

Modernization of Unit for Elimination of VOCs by Catalytic Oxidation

David Jecha^{a,*}, Jan Martinec^b, Vladimír Brummer^a, Petr Stehlík^a, Pavel Leštinský^a

^aInstitute of Process and Environmental Engineering, Brno University of Technology, Technická 2896/2, 616 69 Brno, Czech Republic

^bMomentive Specialty Chemicals, a.s., Tovární 2093, 356 01 Sokolov, Czech Republic
jecha@fme.vutbr.cz

The treatment of waste gases as well as solid and liquid wastes is important activity for environmental protection. Recently, with the tightening emission limits, the pressure to reduce emissions, especially the volatile organic compounds (VOCs), has increased. The reason is not only the impact of these emissions on the "greenhouse effect", but also their negative impact on the environment and human organism. Individual VOCs have dangerous properties, such as: irritant, toxic, and dangerous for the environment, and harmful (Koppmann, 2007). Emissions of VOCs arise mainly in industry processing the organic materials, such as various chemicals, solvents, paints, fuels, cleaning agents and other.

1. Removal of VOCs in a combustion chamber

The treatment of waste gases with high concentrations of VOCs is the case of company Momentive Specialty Chemicals Inc. in Sokolov, Czech Republic. The company produces acrylic acid, acrylic acid esters and acrylate polymers. Two thermal incineration units installed at the site dispose liquid and gaseous wastes from the production. The consumption of natural gas is huge and operating cost very high. This is main reason, why the company has been seeking technologies that decrease the consumption of natural gas while maintaining compliance with existing emission limits. Replacement of the existing combustion chamber (furnace) 2F-630 (see Figure 1) with a catalytic reactor technology seems to be an appropriate solution.



Figure 1: Incineration unit 2F-630 at Momentive Specialty Chemicals, Inc. in Sokolov

The arrangement of the existing technology with combustion chamber is shown in Figure 2. 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.

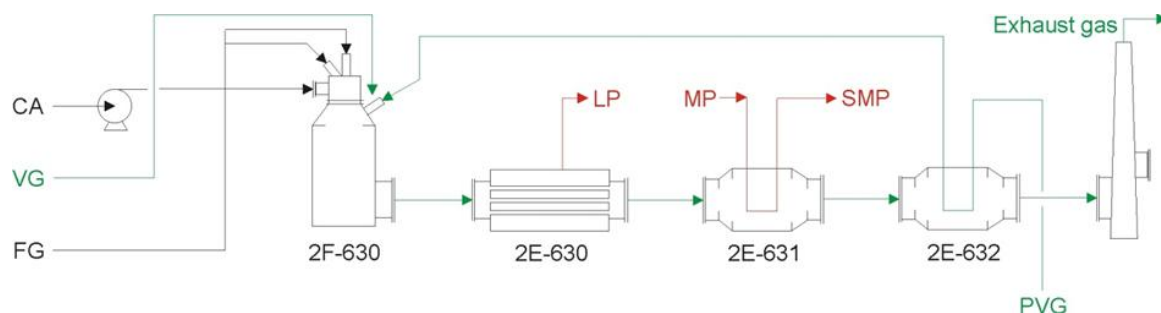


Figure 2: Flow sheet of the incineration unit

The measurement of the composition of PVG-VG mixture was carried out. Knowledge of composition of the off-gas processed is important for the analysis of current technology status and for new technology design. The results of the gas composition measurement are shown in Tables 1 and 2. The concentrations of VOCs were measured by a FID analyzer. The content of O₂, CO and CO₂ was measured by an IR analyzer.

Table 1: Composition of process off-gas PVG

Composition	Composition of PVG off-gas (humid gas)				vol. %
	N ₂ , H ₂ O vol. %	VOC vppm	VOC mg TOC/m _N ³	CO, CO ₂ , O ₂ 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			73 °C		
Absolute pressure			106.325 kPa		
Flow rate			18,279.9 m _N ³ /h		

2. Design of a catalytic oxidation unit for VOCs removal

Catalytic oxidation of organic compounds is a frequently used method owing to low operating cost (Everaert, 2004). Organic compounds are oxidized by oxygen to carbon dioxide and water. The temperature required for the catalytic oxidation during the reaction is dependent on the type of organic compound, space velocity and concentration. Space velocity should be chosen with respect to the desired

degree of conversion (Dvořák, 2006). Catalytic oxidation process economy is advantageous compared to that of thermal (non-catalytic) oxidation. Reaction temperature for thermal oxidation of organic compounds is around 600 °C and higher, whereas reaction temperature for catalytic oxidation is in the range of 150-350 °C (Heck, 2002). Due to this difference, catalytic oxidation has a lower operating cost, while achieving the same degree of VOC conversion.

Table 2: Composition of off-gas VG

Composition	Composition of VG off-gas (humid gas)			
	air vol. %	VOC vppm	VOC mg TOC/m _N ³	vol. %
N ₂	77.10			76.773
O ₂	20.70			20.612
Ar	0.90			0.896
CO ₂	0.10			0.100
H ₂ O	1.20			1.195
Toluene (C ₇ H ₈)		3,602	13,512.9	0.360
Methyl acrylate (C ₄ H ₆ O ₂)		636	1,362.7	0.064
SUM	100	4,238	14,875.6	100.000
Temperature	22 °C			
Absolute pressure	106.325 kPa			
Flow rate	1,820.9 m _N ³ /h			

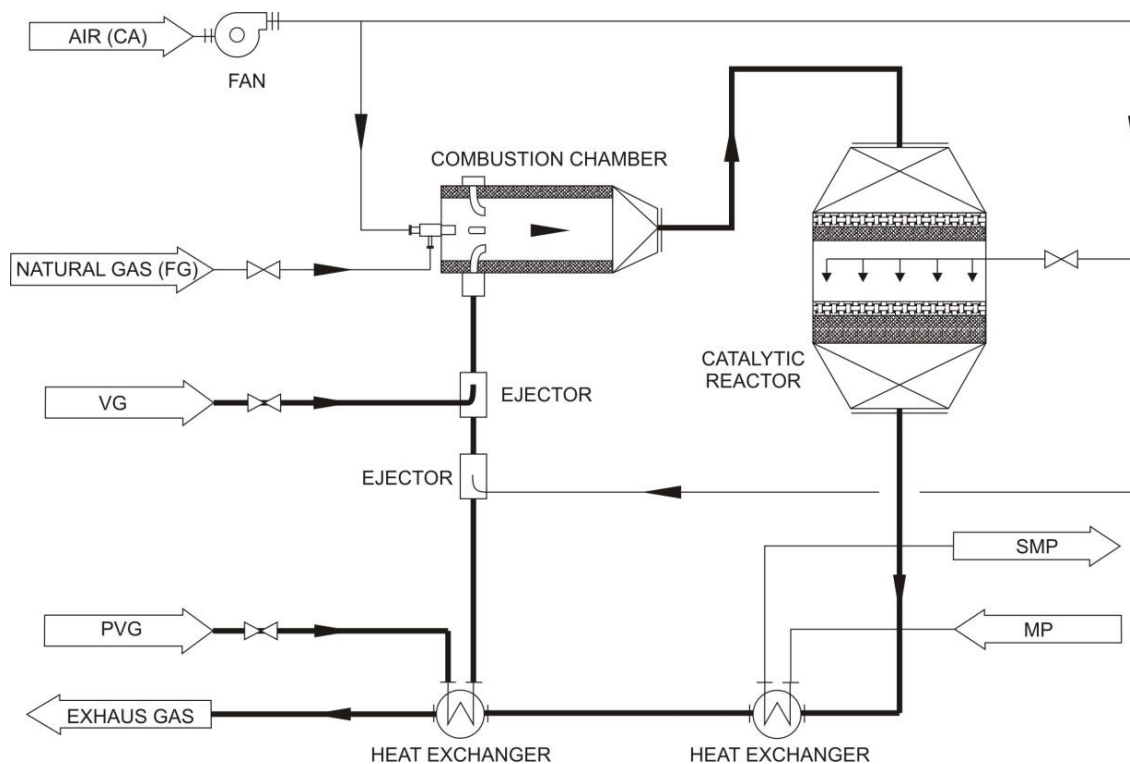


Figure 3: The flow sheet of a catalytic reactor

The technology arrangement of catalytic reactor technology (Figure 3) was designed with regard to composition and flow rate of PVG and VG off-gases (Table 1 and Table 2). The PVG off-gas is fed through a manual valve to the heat exchanger, where it receives heat from the exhaust gas. The heated PVG continues through two ejectors, where it is mixed with air and VG off-gas. The mixture of PVG and VG gases is transported to the combustion chamber, where it is heated-up to the starting temperature of catalytic oxidation reactions. Preheating is done by natural gas burner - the quantity of natural gas (FG) and combustion air (CA) is controlled by a thermocouple installed at the outlet of the combustion chamber. The heated mixture of PVG and VG gas then enters the first catalytic bed in the catalytic reactor, where

the oxidation of VOCs and CO takes place. Dilution/cooling air (CA) is fed into the interspace between the two catalytic layers. Dilution air protects the catalyst against overheating in case of reactor overloading with flammables. The amount of dilution air is controlled according to the temperature measured by a thermocouple at the outlet from the second catalytic layer. Combustion products from the catalytic reactor then enter a heat exchanger, where the heat is transmitted to steam. Later, the exhaust gas pre-heats PVG in another heat-exchanger. Then, the cooled combustion gases enter the smokestack.

The design of the catalytic reactor is further based on the operating parameters of the catalyst EnviCat® VOC-5565. These parameters are listed in Table 3. Starting temperature of oxidation reaction (320 °C used for design) and maximum operating temperature of catalyst (680 °C; 600 °C used for design for safety reasons) were key parameters for the technology design.

Table 3: 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

The catalytic reactor and the combustion chamber for preheating of PVG off-gas to the starting temperature are basic elements of the technology. The off-gas enters the catalytic reactor from the top. The maximum gas flow through the catalytic bed was determined to be 26,997 Nm³/h. The catalytic bed was divided into two catalytic beds with addition of air between these beds. Since most of the present VOCs and carbon monoxide (CO) are oxidized very easily at low temperatures, it is not appropriate to divide the height of the bed evenly. On the other hand, propane achieves high degrees of conversion at high temperatures (see figure 4). For this reason, the catalytic bed was divided in the ratio of 1:3. The catalyst used was the EnviCat® VOC-5565 from Süd-Chemie. This catalyst is a mixture of noble metals, such as platinum and palladium on the Al₂O₃ carrier. This combination is typically used in the industry for cleaning gases containing CO and VOCs (Cordi, 1996). Reduction of the concentration of CO in the first bed also increases the conversion of VOCs in the second bed because CO acts as an inhibitor on the catalytic oxidation of VOC (Liotta, 2010). A layer of inert material before catalytic bed was used for homogenization of flow and protection of both catalytic beds against fouling with solid particles.

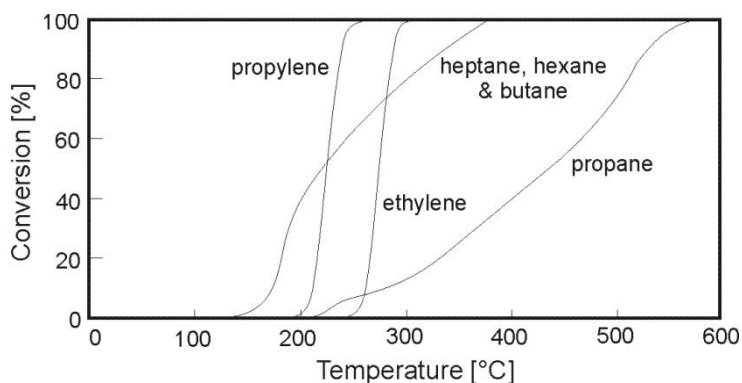


Figure 4: Conversion of propane and other VOCs in dependence on temperature in catalytic bed (Cheremisinoff, 1989).

Table 4 Maximum operating flow rates in the catalytic reactor

Max. flow rate in catalytic bed (for N.T.P.)	26,977 m _N ³ /h
Max. real flow rate on entrance to the catalytic reactor	42,598 m ³ /h
Max. real flow rate on exit from the catalytic reactor	82,144 m ³ /h
Max. real flow rate for air between the catalytic beds	7,323 m ³ /h

The parameters of catalytic bed were calculated based on the maximum operating conditions (Table 4). The volume of catalyst was calculated to be 2.7 m³. The weight of catalyst of 1,620 kg was calculated from specific gravity of the catalyst (Table 4). The cross-sectional area of the catalytic bed of 13.38 m² was

calculated from design linear velocity and maximum flow rate in the catalytic bed (for N.T.P.). Height of the catalytic bed was 200 mm. The height of the first layer of catalytic bed was 50 mm, the height of the second layer was 150 mm. The height of inert protective layer installed before catalytic beds was 100 mm. Raschig rings were used as the inert particles.

The Levy equation (Perry, 2008) was used for calculation of pressure drop in the catalytic beds. The parameters as maximum flow rate through catalytic bed (Table 2), temperature (320 and 600 °C) and pressure (106 kPa) were used for the calculation. The characteristic diameter of catalyst was 5 mm (spheres). The inert particles (Raschig rings) were sized approximately 15x15 mm. The pressure drop for catalytic reactor was calculated as 1.6 kPa for maximal load (temperature 600°C).

3. Verification of the catalytic reactor balance

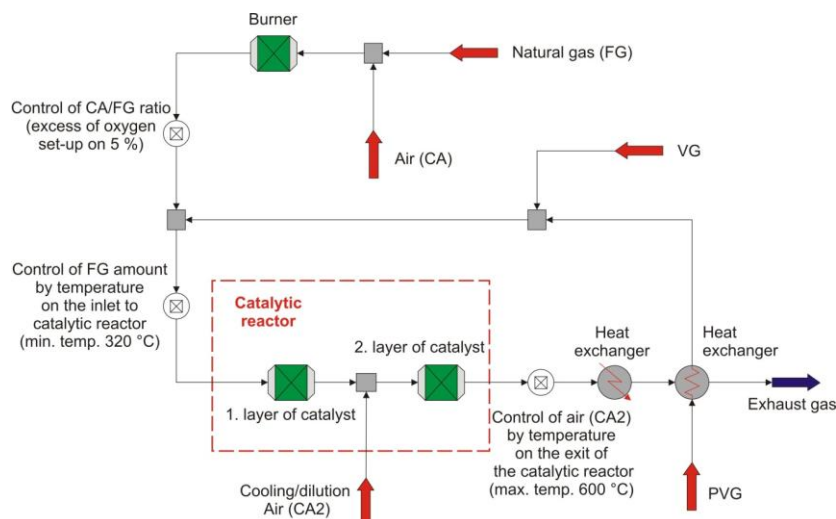


Figure 5: Catalytic unit flow diagram

The mass and heat balance of the catalytic unit was prepared by using ChemCAD process simulator. Unit flow diagram is shown in Figure 5. Four variants were prepared for maximal and minimal gas flow rates, and for high and low vent lower heating value (LHV). The LHV depends mainly on the quality of raw materials used for acrylic acid production.

In the low HV variant, 0.56 vol. % VOC and 0.48 vol. % CO in humid gas was used. In the high LHV variant, 1.03 vol. % VOC and 0.5 vol. % CO in humid gas was considered. The balance with low LHV was calculated for zero feed of cooling air.

4. Conclusions

The technology unit of catalytic oxidation for reduction of VOCs and CO was designed for company Momentive Specialty Chemicals, Inc. in Sokolov. This unit should replace the existing combustion chamber 2F-630 (see Figure 1). The catalytic reactor with two catalytic beds (Figure 3) was designed based on the maximum operating flow rates.

The catalytic bed was divided on two parts with the ratio of 1:3. Between the beds, dilution air inlet was proposed to prevent the temperature increase above 680 °C, which is the upper critical working temperature of the catalyst EnviCat ®. The layers of inert Raschig rings were added in front of each catalytic bed. The pressure drop of catalytic reactor was calculated for process temperatures 320-600 °C and it was in the range of 1.11-1.60 kPa.

The process balance of catalytic reactor was prepared in software ChemCAD. The flow sheet is shown in Figure 5. The input and output data from balance of the catalytic reactor are shown in Table 5. In the heat balance, zero residual VOCs and CO in the exhaust gas at the outlet from the catalytic reactor were considered. From Table 5 it is clear that in case of high content of organics in the vent gas it is necessary to bring the dilution air between the catalytic beds. Without the addition of dilution air to the bed, temperature would rise above 750 °C, with the risk of catalyst damage. On the contrary, cooling air addition is not necessary if the vent gas with low content of organics is treated. In this case, the outlet temperature approaches the minimum operating temperature specified for the catalyst.

Table 5: Maximum operating flow-rates in the catalytic reactor

	Unit	Max. LHV and max. PVG flow rate	Max. LHV and min. PVG flow rate	Min. LHV and max. PVG flow rate	Min. LHV and min. PVG flow rate
PVG flow rate	m _N ³ /h	18,280	16,031	18,280	16,031
VG flow rate	m _N ³ /h	1,821	1,821	1,821	1,821
Temperature before combustion chamber	°C	301.5	298.3	301.3	298.0
Natural gas consumption (FG)	m _N ³ /h	18	19	18	19
Air consumption (CA)	m _N ³ /h	178	186	178	185
Flow rate of PVG+VG to catalytic reactor	m _N ³ /h	20,297	18,057	20,297	18,057
Temperature of PVG+VG before catalytic reactor	°C	320.0	320.1	320.0	320.0
Flow rate of cooling air (CA2)	m _N ³ /h	6,598	5,790	0	0
Temperature of exhaust gas on exit from catalytic reactor	°C	599.4	600.7	558.6	560.9
Theoretical temperature on exit from catalytic reactor without cooling air	°C	752.8	752.6	558.6	560.9
Flow rate of exhaust gas to smokestack	m _N ³ /h	26,895	23,847	20,297	18,056

The investment and operating costs were estimated for the designed technology. The total investment cost is approximately 700,000 € (without catalyst) or 900,000 € (with catalyst). When considering the existing operating cost connected with the operation of the thermal unit and estimated investment cost for the new technology, payback period of 5.5 y results (catalyst included). Due to the potential threat of catalyst fouling by solid impurities, a pilot plant was installed to prove long-term reliability of the catalytic reactor. VOC and CO removal efficiencies of 97.1 % and 97.9 % were achieved at full load. The concentrations of VOCs and CO at the outlet from the pilot unit met the existing emission limits according to Decree No. 205/2009 Coll.

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