

Optimal Design and Modernization of Small Incineration Unit for VOC Abatement

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In premises of company Momentive Specialty Chemicals, Leuna GmbH & Co. KG an operational thermal incinerator of gaseous waste from the manufacture of products on the base of butadiene-styrene and acrylic-styrene is situated. While producing such mixtures, gaseous vapours are discharged to the waste incineration plant. Gas containing organic substances arises (evaporates from the reactor) especially after transportation of the mixture to the reactor and subsequently at each process steps in the strippers (addition of chemicals, stripping, etc.). The operation of the present unit for processing of waste gas is energetically costly because, for its operation a considerable amount of natural gas is consumed.

Therefore, new technologies were sought that could lower the consumption of natural gas and meet the current emission limits. In present time, the existing incinerator has difficulties in complying with the emission limit for NO_x.

In this case, it seems suitable to replace existing combustion chamber either with the catalytic reactor technology or with a new unit for VOC thermal abatement, or to modify the existing thermal incineration unit in order to meet emission limits (particularly for VOC and NO_x), while achieving some savings in terms of operating costs. Currently, the combustion chamber processes two kinds of waste gases - process off-gas 90100 and 90200, which were subjected to technical measurement. These streams differs radically in terms of flow rates and also in terms of composition and pollutants contents trends during production of different kind of products. Technical measurements of waste streams provided the basis for creation of designs that try to deal with the given situation.

On the basis of the measured and processed data, data from the operator and simulation of the process in Hysys environment, utmost conditions have been designed, i.e. input values of composition, temperature, pressure and flow rates of waste gases streams 90100 and 90200, for the design of the technology.

Possibilities of catalytic oxidation usage for this application or modernization of the incinerator were explored, to achieve reasonable operating costs and meet locally applicable emission limits for VOC and NO_x.

1. Introduction

Oxidation is the most frequently used method to deal with pollutants as VOC and CO in industrial waste gas. (Matějová et al., 2012) Catalytic oxidation has some benefits comparing to thermal oxidation. Lower temperatures for light off curves for VOC and CO (Ved et al., 2013) leads to financial saving even with the additional costs for the catalyst. But the possible VOC concentration range that can be treated is lower for catalytic oxidation, because catalyst sintering phenomena occurs at temperatures above 800 °C. (Barbato et al., 2013)

The composition and total VOC content of waste streams differs from case to case and this is the reason for requirement of individual approach and development in VOC treatment. (Ojala et al., 2011) The decision, whether it will be more beneficial to use catalytic or thermal processing of waste gas depends on

total VOC concentration, the individual VOC contents and trend of concentration in gas stream over time.

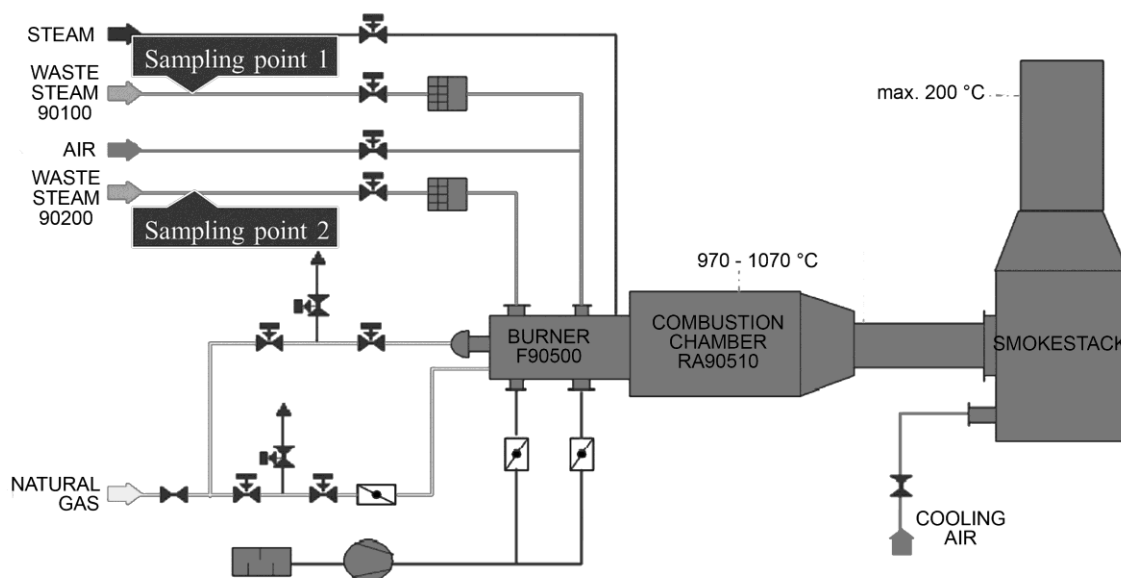


Figure 1: Flow sheet of the combustion chamber of the incinerator with location of sampling points

(Gosiewski and Pawlaczyk, 2014) If VOC loading is uneven during time, it is necessary to count for the design with air cooling in the reactor to prevent catalyst damage in the case of VOC peak.

2. Specifications of inlet and outlet waste gas

Within the examination of the suitability of the catalytic oxidation technology usage for a replacement of the incinerator F90500 in the premises of company Momentive Specialty Chemicals, a technical measurement of selected compounds concentrations in the waste gas streams 90100 and 90200 had to be done. The sampling points used for measurements and relevant part of the technology are shown in Figure 1.

In the waste stream concentrations of O₂, CO, CO₂, SO₂, NO_x and VOC were monitored. Flow rate, humidity, temperature were also measured or taken from the online measurements from the control system of a technology.

3. Composition of inlet streams for the design of new equipment

Because the production is discontinuous (batch type) and several types of products manufactured are alternating, a production schedule is (for a simplification) split into two groups: butadiene-styrene type and styrene-acrylate type. Production phases were usually: addition of a latex, addition of chemical agents, vacuum stripping, steam stripping, vacuum cooling and start of another batch. Due to discontinuous operation and wide product portfolio, trends of VOC in waste gas streams differs for each product and VOC peaks for each production were observed in different production phases (mainly during addition of chemicals, stripping by vacuum or steam). New technologies must be designed with respect for minimal and maximal VOC concentrations in waste gases. The ratio of individual VOC for the composition of streams 90100 and 90200 for both product lines (BS and SA) was used according to the HYSYS process simulation results. Measurement of VOC and evaluation of current state was complicated by the fact that there are many different products and for each product there is different waste gas streams composition and technology is Batch type, so VOC trends also vary very widely with the time. It was also discovered, that VOC concentrations in VOC rich stream 90100 were for the most of the time out of the measuring limits of FID analyser used, so sampling was carried out using a dynamic dilution by air.

Based on the request of the investor, the newly proposed technology is designed for double production, thus also the VOC concentrations doubles. Stream 90100 is already fully saturated with VOC during certain phases of the production and in case of increase in production the flow rate of stream 90100 will raise too. At the current state, the maximum flow during transfer to the reactor is approx. 36 m_N³/h. The estimated flow in the new equipment is 72 m_N³/h and fluctuations of VOC concentration, according to

Table 1: Summary information of mixed waste gas streams (90100+90200) regarding two main production lines for the design of new technology

Butadiene-styrene products line				Styrene-acrylic products line			
Properties	Component [mole %]			Properties	Component [mole %]		
Temp [°C]	26.595	Nitrogen	69.7696	Temp [°C]	26.132	Nitrogen	77.6476
Pres [kPa]	100.995	Oxygen	18.5284	Pres [kPa]	100.995	Oxygen	18.5286
		Argon	0.8497			Argon	0.8497
Vapor mole frac.	1.000	Carbon Dioxide	0.0886	Vapour mole frac.	1.000	Carbon Dioxide	0.0886
Total [kmol/h]	26.382	Water	2.4432	Total [kmol/h]	26.382	Water	2.4432
Total [kg/h]	816.553	Carbon Monoxide	0.0252	Total [kg/h]	763.851	Carbon Monoxide	0.0252
Total std L [m ³ /h]	0.988	Nitric Oxide	0.0009	Total std L [m ³ /h]	0.882	Nitric Oxide	0.0009
		Sulphur Dioxide	0.0248			Sulphur Dioxide	0.0248
Total std V [m ³ /h]	591.320	Styrene	0.2912	Total std V [m ³ /h]	591.320	N-Butyl Acrylate	0.1196
		1,3-Butadiene	7.9487			Styrene	0.2518
		Vinylcyclohexene	0.0297			N-Butanol	0.0198

measured data. The maximum VOC concentration is observed at the current state with a flow rate of about 25 m_N³/h, therefore for future equipment design it will be counted with 50 m_N³/h flow of this stream. For stream 90200 is the situation reversed, the flow of this stream is determined by blower, which performance does not fundamentally alter during the production process. For this stream and current state is the concentration of VOC 0.21 vol. %, for the new equipment design will be counted with double concentrations (0.42 vol. % VOC). For design of primary solution for removing pollutants (in this case VOC) are primarily important their maximum concentrations. From streams 90100 and 90200 compositions a mixed stream was created that will enter the new technology. The resulting mixed stream was determined for the butadiene-styrene and the styrene-acrylic products lines and their parameters are summarized in Table 1.

The possibility to apply biofiltration for VOC disposal was unreal, measured concentrations were much higher than 5 g/m³, which is optimal for biological processes and hydrophobic VOC as styrene are degraded poorly by microorganisms (Muñoz et al. 2012). The applicability of the catalytic oxidation and thermal liquidation of VOC were more promising and were evaluated. Energy and mass balances for current state and also for catalytic technology variant and reconstruction of combustion chamber both for minimal and maximal VOC loading was prepared in Chemcad. Flow diagram for catalytic oxidation technology and maximal VOC loading is showed in Figure 2.

The draft design of a reconstruction of an existing incinerator for thermal destruction of VOC was also prepared. Based on the technical measurements results, limiting compositions of the process off-gas streams 90100 and 90200 for the design of new technologies with a catalytic reactor (for use of catalytic oxidation) or new incinerator (for thermal oxidation) were determined. Resulting specifications that arise from balances with minimal and maximal VOC loading are summarised in Table 2.

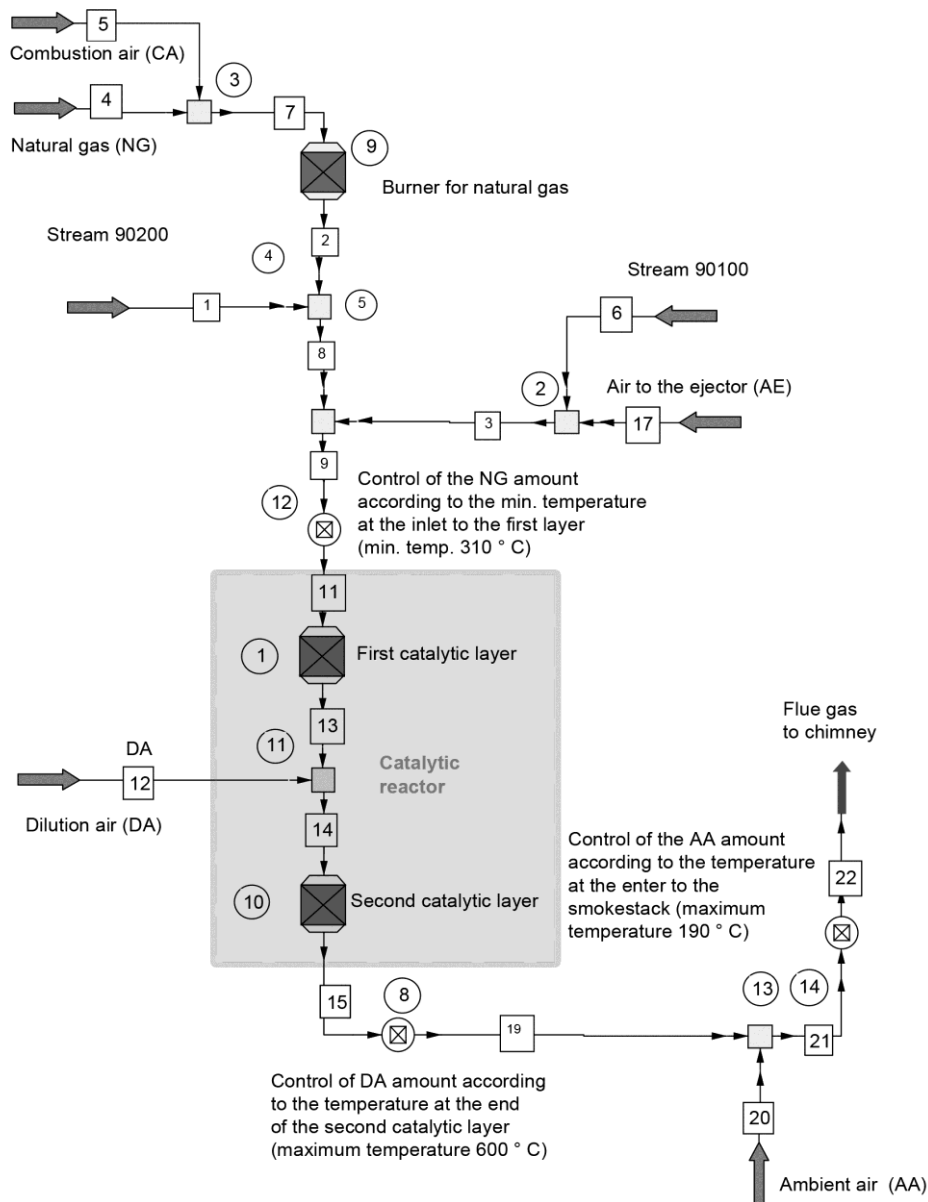


Figure 2: Chemcad flow sheet of the catalytic oxidation technology balance for maximal VOC loading

With the results of balances and operating conditions was then proceeded to calculation and design of individual parts of the technology with a catalytic reactor. Specifically, there were calculations and designs of catalytic reactor and the combustion chamber for preheating of waste gas streams 90100 and 90200 mixture and pipelines. For a given process waste gas streams compositions, the suitable type of catalyst from Süd-Chemie was inquired. The Süd-Chemie did not recommend the specific type of catalyst, but gave comments on the design of the technology that was the foundation for the basic design and estimation of operating and investment costs.

For the decision about an implementation of the project replacing the currently existing combustion chamber for the technology with catalytic reactor it was essential to estimate investment and operating costs of the entire proposed technology. Total investment costs of the technology with a catalytic reactor represent approximately amount of € 776,000 (excluding the first supply of the catalyst) and € 835,000 (including the first supply of catalyst). After processing the operating costs of current technology with the combustion chamber and the incorporation of planned costs of the technology with a catalytic reactor comes payback period of this investment for approximately 18.34 y. This was the main reason for rejecting the catalytic oxidation processing of waste gas for this application. There is also an issue connected with an uneven loading of catalyst bed during production, which could cause technological problems. The

outcome here was very different from another previous case, where waste gas from acrylic acid, esters and related production was processed and payback period for catalytic oxidation was calculated to 5.5 y and catalytic oxidation was suggested to replace current thermal treatment. (Jecha et al., 2013)

Table 2: Specifications for the design that arose from balances for minimal and maximal VOC loadings

Properties	Units	Maximal VOC concentration	Minimal VOC concentration
Flow of the stream 90100	[m _N ³ /h]	50	0
Flow of the stream 90200	[m _N ³ /h]	532	532
Temperature prior the combustion chamber	[°C]	26	26
Consumption of natural gas (NG)	[m _N ³ /h]	9	20
Consumption of combustion air (CA)	[m _N ³ /h]	100	380
Flow of off-gas after the combustion chamber	[m _N ³ /h]	700.5	941.5
	[m ³ /h]	1,503	2,923
Off-gas temperature to catalytic reactor	[°C]	310.9	572.0
Flow of dilution air (DA)	[m _N ³ /h]	6,686	0
	[m ³ /h] at 45 °C	7,421*	0
Temperature of flue gas at the outlet of the catalytic reactor	[°C]	600	572
Theoretical temperature at the outlet of the catalytic reactor without dilution by air (DA)	[°C]	1 663	572
Flue gas flow from the reactor	[m _N ³ /h]	7,413*	942
	[m ³ /h]	23,781*	2,924
Dilution air flow (AA)	[m _N ³ /h]	20,391	2,403
	[m ³ /h] at 30 °C	21,562	2,541
Flue gas temperature at the outlet to the atmosphere	[°C]	190	190
The flue gases flow from the stack	[m _N ³ /h]	27,803	3,344
	[m ³ /h]	47,321	5,692

* values used for the design of catalytic reactor, combustion chamber and pipelines

Thermal disposal of process waste gas streams in Leuna plant was than solved in two different ways. Firstly based on the requirements of the investor to increase the production capacity was designed a new incinerator, secondly, for the existing conditions was recommended a reconstruction of the existing incinerator.

After the conditions were specified, it was approached to simulations of new combustion chamber and consequently to the calculation and design of a new combustion chamber. For the decision about an implementation of the project that replaces the currently existing combustion chamber with new combustion chamber, were estimated investment and operating costs of the proposed technology. Total investment costs of the technology with new combustion chamber represent approximately amount of € 491,000. Payback rate of the technology is not applicable because it is a replacement of the same technology, but for larger amounts of process waste gases. The main benefit is the reduction of monitored substances below a new emission limits.

In case, that investor chooses to maintain the current production volume, i.e., as well also a volume of process waste gas, the possibility of reconstructing of an existing combustion chamber was proposed. Price of reconstruction is highly dependent on the extent of possible use of existing technology. For minor reconstruction that includes only a burner exchange to low-NO_x type with relevant modifications, the

investment costs are estimated to about € 100,000. If the decision has been taken to do complete combustion chamber reconstruction, the investment costs will be approximately € 328,000.

4. Conclusions

The usability of catalytic or thermal deep oxidation for waste gas treatment from manufacture of products on the base of butadiene-styrene and acrylic-styrene was evaluated. At the start, the waste gases VOC concentration trends of Batch type technology were unknown and to know whether it will be favourable to use catalytic oxidation instead of thermal, or just to modernise existing combustion chamber was necessary to decide after the measurement of waste gas streams and creation of process mass and energy balances.

On the basis of the measured and processed data and data from the operator, utmost conditions have been designed, i.e. input values of composition, temperature, pressure and flow rates of waste gases streams 90100 and 90200, necessary for the design of the technology. As the investor requested, it was calculated with an increase in the production, which will affect the composition and quantity of process off-gas streams. The stream 90100 flow was considered as doubled and for the stream 90200 was changed the composition to double the amount of VOC.

According to the design conditions, an arrangement of the technology with a catalytic reactor was created and also two balances for the minimal and maximal VOC concentrations in the waste gases. Because the uneven loading of VOC and peaks of almost 100 % VOC concentration in one of the waste streams, the designed catalytic reactor dimensions were disproportionally large for considered waste gas flow, which led to payback rate of investment - 18.34 y. Total investment costs for technology with catalytic oxidation were estimated to € 835,000 including the first supply of catalyst. Thus, the catalytic oxidation was rejected as a viable solution.

It was discovered that for the decision making process of the suitable technology, it is necessary to take into account not only total and individual VOC content, but also instability in VOC loading, which could lead to bigger necessary catalytic reactor and peripheral equipment and higher investment and operating costs and longer payback rate, which was also this case.

Instead, minor and major reconstruction of combustion chamber was taken into account. For minor reconstruction investment costs was estimated on about € 100,000 including burner exchange to low-NO_x to meet emission limits. The investment costs for complete combustion chamber reconstruction will be approximately € 328,000.

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