CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS AND MALODOROUS ORGANIC COMPOUNDS

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OU LU 2005
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OULUN YLIOPISTO, OULU 2005
Abstract

This thesis describes efforts made on the development of an existing catalytic incinerator. The development work, called process characterization, consists of four general parts. These are the development of measurement methodology, the studying of construction materials, the selection of suitable catalysts and the testing of the effects of process operation conditions. The two application areas for catalytic incineration considered in this thesis are solvent emission abatement (VOC, volatile organic compounds) and chip bin emission abatement (SVOC, sulphur-containing volatile organic compounds).

As a baseline, the process characterization is started with the development of measurement methodology. In general, the methodology will decrease costs and simplify the carrying out of the actual measurements and thereby make the measurement time more effective. In the methodology it is proposed that continuous total concentration measurement should be used in connection with qualitative sampling to obtain reliable measurement data.

The selection of suitable construction materials for the application is very important. As shown in this thesis, the end conversions in solvent emission abatement may even be improved through the selection of the proper construction materials. In chip bin emission abatement, the problem arises from corrosive oxidation products that set limits on the construction materials used as well as on oxidation conditions.

Catalyst selection is based on the following catalytic properties: activity, selectivity and durability. These catalytic properties are studied either at the laboratory or on an industrial scale. The catalytic materials tested are Pt, Pd, Pt-Pd, Cu-Mn oxides, MnO₂-MgO, CuₓMg(1-x)Cr₂O₄ and CuₓCr₂O₄. The most important selection criteria in solvent emission abatement are proposed to be activity and selectivity. In the case of chip bin-SVOC-abatement, these are selectivity and durability. Based on these criteria, catalysts containing Cu-Mn oxides and Pt were demonstrated to be the best catalysts in VOC oxidation, and catalyst containing MnO₂-MgO was shown to be best catalyst in SVOC oxidation.

A study on the effect of process operation parameters (temperature, concentration and gas hourly space velocity (GHSV)) and moisture was carried out with the aid of factorial design. In VOC (n-butyl acetate) oxidation, the most influential process parameter was GHSV, which decreased the end conversion when it was increased. In SVOC (DMDS) oxidation, the effect of temperature was most significant. The end conversions increased as the temperature increased. Moisture slightly decreased the formation of by-products in n-butyl acetate oxidation. In DMDS oxidation, moisture slightly increased the end conversions at a lower temperature level (300°C).

At the end of the thesis, these process parameters are also discussed from the standpoint of the catalysts' activity, selectivity and durability. Finally, proposals for process improvements are suggested.

Keywords: chip bin emission, metal oxide catalyst, noble metal catalyst, process development, process parameters, solvent emission
To my grandfather
Acknowledgements

As note of warning: this list of acknowledgements will be very long, since a great deal of people and companies have contributed to my work during this four-and-half-year period of research.

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Ms. Reeta Ylönen worked as my partner in KATVOC-project, concentrating mainly on flow measurements and CFD modeling. Thanks for your company throughout many measurement/course trips and for all the hilarious moments!

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Research also needs financial support. I have been fortunate to receive a four-year funding from the Graduate School of Chemical Engineering (GSCE), which is greatly acknowledged. Thanks are also due to the following organizations for their financial support: the Academy of Finland, Tekes, the Finnish Catalysis Society and foundations of Tauno Tönning, Kemira, TES, Gustaf Komppa and Konkordialitto. In addition to funding my research, they made it possible to travel to conferences and present the results as well as to find out the latest developments in the fields of catalysis and chemical engineering.

To the personnel of Laboratory of Mass and Heat Transfer: the importance of coffee breaks is definitely underestimated! Discussions starting from daily news to lunch recipes really stimulates the mind. And if so, we should truly develop a continuous-flow coffee machine! Thanks to you all (and Robert Paulig) for all the refreshing moments!

At this moment my good friend and advisor Dr. Ulla Lassi probably thinks that I have forgotten her, but this is not the case! Thank you Ulla for your invaluable help during my research. You were always there, by the phone if not personally, answering my questions and listening to my problems.
Finally, my warmest thanks go to my family: my partner Tommi, my parents Tapio and Päivi as well as to my little sisters Riitta and Marisa. This thesis is dedicated to my grandfather who encouraged me to start post-graduate studies, but unfortunately passed away a while before I finished up my thesis.

After this long list of thanks I am still not sure if I have acknowledged everyone I wanted to. I consider myself to be very fortunate, since many have contributed to my work by showing me their points of view, helping with experimental work, organizing pilot tests or just giving me possibilities to concentrate on other things than research from time to time. All your contribution has been very important and will not be forgotten!

I would like to end with the inspiring words of wisdom from Mr. Donald Trump:

‘Without passion you won’t have energy,
without a positive attitude
you won’t even be successful!’

Oulu, October, 2005

Satu Ojala
### List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller-method</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda-method</td>
</tr>
<tr>
<td>CEN</td>
<td>The European Committee for Standardization</td>
</tr>
<tr>
<td>DMDS</td>
<td>Dimethyl disulphide</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethyl sulphide</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FPD</td>
<td>Flame Photometric Detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas Hourly Space Velocity</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Electron Spectroscopy</td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>MM</td>
<td>Methyl mercaptane</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>MSD</td>
<td>Mass Selective Detector</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NMVOC</td>
<td>Non-methane Volatile Organic Compound</td>
</tr>
<tr>
<td>PGMME</td>
<td>Propylene glycol monomethyl ether</td>
</tr>
<tr>
<td>PGMMEA</td>
<td>Propylene glycol monomethyl ether acetate</td>
</tr>
<tr>
<td>PID</td>
<td>Photo Ionization Detector</td>
</tr>
<tr>
<td>SVOC</td>
<td>Sulphur-containing Volatile Organic Compound</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TD</td>
<td>Thermodesorption</td>
</tr>
<tr>
<td>TG</td>
<td>Thermo Gravimetric analysis</td>
</tr>
<tr>
<td>TVOC</td>
<td>Total Volatile Organic Compounds</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
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</table>
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1 Introduction

1.1 Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are one of the major contributors to the formation of photochemical ozone (Derwent et al. 2003). They are emitted into the atmosphere from thousands of sources. Generally, these sources are classified into three groups: point, area and mobile sources. Point sources are large, discrete stationary sources such as chemical plants, petroleum refineries, and power plants. Even though they are often considered to be large emission sources of VOCs, they emit less VOCs than other sources. Area sources i.e. small, widespread stationary sources such as gas stations, dry cleaners, residential heaters and even backyard grills and home fireplaces collectively contribute to a significant portion of VOC emissions. Mobile sources of VOC emissions range from on-road automobiles, trucks and motorcycles to non-road airplanes, trains, marine vessels, farm and lawn equipment. (Moretti 2001) One should not forget that a significant share of VOC emissions is emitted into the atmosphere from natural sources such as forests and plants, which naturally emit VOCs in the presence of sunlight. (Moretti 2001, Seinfeld & Pandis 1998) In Finland, natural VOC emissions may be as high as 71% of all the VOCs emitted (Degobert 1992).

There are a number of official definitions of VOCs that vary depending on the country. According to the EU’s VOC Directive (99/13/EC), ‘a volatile organic compound shall mean any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use…’ VOCs include a great variety of different organic compounds including alcohols, ethers, esters, chlorinated hydrocarbons and odorous compounds containing sulphur (Khan & Ghosal 2000).

In Europe the implementation of the Directive on Reduction of Motor Vehicle Emissions of VOCs (UN ECE 1991) has resulted in the reduction of emissions of certain organic compounds in 1990s (Derwent et al. 2003). In Finland, the emissions of VOCs started to decrease in the 1990s. Nevertheless, the obligation under the Geneva VOC protocol, which was signed in 1991, i.e. 30% reduction on the 1988 level of VOCs by 1999, proved to be more difficult to attain than anticipated partly due to the fact that old
vehicles have not been replaced at the rate that was envisaged. However, emissions of VOCs decreased by close to 30% in the 1990s, down to about 160,000 tonnes per year. The emission limit for 2010 is 130,000 tonnes. Table 1 summarizes the emissions of VOCs since the Geneva protocol reference year 1988 (Ministry of the Environment 2002). Fig. 1 gives non-methane VOC emissions (NMVOC) from 1990 to 2003 (Finland’s environmental administration 2005). The corresponding methane emission values during the years have been decreased from 6.4 (million tonnes of CO₂ equivalent) to 5.0 (Statistics Finland 2005).

*Table 1. Emissions of VOCs since the Geneva protocol reference year (1988) in Finland, kt a⁻¹ (Ministry of the Environment 2002).*

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Transport</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Road</td>
<td>64.9</td>
<td>63.9</td>
<td>51.9</td>
<td>39.9</td>
</tr>
<tr>
<td>Volatile</td>
<td>16.9</td>
<td>17.8</td>
<td>14.3</td>
<td>10.1</td>
</tr>
<tr>
<td>Other</td>
<td>7.7</td>
<td>8.7</td>
<td>9.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Total</td>
<td>89.5</td>
<td>90.4</td>
<td>75.4</td>
<td>59.0</td>
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<tr>
<td>Solvent use</td>
<td>54.1</td>
<td>52.6</td>
<td>35.5</td>
<td>32.0</td>
</tr>
<tr>
<td>Industrial processes</td>
<td>28.6</td>
<td>26.5</td>
<td>23.8</td>
<td>16.4</td>
</tr>
<tr>
<td>Heating for housing and service buildings</td>
<td>27.5</td>
<td>27.6</td>
<td>27.4</td>
<td>27.7</td>
</tr>
<tr>
<td>Non-road machinery (incl. farm machinery)</td>
<td>15.6</td>
<td>17.0</td>
<td>16.4</td>
<td>16.1</td>
</tr>
<tr>
<td>Fuel distribution</td>
<td>7.6</td>
<td>7.7</td>
<td>7.4</td>
<td>4.0</td>
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<tr>
<td>Other</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Total emissions</td>
<td>224.9</td>
<td>223.9</td>
<td>187.8</td>
<td>161.3</td>
</tr>
</tbody>
</table>
In 1999, the EU adopted the VOC Solvent Emissions Directive (1999/13/EC), which seeks to reduce VOC emissions from solvent-using installations by 67% by 2007, as compared to the 1990 VOC levels. The purpose of the VOC directive is to prevent or to reduce the direct and indirect effects of VOCs on the environment, mainly air, and the potential risks to human health. This directive includes the emissions from e.g. different coating and painting processes, the manufacturing of coating agents and the production of shoes, drugs and fat. (Directive 1999/13/EC)

If the primary emission control methods are not feasible, the abatement of VOCs from stationary sources may be carried out in several ways. If the emissions only contain a few compounds, and in quite large concentrations, recovery of the emissions may be beneficial. Sometimes it is even possible to use VOC emissions as an energy source (Wherrett & Ryan 2004). However, quite often the emissions are mixtures of several compounds, concentrations are rather low, and recovery is not economical. In those cases destruction-based technologies such as thermal and catalytic incineration or biodegradation are available. (Moretti 2001, Moretti 2002, Ojala 2003) On an industrial scale, catalytic oxidation is the most economical solution if the emissions that should be treated are mixtures and the concentrations vary from low to relatively high. Other abatement techniques are discussed elsewhere (Ojala 2003).

The selection of the most feasible VOC emission reduction strategy should be based on accurate emission measurements from industrial sources. Measurement techniques include both continuous and sampling-based techniques. For example *in situ* flame ionisation detectors (FID), photo ionisation detectors (PID) and Fourier transform infrared spectrometry (FTIR) are used as continuous measurement methods, whereas sampling includes adsorption of VOCs on a solid sorbent and gas sampling in different kinds of containers.
This thesis concentrates particularly on the catalytic abatement of two different types of VOC emissions. First, solvent emissions from wood-coating processes, and second, malodorous organic sulphur emissions (later denoted as SVOCs) originating from a pulp mill chip bin are studied. Furthermore, in this thesis, methane is included in VOC compounds, and methyl mercaptane (MM) in SVOCs.

1.2 Catalytic incineration of VOCs

Catalytic incineration is a rather mature technology that has been used since the 1940’s. Over the years improvements in catalysts etc. have made the catalytic incineration a cheaper and more energy efficient technology. (Jennings 1985) In catalytic incineration, VOC emissions are oxidized to CO2 and H2O, and, in the case of SVOCs, also to SO2, as is the case in thermal oxidation as well. However, the catalytic oxidation proceeds without a flame, and the required temperatures are significantly lower than those needed in thermal oxidation. Because the temperatures are lower, the demands on construction materials are not so severe, and the concentrations of emissions can be lower in turn. In addition, the cleaning efficiencies can be over 95%, which is especially important for malodorous VOCs since they are odorous at very low concentrations. (Hynninen 1998, Ojala 2003, Ojala et al. 2005a)

The method for contacting the waste gas with the catalyst can be different in catalytic oxidation systems. Both fixed-bed and fluidized-bed systems are used. Fixed-bed catalytic oxidizers may use a monolithic or a packed-bed catalyst, of which the monolithic oxidizers are more widely used. Monoliths offer the advantages of minimal attrition resulting from thermal expansion and contraction during the start-up or shutdown and a low overall pressure drop. Fluidized-bed catalytic oxidizers have the advantage of a very high mass transfer rate, although the overall pressure drop is somewhat higher than for a monolith. (Moretti 2001, Hayes & Kolaczkowski 1997) This thesis mainly considers fixed bed–type monolithic catalysts, but granules and pellets are also tested in the laboratory-scale studies.

The heat produced during the combustion of VOCs in the catalyst bed can be recovered. The recovered heat can be used:

− to heat the waste gas and to reduce the energy needed for the preheat burner,
− to heat the process itself by recycling the exhaust back to the process,
− to produce steam or hot water in a waste heat boiler (Jennings 1985 ), and
− to heat the endothermic reaction e.g. methane steam reforming in the coupled reactor concept (Kolios et al. 2002).

The use of heat recovery equipment in the incineration system reduces the energy usage of the incinerator and thus greatly increases the energy efficiency of the incineration process. Heat recovery may be accomplished through recuperative, regenerative or recycle heat exchanges, or through waste heat boilers. (Jennings 1985)

The catalytic incinerator used in this study is a regenerative flow-reversal -type reactor. It consists of two honeycomb systems that include catalysts and heat exchangers. The heat exchangers are considered regenerative since they temporarily store energy from a hot gas stream. This hot gas is produced during exothermic oxidation reactions in the
catalyst bed and stored in a heat sink such as that created by metal honeycombs. The hot stream is introduced into the bed until the temperature of the bed almost reaches the temperature of the hot stream. The direction of streams is changed, and a cold gas stream is passed through the hot bed. Thus the cold stream is heated up to the required reaction temperature by the hot bed. When the bed cools down, the direction of streams are reversed again, repeating the cycle. This kind of operation does not need any external heating if the VOC concentrations of the emission gases are high enough. The lowest concentration needed for oxidation without extra heating the so-called ‘autothermal point’, is about 0.7 g m\(^{-3}\) of VOC. If the concentration of VOC exceeds approximately 8 g m\(^{-3}\), extra dilution air is needed to keep the emission gases outside the explosion limits. The normal operation temperature of an industrial scale catalytic VOC incinerator is about 350\(^\circ\)C, but it varies depending on the VOC compounds to be oxidized. For example, the oxidation temperature should be over 400\(^\circ\)C in the oxidation of chip bin emissions. (Ojala et al. 2005a)

The catalysts used for VOC abatement include metal oxides or precious metals such as platinum (Pt) and palladium (Pd). Precious metals have a longer lifetime and they are more resistant to poisoning and fouling than less expensive base metal catalysts. (Moretti 2001, Ferrandon et al. 1999, Papaefthimiaou et al. 1997, Spivey 1987) In this thesis both metal oxides (Cu-Mn, Mn-Mg, Cu-Mg-Cr, Cu-Cr) and precious metal catalysts (Pt, Pd, Pt-Pd) are studied.

## 1.3 Aims of the work

The aim of this work is to develop an existing catalytic incineration process with the aid of the characterization of different aspects related to this process. The process characterization is divided into four major parts as described in Fig. 2. These parts are developing the measurements, studying the construction materials, catalyst research and consideration of process operation parameters. The combined information derived from these parts may be further used in the process development work.
Fig. 2. Process characterization (measurements, construction materials, catalyst research and process parameters) as a tool in process development.

The process characterization work starts first with the development of a feasible measurement methodology. The measurement of VOCs and SVOCs is even today still quite difficult, and emissions are very often measured in total concentrations without information on the composition of the emissions. One aim of this thesis is to propose and test a simple and a cost-effective measurement methodology for the measurement of VOCs and SVOCs.

Second, different construction materials are tested in the abatement of solvent and chip bin emissions. Construction materials may have a positive or negative effect on the oxidation result. Furthermore, the durability of construction materials in operation conditions of catalytic incineration is important to study. The second aim of this thesis is to bring out the possible effects of construction materials on the catalytic incineration of VOCs as well as information on the effects of oxidation products or conditions on the durability of construction materials.

Third, the selection of the most optimal catalysts for certain oxidation processes is considered. In this case, three aspects are considered: the activity, selectivity and durability of the catalysts. One aim of this thesis is to suggest the most optimal catalysts for solvent emission and for chip bin emission abatement from the catalysts included in the research. This suggestion is based on the activity and selectivity of the catalysts and knowledge of the durability of the catalysts.

Fourth, the process operation is considered in more detail. Different kinds of VOCs require different kinds of conditions for complete oxidization. Temperature, gas hourly space velocity, concentration and moisture are selected for different factors. In this
chapter catalysts’ operation in transient conditions is also discussed. In addition, the information elicited from laboratory studies is applied to a process operation in order to give suggestions for improving the performance of the existing incinerator.

1.4 Scope and outline of the work

This thesis concentrates on the development of the catalytic oxidation process. It takes into account four different aspects, and this comprehensive approach is called process characterization. Process characterization consists of the development of measurements, a study on construction materials, a selection of catalysts and a study on process operation conditions. In this thesis, it will be proved that all these four parts are important in the development work and are sometimes interlinked with each other.

Measurement of VOCs as well as SVOCs is very difficult and the usage of only one piece of equipment in sampling or in measuring of the emissions is not yet widely available. According to a rather new EU Solvent emission directive, fairly small companies are required to measure emissions and this can be quite expensive. This thesis proposes a measurement methodology, which helps in acquiring reliable measurement data in a short amount of time using existing technology and thus with moderate expenses.

Different operating conditions and application areas of catalytic incineration impose different requirements for construction materials. The thermal durability as well as corrosion resistance of materials becomes important especially in SVOC oxidation. Sometimes construction materials may affect the oxidation results, which will be shown in this thesis in the case of VOC oxidation.

The selection of suitable catalysts is based on three different views: the activity, selectivity and durability of a catalyst. The significance of these aspects is different in the cases of VOC and SVOC oxidation. The discussion on the selection of the catalysts is based on experimental results as well as literature data and at the end of the thesis, suitable catalysts are proposed for both cases.

Finally, the effect of three process operation parameters: GHSV, temperature and concentration, as well as the effect of moisture on oxidation results are studied. It will be shown that these factors are also linked to the activity and selectivity of the catalyst, as well as to the durability of construction materials.

When information of all of these four parts is combined, the most optimal operation of catalytic incineration in solvent VOC and chip bin SVOC emission abatement will be achieved.

This thesis is composed of six chapters. All sections are composed of a literature review, the applied experimental methods and a results and discussion part. Chapter 1 gives a general overview of volatile organic compounds and catalytic incineration. The subsequent chapters contain different process development aspects included in this work, which are: measurements (Chapter 2), construction materials (Chapter 3), catalysts’ performance (Chapter 4), and process parameters and operation (Chapter 5). At the end, Chapter 6 summarizes the most central results and conclusions presented in the previous chapters.
2 Measurement of VOCs and Sulphur-Containing VOCs (SVOCs)

An often forgotten yet essential part of process characterization is the one, which gives foundation for experimental research efforts. This is the development of accurate and reliable measurement techniques, or sometimes even a systematic measurement methodology, to carry out the measurements. At its best, the measurement methodology is considered prior to action and then further developed by means of practice. This chapter provides a short review of the previous research carried out in the development of different measurement techniques and applies knowledge from literature and practice to develop a simple and reliable measurement methodology. This methodology is also proposed and tested in the measurement of solvent emissions.

2.1 Introduction

Several research groups (e.g., Wolkof et al. 1998, Moretti 2001) have reported on the difficulty of VOC as well as odour measurements. Both of these emissions are normally mixtures, and furthermore, people sense odorous compounds even before many analytical techniques are able to detect them. Sigrist (1995) has listed the requirements for the ideal measurement technique in general. These requirements are feasibility of measuring different compounds with a single instrument, high sensitivity permitting the detection of ppb (10^{-9}) or even ppt (10^{-12}) concentrations, high selectivity permitting clear differentiation between compounds, large dynamic range to measure low concentrations in rural areas and high concentrations near emission sources, good time resolution permitting quasi-continuous measurements, and portability for in situ measurements or remote monitoring and automatic operation. Even though the requirements were noted several years ago, even today there is still no single technique available that meets all these requirements.

Accurate VOC emission measurements are essential in, for example the selection of the most feasible VOC abatement method. Furthermore, information about possible catalyst poisons or other components (particulates etc.) that affect a catalyst’s performance are needed prior to the selection of an optimal catalyst for a catalytic
incinerator. Significant research efforts are directed toward finding proper techniques for the measurements of the VOCs in diluted concentrations (Dewulf & van Langenhove 1999; Czaplicka & Klejnowski 2002, Kim et al. 2004). VOCs include organic compounds that have very varied properties when compared to each other, and this is one reason why there is no single measurement method that allows e.g. sampling of the whole range of volatile organics (Wolkof et al. 1998). The VOC and SVOC emissions studied in this research, i.e. solvent emissions and pulp mill chip bin emissions, have some consistent and some characteristic features. These features are presented in the following sections in connection with measurement methods.

One common feature of emissions studied here, in addition to they’re being mixtures, is that both are present in relatively large concentrations. Owing to that, the detection of the diluted compounds is not so central matter. However, it cannot be entirely excluded, since sensitive measurements are needed in checking the concentrations after the catalytic oxidation of emissions.

It is good to keep in mind that in some emission sources the use of material balances is the only practical method to estimate VOC emissions accurately. When emissions are intermittent, diluted, or fugitive the source testing may turn out to be difficult and expensive. (Moretti 2001) For example the emission limits mentioned in the Solvent Emission Directive are determined by material balances, as they are based on the amounts of used solvents and concentration limits for emissions. The usage of material balances is one example of indirect emission measurement techniques. In the following sections, only direct measurement techniques are considered.

### 2.1.1 Continuous measurement methods

Direct measurement techniques include source testing and the continuous monitoring of VOC emissions. The quantity of emissions through a stack or vent may be calculated from the measurement results of emission total flow [e.g. m³ h⁻¹] and analysis results of emission samples [e.g. g m⁻³]. (Moretti 2001) Continuous measurements give, however, a better general view of emissions during fluctuating process conditions (Moretti 2001, Ojala 2003, Ojala et al. 2005d). These continuous measurement techniques often measure total VOC concentration (TVOC) and they are calibrated with one selected compound which should represent all the different compounds in an emission stream. For example, the *in situ* photo ionization detector (PID) and *in situ* flame ionization detector (FID) measure TVOCs and usage of the latter technique is required in many CEN (The European Committee for Standardization) measurement standards (Salmikangas 2004). A rather new technique *in situ* measurements is FTIR, which can be used to continuously measure several compounds simultaneously with a single piece of equipment (Anon 2005b).

The measurement of total volatile organic compounds (TVOCs) is frequently used to assess indoor air quality because the interpretation of a single parameter is simpler and faster than the interpretation of the concentrations of the several dozens of VOCs typically detected indoors. The concept can be useful in many cases in which there is some knowledge about the VOC profile. Non-speciated TVOC measurements may be useful for monitoring the effectiveness of physical changes in a building. In this case, the
selected calibration gas is critical in determining whether the TVOC is a good indicator of the real pollutant level. (Guo & Murray 2001)

According to Gostelow et al. (2001), odour measurement techniques, in which SVOC measurements may also be classified can be divided into two classes: sensory and analytical measurements. Sensory measurements employ the human nose and measure the effects of the odour as perceived by an observer. Analytical measurements characterize odours in terms of their chemical composition and attempt to quantify the odorants present. The dimensions of an odour refer to the measurable parameters of an odour, which are concentration of odorants, intensity (magnitude of perceived sensation), character (characteristic properties distinguishing one odour from another) and hedonic tone (pleasantness or unpleasantness of odour). Odorant concentration is the only odour dimension that can be measured analytically. The remaining parameters can be measured using sensory methods.

One sensory method for odour evaluation is olfactometry, in which a panel of experts tests the presence of odour in progressively diluted environmental air samples in order to estimate the lowest concentration at which the odour is perceived (Davoli et al. 2003). Another sensory method is an electronic nose, which tries to mimic the human nose by applying arrays of e.g. polymer or metal oxide sensors to detect gaseous odorous compounds (Shaham et al. 2004, Ampuero & Bosset 2003, Di Francesco et al. 2001, Nicolas et al. 2000). These electronic noses are normally less powerful than human noses, yet they offer some significant advantages in analysis such as in instrumental classifications based on hedonic or sensory analysis and in potentially automated on-line monitoring of volatiles (Ampuero & Bosset 2003).

Since the perception levels of the human nose are very low, even as low as the ppt level, analytical techniques are not always sensitive enough to ensure a direct detection of all malodorous compounds at such concentration levels (Davoli et al. 2003). Moreover, a person’s response to an odour is highly subjective – different people find different odours offensive, and at different concentrations. (Ampuero & Bosset 2003) However, at these detection levels of the nose the toxicity of the compounds is negligible (Bordado & Gomes 1998, Bordado & Gomes 2002). If the concentrations of odorous compounds are in the range of odour threshold limits, a pre-concentration of samples is often used to facilitate the analytical detection of individual compounds. Pre-concentration is also sometimes used in VOC analysis.

In general, analytical measurements have the advantages of objectivity, repeatability and accuracy when compared to sensory methods. Furthermore, importantly they can be used for theoretical models relating to odorant formation and dispersion (Gostelow et al. 2001). This is one reason why analytical measurements were applied in this research.

2.1.2 Sampling and analysis

Solid adsorbents, one of the sampling methods used in this study of VOC sampling, is the most commonly used method for low-concentration organic components sampling, particularly for indoor air. In this technique the sample is adsorbed on a solid adsorbent, then the adsorbed compounds are desorbed and analysed e.g. by gas chromatography (GC). A wide range of VOCs can be adsorbed by using multiple sorbents. (Dewulf & van Langenhove 1999)
As was mentioned, the adsorbed sample must be desorbed prior to analysis either by thermal desorption or by solvent extraction. Solvent extraction requires an adsorbent with a fixed volume of solvent for extracting the sample and injecting the extract into the GC. Thermal desorption extracts VOCs from the sample by using a purge gas stream. The filled sample tube is heated rapidly to release organics into the GC column. (Reeve 1994) In thermal desorption a second pre-concentration step may be necessary in order to achieve a good chromatographic separation. This is frequently done by cryogenic trapping, but electrically cooled traps are also used. (Dewulf & van Langenhove 1999, Rottweiler 2003) Using thermal desorption, detection limits are enhanced by a factor of $10^2$-$10^4$ over solvent extraction (Rottweiler 2003).

Another sampling method used in this study is bag sampling. For example, Tedlar bags (polyvinylfluoride material) are quite commonly used as sample collection bags. They are also commonly reused for multiple sample collection and event storing. The problem that arises with the multiple use of the same sampling bag is that bags sometimes cannot be thoroughly cleaned or flushed after sampling. It has been reported that some compounds tend to adsorb onto the surface of the bag and are very difficult to remove from the bag surfaces, e.g. methanol. McGarvey & Shorten (2000) concluded that methanol or other alcohols with low molecular weight should be analysed within the first 24 hours in order to ensure the accuracy of results. The reuse of Tedlar bags was considered to be reasonable in the collection of alcohols of a higher molecular weight after adequate flushing. Some problems with some substituted aromatic compounds were also found. Styrene and ethylbenzene caused a hysteresis effect in flushing. According to McGarvey & Shorten (2000) Tedlar bags may be used to collect ether samples, and they may be cleaned and reused without compromising subsequent analyses. Sample holding time did not appear to affect the observed concentration of ethers in Tedlar bags. However, long-term storage of contaminated samples, followed by cleaning and reuse of those bags, can lead to significant off gassing of contaminants into subsequent samples.

Canister sampling usually requires a subsequent adsorbent or cryogenic concentration stage in the laboratory. The major advantage of canister sampling, as with bag sampling, is that they make it possible to analyse a single collected sample several times, which is not always the case for a cryogenically collected or adsorbed sample. However, equipment that re-collects the desorbed sample after the first analysis, and thus allows several analysis of a single sample, is available (Rottweiler 2003). The critical points in the canister sampling technique are humidity, wall adsorption and conditioning. In addition, canister sampling involves a relatively high cost (e.g. transportation) and requires sophisticated equipment for the cleaning procedure. (Dewulf & van Langenhove 1999)

In recent years, quite a lot of research has been carried out on the sampling of odorous emissions. For example, it has been proven (Sulyok et al. 2001) that Tedlar bags are not suitable for sampling of SO$_2$ and H$_2$S gases, but the stability of other compounds such as mercaptans is high enough even when collecting ambient air samples. Sulyok et al. (2001) performed a study on different sampling containers: Tedlar sample bags, black/clear layered Tedlar sample bags and Silicosteel sample cylinders. They found that the stability of SVOCs in the standard Tedlar sample bags is sufficient enough if the analysis is carried out within 24 to 48 hours. Light protection is not necessary since the relevant SVOCs are stable over this storage period. In contrast to this, the use of black/clear layered Tedlar bags results in significantly lower recoveries presumably due to the uncontrolled adsorption of SVOCs to the black carbon filled Tedlar layer. A
passivation technology, named Silicosteel treatment, bonds a layer of silica onto the inner surface of the stainless steel parts to make the parts inert to sulphur compounds. According to Sulyok et al. (2001) the use of Silicosteel sample cylinders is also acceptable in this kind of sampling since cylinders demonstrate good performance in terms of the stability of methyl mercaptane. Another technology of passivation is the Sulfinert treatment, which enables the sample storage of sulphur gases at a low ppbv level, which is not possible even on inert fused silica-based coatings.

Zemmelink et al. (2002) conducted a study on the dimethyl sulphide (DMS) sampling. They used Tenax as a solid sorbent and Tedlar bags as samplers, and concluded a high stability of the DMS in the Tedlar collection bags, i.e. it preserves well. They allowed at least a one-week storage time; therefore the analysis could be performed away from the sampling site. DMS is a relatively unstable compound when pre-concentrated together with atmospheric oxidants, leading to significant losses unless oxidants are removed prior to trapping.

In addition to adsorption on the sampler surfaces and the unstability of sampled compounds, the moisture content of the emission gas may also cause some difficulties. A compound with sufficiently large water solubility may be partially absorbed into the aqueous phase and may not be recovered if water is condensed on the sampler surfaces (Ochiai et al. 2001). However, it has been reported that water vapor may also act as the main competitor for the inner surface adsorption of samplers, and thereby minimize the loss of sampled emission compounds by wall adsorption (Dewulf & van Langenhove 1999, Monod et al. 2003).

Due to the above-mentioned problems, all the materials used during the sampling and analysis should be as inert as possible. This is especially important with SVOCs, but similar problems may arise in VOC sampling. If the concentrations of VOCs and SVOCs are in the mg m$^{-3}$ range, as in our case, direct analysing after collection in suitable containers is possible by a gas chromatograph. However, pre-concentration was used when the analysis method was GC-MS.

Ultimately the possible error sources for a single sample are: sampling errors arising from the sample line, errors in sample collection, solvent evaporation, incompleteness of chemical reaction during sampling (sometimes needed for sample collection), transportation of sample, physical and chemical changes in the sample during the transportation and storage, as well as calibration and measurement errors in analysis. (Niskanen 1985)

The first task in sampling VOC or SVOC emissions is the collection of a sample, which is as representative as possible. The possible errors caused by environment, interfering components of the emission stream (e.g. moisture, particulates), the measurer himself etc. should be eliminated. In addition, time for sample collection should be adequate – not too long or short. Too short a sampling time will not give a representative portrayal of emissions and too long a sampling time may cause e.g. overfilling of solid adsorbents.

Second, storage of the sample should be appropriate for the sampler used. The selection of a suitable sampler should be based on the knowledge of the emissions to be measured (i.e. possible concentration level and components within the emission stream). Possible samplers may be for example canisters, sampling bags or solid adsorbents. Canisters and sampling bags should be stored in a warm place in order to avoid possible condensation of emission compounds or water on the sampler surfaces.
Third, analysis of the samples in the laboratory is very often carried out by GC (Pérez Ballesta et al. 2001, Dewulf & van Langenhove 1999). In the GC column, the emission mixtures are first separated and then identified and quantified by a suitable detector. Practice has shown that if there is no information available on the emission prior to sampling, at least the identification of the emission compounds by a mass selective detector (MSD) is of crucial importance. Further analysis may be carried out by other GC detectors, such as by FID for organic compounds, by flame photometric detector (FPD) for sulphur containing compounds and by thermal conductivity detector (TCD) for e.g. water. If the concentrations are low, pre-concentration of the samples is needed prior to analysis. The most widely applied pre-concentration procedures used in ambient-air sampling are based on adsorbents or cryogenic techniques. Desorption of samples is then performed thermally or by using a suitable solvent (Santos & Galceran 2002, Dewulf & van Langenhove 1999).

2.2 Basis for methodology development

The most sensible way to minimize time and possible problems in on site measurements is to start the collection of process information prior to measurements. Information about the process operation mode (continuous or intermittent), measurement sites and chemicals used will make the actual measurements, as well as selection of sampling and analysis methods easier. The proposed measurement methodology starts from this point (steps 1-3). This background information is also needed when evaluating the costs of the measurements. Second, the actual selection of measurement methods is done (step 4, Fig. 3). As it was discussed before, and will be shown further, a combination of continuous and sampling methods is affordable, since there is not yet a single method available to detect and measure all the compounds in emission mixtures. Even though the in situ FTIR method demonstrates this kind of ability, it is not yet widely used.

In the actual measurements, timing is important. The duration of continuous measurement should be long enough to eliminate the possible impact of transition states in the process performance on averaged values. Furthermore, sampling times should be recorded since the results should be comparable with the continuous measurements (step 6, Fig. 3). Continuous measurements give information about the process state, and explain the possible differences between the samples.

In conclusion, it is proposed that sampling in this measurement methodology be used mainly in qualitative analysis and for calculating the relative amounts of detected compounds. In that case the continuous and averaged total concentration measurements are used as the quantitative emission measure. These above mentioned phases are connected in Fig. 3 to generate a measurement methodology.
Fig. 3. Measurement methodology, steps 1-10 (Ojala et al. 2005d).
2.3 Experimental

The measurement methods used in this research included both continuous and sampling methods. The measurement methods, described below, were tested both in a laboratory and in industrial measurements.

In the industrial VOC emission measurements two *in situ* PIDs (PID1 and PID2) were tested as continuous measurement techniques. PID1 was also used in laboratory experiments as a continuous measurement method, and tested in chip bin emission measurements, where it was not used further due to an accumulation of sulphur compounds and defective measurement data. The calibration compounds of the PIDs were selected depending on the measurements; usually isobutene was used in industrial measurements and n-butyl acetate at the laboratory. A 10.6 eV lamp was used in both of the detectors. The PID responds to compounds with a photo ionisation potential equal or less than that of the energy source (Hobbs *et al.* 1995). According to manufacturer PID1 has repeatability of +/- 1% (isobutene). (Anon 1993)

In addition to PID, other techniques were used in the measurement of inorganic compounds in connection with VOC emission as well as SVOC emission measurements. For example, in the chip bin emission measurements the concentration of O₂ was measured by an electrochemical cell and CO and CO₂ were measured with an IR analyzer. The SO₂ measurements were based on UV fluorescence, and the NOₓ measurements on chemiluminescence. (see Ojala *et al.* 2005a) However, these measurement methods are beyond the scope of this research and are not considered in more detail later.

In this study, different sampling methods were applied, tested and evaluated. One of the techniques used was the adsorption of gaseous sample on a solid adsorbent. Tenax and activated carbon were used for adsorbent materials. The analysis of the adsorbent tubes was carried out by a GC-MS at the Oulu Regional Institute of Occupational Health, Finland. The extraction of the sample from the adsorption tubes was carried out with thermal desorption. The desorption procedure was as follows: the adsorption tubes were heated up to 60°C where temperature was kept constant for 1 minute, then the tubes were heated up first to 150°C at a rate of 10°C s⁻¹ and secondly to 250°C at a rate of 20°C s⁻¹, where it was kept for 2 minutes. This kind of procedure should guarantee total desorption of the adsorbed compounds. Adsorption sampling was used only in solvent emission measurements, even if in principle, it could have been applied to SVOC sampling, too (Zemmelink *et al.* 2002).

Sampling was also done in different kinds of sampling bags. Two different bag materials were used. The laminated metal foil bags (with volumes of 7 dm³ and 10 dm³) were manufactured in the ‘TESO koulutus’ workshop in Imatra, Finland. The metal foil bags are made from aluminium foil and coated with gold varnish + PETP (12 μm) and varnish + PE-film (85 μm). (N. Pesonen, personal communication) A simple rubber valve was used for the sample-introducing valve. The Teflon bags (with the volume of 3 dm³), manufactured by SKC Inc, USA, were used as a reference material. The Teflon bags were equipped with a Teflon fitting. The sampling procedure was as follows: prior to the sampling, the bags were flushed twice with the gas to be sampled. The sampling was carried out with a sampling pump (Thomas, Model No. 607CD22). Teflon lines were used in order to avoid adsorption of emission compounds on tubing surfaces. Even though no significant off-gassing of sampled emission compounds was observed when a
sample bag was flushed with nitrogen after sampling, the sampling bags were not re-used. Bag sampling was used in solvent emission measurements as well as in chip bin emission measurements.

An analysis of bag samples was carried out by a gas chromatograph equipped with a flame ionisation detector and a flame photometric detector (GC-FID-FPD) (Agilent Technologies, Model 6890N) or by a gas chromatograph equipped with a thermal desorption unit and a mass selective detector (TD-GC-MS) (Agilent Technologies, Model 6890N GC, Model 5973N MS). The operating conditions for both of the gas chromatographs were the same. The capillary column was J&W DB-VRX and the carrier gas (He) flow was 1.5 ml min⁻¹. The oven temperature was 150°C (isothermal operation) and the FID, used in the VOC analysis, operated at a temperature of 250°C. With the FPD detector, which was used to analyze SVOCs, the column was a packed column made of Teflon (Carbopack B 2%, Carbow 20 M + H₃PO₄ 0.5%) and later, in catalyst activity tests, another packed column (12% Polyphenyl ether and 0.5% H₃PO₄ on Chromosorb T 40/60 with a length of 26’ and diameter of 1/8” FEP). In the FPD analysis the initial oven temperature was 100°C, where it was kept for 2 min. Then the oven was heated at a rate of 20°C/min to 150°C, where it was kept for 10 min. The detector temperature was 240°C. In the TD-GC-MS system, the feed of the bag sample was carried out via the TD system (Tekmar 6000: AERO Can + AERO Trap Desorber + CRYO Focusing Module). In the TD unit, the bag sample was adsorbed and concentrated on a Porapak-QS adsorbent at a temperature of -160°C. Next, the sample was desorbed by heating up the adsorbent (to 200°C) and fed into the focuser where the sample was condensed into a capillary column at -185°C, in order to achieve a sharp feed. The analysis was carried out by the GC-MS. The TD-GC-MS was used only in the qualitative analysis.

### 2.4 Development of measurement methodology

#### 2.4.1 Collection of background information and process analysis

This section gives an example of the collection of background information and process analysis in methodology steps 1, 2 and 3 (See Fig. 3).

The solvent emission sources selected for this research are different coating processes. These coating processes are parts of the manufacturing processes of furniture and plastic products. The emissions originate from the painting and drying phases of the processes. In every case the majority of emissions are collected and released to the air via piping. In some cases some of the solvents are collected with the aid of water absorbers.

The solvents and coating agents used in these processes include ethanol (one of the major compounds), ethyl acetate, p-toluene sulfonic acid, sulfuric acid, n-butanol, butyl acetate (one of the major compounds), 1-methoxy-2-propanol, isobutanol, carbamide resin, melamine resin, propylene glycol monomethyl ether (PGMME), butyl glycol, 2-amino-2-methyl-1-propanol and 2-butoxyethanol. Furthermore, according to product information, in coated plastic products xylenes, propylene glycol monomethyl ether acetate (PGMMEA), some synthetic binder and polymers (PUR, polyester), organic pigments and fillers, hexamethylene diisocyanate, ethyl benzene, 1,6-hexamethylene diisocyanate
homopolymer, glycoethers, acetone, methyl ethyl ketone (MEK), toluene and isopropyl acetate were included. Sometimes the total amount of aliphatic hydrocarbons was also given. The amounts of the different compounds depended on the coating agent used. The emissions may also contain moisture and particulates e.g. wood dust from grinding.

The operations of processes are both continuous and intermittent. Lunch breaks etc. may stop the process and affect the release of emissions. However, fugitive emissions in a working place have certain minimum concentrations during working days. Prior to the measurements, the measurement sites were selected based on process layout drawings and photographs supplied by the factory.

The pulp mill chip bin was selected as the source of SVOC emissions since in many pulp mills the chip bin is not included in the collecting system of malodorous emissions. Few pulp mills in Finland collect diluted malodorous gases, which are oxidized in a recovery boiler or in a separate incinerator (Ojala et al. 2004a, Ojala et al. 2005a, Ojala et al. 2005e). However, malodorous gases are released into the air in process shutdowns or in cases when the recovery boiler is not operating normally.

Pulp mill chip bin emissions may contain volatile organic compounds such as methanol and terpenes, sulphur-containing organic compounds; mercaptanes and other organic sulphides; as well as inorganic sulphides such as hydrogen sulphide. Chip bin emissions also contain moisture and solids in notable amounts.

The operation of a process is continuous with only a few planned shutdowns during the year. Even if the pulping process is down, it does not entirely remove emissions, and furthermore, the emissions are released into the air since they cannot be treated in a recovery boiler. The measurement site is in a chimney on the top of the chip bin and extra precautions are needed due to the site (e.g. helmets and safety shoes).

2.4.2 Testing of continuous measurement methods

The following Sections 2.3.2 and 2.3.3 describe the testing and selection of continuous and sampling methods in measurement methodology step 4 (see Fig. 3).

PID1 and PID2 analyzers were tested at Topi Kalustaja furniture company in Finland. Measurements were carried out in the painting house, where the furniture parts are coated. The results of on-site comparisons are presented in Figs 4a and b. These figures show clearly one of the main difficulties in VOC measurements. Different measurement techniques, even analyzers that operate based on the same operation principle, may give different results. PID2 did not respond sufficiently to the changes in emission concentrations (see Fig. 4a). In addition, Fig. 4b indicates that PID2 did not respond to the change in VOC concentration during the mixing of paint either. Both of the measurements were performed at the same time, and the probes were placed closely to each other. 10.6 eV lamps were used, and both of the detectors were calibrated with 100 ppm of isobutene. Therefore, the results should be comparable. As can be seen in Figs 4a and b, the PID1 analyzer is more sensitive, and probably gives results that are more accurate than the PID2 analyzer. These kinds of inaccuracies or failures in measurements cannot be observed without comparative measurements.

Figs 4a and b also show that the calibration concentration i.e. 100 ppm is representative of these emissions. This should be checked prior to the actual measurements in step 5 of the measurement methodology.
Fig. 4. Total VOC concentrations at Topi-Kalustaja Oy as measured by PID1 and PID2 (a) coating line, painting, (b) indoor air, close to paint mixing; PID detectors calibrated with 100 ppm of isobutene (Ojala 2003, Ojala et al. 2005d).
After observing the possible problem described above, the performance and accuracy of
the PID1 analyzer was also tested in several laboratory scale experiments. Fig. 5 shows
the results of the measurements of total VOC concentration in a catalytic oxidation
experiment. The total VOC concentration was followed by PID1 and by GC-FID at the
outlet of the catalytic reactor. The temperature of the continuous flow catalytic reactor
was increased from room temperature up to 500°C during the experiment, which causes
the light-off of catalytic reactions and at the same time a decrease in the feed compound
concentration at the reactor outlet as the reactions proceed.

![Fig. 5. Total VOC concentration at the outlet of the reactor in catalytic light-off experiments
as measured by GC-FID and PID1 analyzers (Ojala 2003, Ojala et al. 2005d).]

Fig. 5 clearly indicates that the PID1 analyzer gives similar total VOC concentrations as
with the GC-FID analyzer. However, higher concentrations are underestimated. In these
experiments, PID1 was calibrated with n-butyl acetate (2000 ppm) that was used as a
model compound in the oxidation experiment and the concentration value measured by
PID1 was put down at the moment of the sample injection for the GC.

In spite of the fact that the use of FID in continuous measurements is recommended in
the measurement standard (Salmikangas 2004), PID1 was selected as a continuous
measurement method due to its simplicity and rather good accuracy. Furthermore, it gives
sufficiently accurate data about process changes. The reported detection level for the PID
used was 0.5 ppm of isobutylene (Anon 1993). The only problem that may occur in
measurements after the catalytic oxidation is that PID also gives response to nitrogen
oxides. However, the formation of nitrogen oxides is reported to be insignificant in
catalytic oxidation of solvent emissions, as it was also observed in our measurements
(Moretti 2002, Ojala 2004b, Ojala et al. 2005a). It is however important to notice, that if
the feed stream contains nitrogen-containing compounds, the formation of nitrogen oxides may occur (i.e. Fuel-NOx).

2.4.3 Testing of sampling methods

Prior to bag sampling the sample durability was tested at a laboratory. The bags were first tested with nitrogen gas to confirm the inert quality of the bag coating. In these tests, no desorption of any compounds from the bag surface was observed when nitrogen was stored for 4 days and the sample was analysed with a gas chromatograph equipped with a mass selective detector (GC-MS).

Sample durability tests were carried out both for a representative VOC mixture and a SVOC mixture. The SVOC test mixture included H₂S (~600 mg m⁻³), methyl mercaptane (MM) (~2800 mg m⁻³), dimethyl sulphide (DMS) (~550 mg m⁻³) and dimethyl disulphide (DMDS) (~450 mg m⁻³) and the VOC test mixture methanol (~30 ppm), ethanol (~180 ppm), i-butanol (~80 ppm), toluene (~13 ppm) and n-butyl acetate (~1500 ppm). The concentrations of the compounds were measured after introducing the sample mixture inside the sampling bags and after certain storage times. The results of sample durability tests are presented in Figs 6a and b. The analysis of each sample was carried out at least twice and the repeatability of analyses was ~5% (in Fig. 6a) and less than ~0.5% (in Fig. 6b). Averaged values of the analysis results have been used in the calculations. Separate bags were used for different storage times in order to avoid possible dilution or slip during the analysis.
Fig. 6. Sample durability a) VOC mixture durability in laminated foil and Teflon sampling bags and b) SVOC mixture durability in laminated foil sampling bags with different storage times from three hours to three days.
Figs 6 show that in general, the durability of the sample is very good. The experiments with the VOC mixture showed that the sample durability was surprisingly good in the laminated foil bags when compared to the sample durability offered by Teflon bags (Fig. 6a). Fig. 6a shows that the initial concentrations of compounds included in the testing sample decreased approximately by 10% during a one-day storage. After three days of storage, the concentrations are further decreased in Teflon bags by an average of 65% and in metal foil bags by approximately 20%. It can be concluded that, in general, the sample durability is better in laminated foil bags than in Teflon bags. In the case of the SVOC mixture, the sample durability is even better. The concentrations of the model compounds decrease only very slightly after two days of storage in a metal foil bag. In these experiments, VOC concentrations were measured by GC-FID and SVOC concentrations by GC-FPD. Sample durability and repeatability were also tested with industrial samples (Figs 7a-b).

Fig. 7. Emissions of a) painting, b) drying.
Figs 7a and b show the analysis results of industrial samples in laminated foil bags. Analyses 1 and 2 were carried out during the same day; analyses 3 and 4 were performed the next day, and analyses 5 and 6 after 3 days of storage. The amounts of detected compounds did not significantly decrease after one day of storage, only a 5% decrease was observed. In contrast, after 3 days of storage, the concentrations decreased to less than half of the initial value and some of the VOC compounds were not detected at all (e.g. n-butyl acetate in Figure 7a). This is probably due to sample leakage or dilution of the sample during analysis, since all these analyses presented in Figs 7a and b were carried out from the same sample bags, which was not the case in Fig. 6a. In addition to sample durability, Figs 7a and b show that the reproducibility of the GC analysis is very good.

Sample durability in adsorption tubes was not tested since the measurement and analysis procedure as well as analysis of the adsorbent tubes was carried out at Oulu Regional Institute of Occupational Health. Comparison of the analysis results of adsorption tubes with the analysis results of bag sampling and continuous measurements was carried out in connection with the solvent emission measurements. The results of these comparisons are discussed in the next section, Section 2.5.

The experiments also demonstrated that the calibration procedure of the GC is of crucial importance in the quantitative analysis of VOC compounds. The calibration of single compounds should be carried out in a similar fashion to the feeding of a sample. Tests showed that if the sample contains mostly air, the calibration of different compounds should also be carried out with an air mixture. If the VOC calibration is done by vaporizing the liquid compound, which is then mixed with an inert gas (e.g. He), the analysis results were different from when calibrated with a VOC-air mixture. The concentrations were also dependent on how the sample was fed. If the sample was fed from a pressurized sampler, the calibration should also be done under pressurized conditions, preferably via a similar sampler. More reliable results were achieved by sucking the sample with a pump. However, the calibration should also be done the same way. Additionally, the calibration of a GC by the response factor method, as was done in our case, may result in over-estimation of small concentrations and under-estimation of high concentrations (Pérez Ballesta et al. 2001). Furthermore, the GC-MS is a very important piece of equipment in identifying the VOC compounds, since different VOC compounds may have the same retention times in a GC column and those compounds are easily falsely detected when using only GC-FID. After identification of the compounds, the GC-FID was used in quantitative analysis.

The sampling in metal foil bags was selected for further use. This selection is reasonable, since the sample durability for both VOCs and SVOCs is good and the analysis is reliable enough. The sampling in metal foil bags is also suitable in this case, since emission concentrations are rather high. Solid adsorbents are easily overfilled, and thus the sampling time is short, which results in considerable sampling errors. However, they are suitable in the fugitive emission sampling in a working place. Identification of the compounds within an unknown sample should be carried out with GC-MS but the further analysis may be carried out with GC-FID. In addition to the faster analysis with the FID-detector, it is more sensitive than the GC-MS used in the scan-mode.
2.5 Results of emission measurements and discussion

This section describes the results of different emission measurements and connects the results to background information. In addition, the results are evaluated by comparing different measurement methods. The section includes steps 6-10 in the measurement methodology (see Fig. 3).

The emission measurements in solvent emission sources showed that continuous measurement of emissions by PID gives a good estimate of the emission level of the process. It also gives on-line information, which can be used in the selection of the suitable moment of sampling. This is essential with an intermittent process operation.

In general, the VOC emissions from the two furniture manufacturers were similar. The compounds detected according to adsorption sampling, compared with the compounds mentioned in the product information, are presented in Table 2. Fig. 8 shows the combined relative amounts of detected compounds from both of the companies.

Table 2. Detected compounds in adsorption sampling and the compounds mentioned in product information. (1 – most dominating, 2 – second dominating, 3 – third dominating, x – detected)

<table>
<thead>
<tr>
<th>VOC compound / in product information</th>
<th>Topi-Kalustaja / measured VOC</th>
<th>Incap Furniture / measured VOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Painting</td>
<td>Drying</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>x</td>
<td>3</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamide resin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melamine resin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGMME**</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Butylglycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>i-Propanol</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>Methyl cyclohexane</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

* not determined, ** propylene glycol mono methyl ether (1-metoxy-2-propanol), *** mixture of aliphatic hydrocarbons with boiling point level of 82-108°C
Fig. 8. Relative amounts of detected solvent VOC compounds (combined emissions from Topi-Kalustaja and from Incap Furniture Varpaisjärvi factory).

In surface coating operations, the majority of emissions are released during application and curing, which was also observed in these measurements. The two most dominant compounds are ethanol and n-butyl acetate, of which ethanol is released mainly during application and n-butyl acetate during curing. The detected compounds, presented in Table 2, deviate in part from the product information. In addition to five matching compounds, seven of the detected compounds are not mentioned in the product information; furthermore, one compound could not be identified for an unknown reason. There are also eight compounds mentioned in the product information that were not detected.

One of the coating processes operates continuously and thus the average emission values for painting, ~569 mg m$^{-3}$, and drying ~565 mg m$^{-3}$, give quite a good approximation of the total VOCs emitted. In this case the sampling methods, too, give more realistic emission concentrations than in the intermittent operation of a process. The comparison in Tables 3 and 4 shows that the measurement results achieved by different measurement methods deviate from each other significantly. (Ojala et al. 2005d)
Table 3. Comparison of total VOC concentrations at Topi-Kalustaja Oy measured by PID1 and according to the metal foil bag (10 dm$^3$) sampling analyzed by GC-FID (Ojala 2003, Ojala et al. 2005d).

<table>
<thead>
<tr>
<th>Measurement site</th>
<th>GC-FID analysis of metal foil bags (on the same day)</th>
<th>Total VOC concentration as measured by PID1 (isobutene equivalent) [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total VOC calculated as isobutene</td>
<td></td>
</tr>
<tr>
<td>1 (painting)</td>
<td>205</td>
<td>83</td>
</tr>
<tr>
<td>2 (drying)</td>
<td>263</td>
<td>135</td>
</tr>
<tr>
<td>3 (drying)</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>4 (drying)</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>5 (painting, fugitive)</td>
<td>112</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 4. Comparison of total VOC concentrations at Incap Furniture Oy as measured by PID1 at the moment of sampling and total VOC concentrations according to Tenax samples analyzed by GC-MS (Ojala 2003, Ojala et al. 2005d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total VOC concentration by GC-MS (includes compounds between hexane and hexadecane) [ppm]</th>
<th>Total VOC concentration in continuous measurements by PID (isobutene equivalent) [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenax 1</td>
<td>14</td>
<td>40</td>
</tr>
<tr>
<td>Tenax 2</td>
<td>17</td>
<td>41</td>
</tr>
<tr>
<td>Tenax 3</td>
<td>14</td>
<td>41</td>
</tr>
</tbody>
</table>

Table 3 indicates that the total concentrations measured by PID1 are smaller for higher concentrations and larger for smaller concentrations than the total concentrations measured by the metal foil bag sampling and GC-FID-analysis. The total concentrations achieved by the sampling methods in Table 4 (i.e. Tenax + GC-MS analysis) are smaller than the total concentrations measured by PID. The differences may be due to the selection of the PID1 calibration compound (isobutene) and its concentration (100 ppm), as well as to the calibration area of compounds in GC-MS or GC-FID analyses. If the calibration compound and concentration were similar to that measured, GC-FID and PID1 gave similar results, as presented in Fig. 5. Furthermore, in Tenax sampling, low volatility compounds or compounds that form strong bonds with the adsorbent may not be displaced in thermal desorption (Brown 2002). Table 4 also shows that in solvent emission measurements it is probably not enough to scan the compounds within the range of hexane - hexadecane, since, in painting, for example, the most dominating compound, ethanol, will be excluded.

Teflon-made sample lines were used in sampling and in continuous measurements. With a silicon-made sample line, accumulation of VOC compounds on the inner surfaces of the sample line was observed. This impairs the PID read-out when measuring mixtures of several compounds. In addition, desorption of some compounds in the tubing surface may cause false detections during successive emission measurements. Some difference in the results may also arise from the ionization potentials of different compounds. A 10.6 eV lamp does not detect ethane, formic acid, methane, methanol, propane, sulfur
oxides and water (Anon 2001a) and the sensitivity of PID increases as the carbon number increases (Anon 2001b). If these low carbon number compounds are present in the measured emissions, PID might give smaller total concentrations than the GC-FID analysis. However, these compounds were not observed from the bag samples from Topi-Kalustaja Oy (Figs 7a and b). In addition to organic compounds, PIDs can be used to measure some inorganic compounds such as ammonia, arsine, phosphine, hydrogen sulfide, nitric oxide, bromine and iodine (Anon 2001c). If these compounds are present in the VOC stream, a PID gives larger total concentrations than a GC-FID. None of these compounds are likely included in solvent emissions. Nitric oxide was not observed after the catalytic oxidation of solvent emissions in industry, which suggests that it does not affect the results of PID measurements presented in Fig. 5.

The main practical problem that occurred with solid adsorbents was the possibility of overfilling the adsorbent. The Tenax and activated carbon are good adsorbents when measuring indoor fugitive emissions. The problem arises when the samples are taken directly from the process vent gases. The Tenax adsorbent is easily overfilled and, therefore, the possible sampling times are very short, only dozens of seconds with a standard sampling pump. Longer sampling times were used with activated carbon, and thus the sampling error was smaller. Another drawback with these adsorbents is that they do not adsorb light hydrocarbons very well. For this reason ethanol may be excluded. Tenax is a commonly used adsorption material; however, it is not suitable for highly volatile or strongly polar compounds due to its low capacity for those compounds (Health and Safety laboratory 1995, Brown 2002).

VOC emissions from the company that produces plastic products did not deviate much from furniture manufacturers’ emissions. The emissions contain acetone, alcohols (methanol, ethanol and n-propanol), toluene and esters (ethyl acetate and n-butyl acetate), heptane, methyl ethyl ketone (MEK) and xylene. Aromatic hydrocarbons were also detected. These detections are consistent with the product information. Total concentrations varied according to the process operation from a few ppm to more than 1000 ppm. Fig. 9 presents the total VOC concentration and the temperature of the gas flow close to the inlet of the catalytic incinerator. These emissions represent the total VOC emissions from the coating process.
The emission measurements from a chip bin showed that a PID is not a reliable measurement method for the organic compounds included in these emissions whether the calibration is done with isobutene or with methyl mercaptane. When the PID was calibrated with methyl mercaptane, it was observed that some odorous compounds accumulated into the detector and the concentration increased as a function of time. The error due to the accumulation was so large that the results were not reliable. Furthermore, after the measurements, the cleaning of the PID detector took a lot of time. Due to these facts, the PID analyzer was not further used in the pulp mill emission measurements. Another continuous measurement method, for example in situ FTIR would be more suitable in this case.

Based on the continuous emission measurements, it was observed that the emission gas from the chip bin at the inlet of the catalytic incinerator included water (14 g kg⁻¹ of dry gas), and its solid content was 0.003 kg h⁻¹. The temperature of the sampled emissions was 11°C, which means that the gas was supersaturated since the water content was over 8.2 g kg⁻¹ of dry gas. The temperature of the laboratory at the time of analysis was 24°C. The moisture content (absolute humidity) of 24°C air in 1 atm for saturated vapor can be ~617 g(H₂O) kg⁻¹(dry air), which means that when the sample is stored at the laboratory temperature it is not likely that condensation of water occurs inside a sampling bag. Furthermore, condensation of water on the inner surfaces of sampling bags has not been observed. In addition to water (~2 vol-%) and solids, the emission gas also contained 21 vol-% of O₂, 0.2 vol-% of CO₂ and ~10 ppm of CO. Nitrogen oxides were not detected. A small amount of SO₂ was observed in continuous measurements, but most probably the detected concentrations were due to other sulphur-containing compounds rather than SO₂ since SO₂ was not observed in the analysis of the bag samples.
According to the metal foil bag sampling and analysis by GC-FPD the emissions contained hydrogen sulfide (H₂S), COS, methyl mercaptane (MM), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) as illustrated in Fig. 10.

Fig. 10. Analysis results of 7 dm³ laminated foil bag samples taken from the scrubber, from the inlet and from the outlet of the catalytic incinerator at the oxidation temperature of ~350°C. MM = methyl mercaptane, DMS = dimethyl sulphide, DMDS = dimethyl disulphide.

Analysis results of the bag samples shown in Fig. 10 indicate that there is a significant difference in the inlet concentrations between the samples analyzed at the University of Oulu (indicated as “OU”) and those analysed at the pulp mill laboratories (indicated as “SE”). This is due to the dilution of samples at the pulp mill laboratory. As the results show, in this case the detected concentrations are relatively high, at the mg m⁻³ level, and thus direct bag sampling without any pre-concentration steps prior to analysis should be adequate enough to give sufficient measurement accuracy.

These measurements as well as the laboratory experiments presented in the previous section (Section 2.4.2) showed that the sampling in laminated foil bags and subsequent analysis by GC-FID-FPD or GC-MS provide reliable qualitative and quantitative results on both solvent and chip bin emissions. Therefore, it can be selected as a sampler in step 4 of the measurement methodology. The usage of adsorbent tubes in qualitative analysis is also possible, but for quantitative measurement purposes they are too easily overfilled because of high emission concentrations, as in this case. PID is a suitable continuous measurement method for solvent emissions, but another method, e.g. in situ FTIR is a better choice in the case of chip bin emissions.
2.6 Conclusions and application

In this chapter, conclusions from all the methodology steps are drawn, advantages and disadvantages are discussed and application of the methodology is suggested.

As a summation, Fig. 11 presents the idea of combining continuous and sampling methods. Short-term sampling, as illustrated with the six sampling points in Fig. 11, cannot give an accurate account of emissions and, therefore, if sampling is used without connection to continuous measurements, the results should be used only as qualitative information about the emitted compounds. Continuous measurements can easily indicate changes in emission concentrations caused by the process operation.

![Fig. 11. Comparison of continuous measurements and sampling methods. Continuous measurements were carried out with a PID1 analyzer (solid line), sampling was done with 10 dm³ of laminated metal foil bags and analyzed by GC-FID and GC-MS-FID (arrows).](image)

Furthermore, even if the measurements confirmed that continuous PID1, which is a rather inexpensive apparatus to purchase and use, gives rather reliable results, it does not by itself give results that are sufficiently representative. The sampling in laminated metal foil bags and analysis by GC-MS can be used to provide qualitative information about the emitted compounds. In addition, analysis by GC-FID will bring out compounds that are not detected with a PID, and thereby reveal the possible falsies in TVOC measurements.

Collection of the background information about the process and the coating agents used is needed for selecting a proper calibration compound to the PID. The importance of the background data collected increases when the reliability of the measurement techniques decreases.

The measurement methodology described in Fig. 3, can be used in routine measurements, and it will simplify executing VOC as well as SVOC emission
measurements in industry. In addition, the following recommendations will reduce the total costs of the measurements:

- Collection of background information on the coating agents (Information on coating agents will ease the selection of suitable measurement technique, and may also allow selection of cheaper measurement technique.) and process operation used (Information on process operation will ease the timing of measurements. For example moments of sampling etc. may be selected beforehand and the time for measurements can be optimised.);
- Usage of laminated foil bags;
- Usage of a PID as a continuous measurement technique for indicating process changes.

In addition to savings in time and money, the advantage of the methodology is that, the combination of different measurement methods helps in determining whether some single method is not feasible for the case in question.
3 Construction materials

The second part of the process characterization focuses on construction materials. It has been reported that selection of construction materials for catalytic incineration is easier and more economical than for thermal oxidation (Hayes & Kolaczkowski 1997, Jennings 1985, Moretti 2001). In general, the temperatures are lower, and thus the operation conditions are not as demanding as in thermal oxidation. The selection of construction materials for industrial processes should, however, be done carefully. The operation conditions must be taken into account as well as the compounds, which are oxidized. For example in the oxidation of SVOCs and chlorinated VOCs, acidic compounds may also be formed. (De Nevers 2000) In this chapter the operation of the catalytic incineration process related to this research, is discussed in more detail to give an idea of the process conditions. Different aspects related to construction materials are discussed and experimental results are presented later.

3.1 Introduction

As already mentioned in Section 1.2, the catalytic incinerator related to this research operates with flow-reversal. The flow-reversal concept was originally patented by Cottrell in 1938 in the USA (Cottrell 1938) and further developed and applied to different purposes (e.g. catalytic VOC oxidation, NO reduction, SO₂ oxidation) by several researchers, for example Matros and co-workers (Ben-Tullilah et al. 2003). The flow-reversal system operates in transient conditions. It has been reported that a temperature maximum is developed inside a catalyst, which slowly oscillates towards both ends of the catalyst bed when flow directions are reversed. (Salomons et al. 2003, Salomons et al. 2004, Ben-Tullilah et al. 2003) This may be beneficial for oxidation reactions. Using an inert material at both sides of the catalyst can minimize the amount of catalyst and energy supply. Furthermore, when inert material is used, the main temperature changes occur in the inert zones and the catalyst temperature is rather constant, which may prolong the catalyst lifetime. (Matros et al. 1993)

The time for the flow reversal should be selected so that the temperature maximum does not escape from the catalyst bed or catalyst-inert bed. The flow reversal time may be
operated automatically, after certain time intervals, based on temperature measurements and according to manual signals. (Matros et al. 1993) The catalytic incinerator in connection with this research is operated based on temperatures. The flow directions as well as the inlet valve of dilution air are controlled by temperature sensors. The setting values for temperature, e.g. minimum inlet temperature, when flow should be reversed and the temperature when the dilution air valve should be opened are selected depending on the application area. In general, in VOC incineration the setting values for temperatures are lower than in SVOC incineration.

In VOC and SVOC oxidation conditions, the temperatures within the reactor are different according to the process operation and the location in the incinerator. They are also dependent on the temperature of the gas flow. At the inlet, the temperature of the gas flow is rather low, depending on the temperature of the incoming emission stream and surrounding temperature. Thus, piping materials at the inlet part of the incinerator rarely meet temperatures over 100°C.

When the gases at the inlet reach the first heat exchangers (heated up in the previous flow cycle) and pass through them, the gas temperature will increase up to the setting value of the incinerator and even higher within the catalyst. This is due to exothermic reactions and the locations of the temperature sensors. In the catalysts and in the heat exchangers after the catalysts, temperatures are thus also dependent on the concentration of the compounds and the gas flow velocity. Materials close to the catalysts are exposed to the maximum level of temperature.

After the catalysts, the temperature of the gas flow will start to decrease when the reaction heat is stored in the heat exchangers following the catalysts. When the gas reaches the blower, its temperature is decreased to the maximum value allowed of ~200°C, or less, depending on the efficiency of the heat exchangers. With regenerative heat exchangers, as used in this application, up to 90% heat recoveries are possible (Eigenberger 2005).

The maximum temperatures in the normal operation of an incinerator in VOC oxidation are close to 520°C, and in SVOC oxidation as high as over 600°C. However, these values are highly dependent on the setting values of the operation, compounds and their concentrations. In addition, as was mentioned earlier, catalyst surface temperatures may be even higher. In addition to temperature, other special requirements for construction materials may arise from particulates, which may cause fouling, for example; and from possible corrosive compounds, e.g. water and sulphuric acid, as in this case. Furthermore, some unwanted reactions might occur during incomplete combustion and may also cause fouling of the heat exchangers. Usually, particulates included in emission stream are filtered before the gas enters the first heat exchangers.

In the present catalytic incinerator, Al-Zn-Si –coated steel (referred to as Aluzinc) is used as the heat exchanger material. Aluzinc coating contains approximately 55% Al, 1.6% Si and the rest Zn. 1.6% Si is added to the coating to prevent an exothermic reaction at the coating’s overlayer/substrate steel interface during the hot-dip process. (Marder 2000, Carlsson 2005) The surface of Aluzinc contains characteristic spangles that consist of aluminum dendrites, Zn-rich interdendritic regions and a fine dispersion of Si particles (Marder 2000). Furthermore, it has been found that a few nanometers thick layer of aluminum oxide, γ-Al₂O₃, is formed on the surface immediately after the substrate steel strip has been immersed in the metal bath in the hot-dip coating. (Carlsson 2005) Aluzinc has been reported to have a high long-term durability especially in atmospheric conditions (Carlsson 2005, Palma et al. 1998, Anon 2005a). The good corrosion
resistance of this coating is a result of the barrier protection due to the Al combined with the galvanic protection, due to Zn (Rocco et al. 2004). However, black rust forms on the Aluzinc plates during storage in damp conditions (Odnevall Wallinder et al. 1999). This rust consists of bayerite (Al(OH)$_3$) mainly precipitated on aluminium-rich dendrites and zinc aluminum carbonate (Zn$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O) on the zinc-rich interdendritic regions. (Carlsson 2005, Odnevall Wallinder et al. 1999)

In VOC incineration, higher conversions of VOCs are sometimes observed than expected based on the laboratory studies. This may be due to the flow-reversal operation of the incinerator, but also partly due to construction materials. When the concentrations of VOC compounds were measured before and after the heat exchangers, it was observed that the total VOC concentration (TVOC) decreases further within the heat exchangers placed after the catalysts. The concentration before the heat exchangers was once measured to be 60 mg m$^{-3}$ and after the heat exchangers 8 mg m$^{-3}$ (Ojala 2003, Ojala et al. 2005b). Therefore, in addition to the thermal durability of construction materials, this chapter also investigates the possible effect of construction materials on the end conversions. Furthermore, the fouling of the heat exchangers is considered in the incineration of chip bin emissions. Both Aluzinc plates and AISI 304 stainless steel are included in this study, since other constructions of the catalytic incinerator are made of AISI 304 stainless steel. In addition to Fe, AISI 304 stainless steel contains a maximum 0.05w-% of C, approximately 17.0-19.0 w-% Cr, 8.0-11.0 w-% Ni, max. 1% Si, max. 2.0% Mn, max.0.045% P and max. 0.030% S (Kyröläinen 2004).

### 3.2 Experimental

#### 3.2.1 Thermal durability of Aluzinc

The thermal durability of Aluzinc was tested in a muffle furnace in air atmosphere. The Aluzinc plates were heated starting from room temperature to 900°C. Prior to experiments, the tested material was cut into 65x75 mm plates and placed on a tray. In the experiment seven plates were placed inside the furnace. First, the furnace was heated up to 300°C and kept there for 30 minutes. Next the first plate was taken out from the furnace. After the first plate, the furnace was heated by 100°C up to 400°C where it was kept for 30 minutes before the second plate was taken out etc. The temperatures used were 300, 400, 500, 600, 700, 800 and 900°C. At the end, the last plate was kept in the furnace approximately for six hours. After the experiments the durability of plates was evaluated visually, which allows rough observation of the changes on the surfaces of the plates.
3.2.2 Laboratory set-up for testing of catalysts and construction materials

The effect of different metals as well as inert material on the oxidation of n-butyl acetate (a model VOC compound) was tested in the laboratory. The experiments were carried out in a tubular continuous flow quartz reactor placed inside a tubular oven. The n-butyl acetate was fed by a calibrator in which a syringe pump injected the liquid phase compound to the heater to be vaporized and mixed with air. The airflow was regulated by a mass flow controller. The temperature of the oven was increased from room temperature to ~800°C, except with glass granules to only ~600°C due to a softening of the granules. The outlet gas flow was analyzed by using the GC-FID (Agilent Technologies Model 6890N). A similar arrangement was used in the light-off tests with catalysts.

The experiments in testing the effect of construction materials were carried out with and without a catalyst, with different metal plates, with inert glass granules and without any packing material, the latter called a thermal experiment. The experiment with glass granules was performed with two different packing sizes (30 and 60 pcs). While the different materials were inserted into the reactor, thus changing the packing volume, the catalyst volume and gas flow (1 dm$^3$ min$^{-1}$) were kept constant, in order to maintain the same space velocity (GHSV; 31,500 h$^{-1}$) within the catalyst honeycomb. The GHSV of 31,500 h$^{-1}$ is similar to the theoretical industrial scale GHSV. Fig. 12 shows the experimental set-up, which was also used in the testing of catalytic materials.
3.2.3 Fouling of the materials

The possible formation of polymer due to incomplete oxidation of terpenes was tested at a laboratory with a set-up similar to the one described in Fig. 12. In addition to experiments on polymer formation, the turpentine oxidation activity of a catalyst similar to the one used in the industrial-scale in the chip bin emission abatement was tested. Wood-based turpentine was used as the representative compound in both catalytic activity tests and polymer formation tests, since the terpenic emissions from the chip silo contained mostly α- and β-pinenes (Ojala et al. 2005a). In activity tests the GC-FID was calibrated with α- and β-pinene. Since the used model compound was ‘French turpentine’, the calibration was carried out with that ‘certain’ turpentine and not with pure compounds. However, the other data needed in the calibration was the data for the pure compounds. This may cause some systematic error in all of the experiments, nevertheless the systematic error is the same in all the experiments and the results are therefore comparable with each other. The concentration of α-pinene in turpentine was around...
1650 ppm and in β-pinene approximately 350 ppm. In general, the GHSV of ~31,500 h\(^{-1}\) was used in the experiments.

Fouling of the materials in the oxidation of chip bin emissions was monitored in an industrial scale incinerator with metallic test sticks. The sticks, made of Aluzinc and AISI304 steel, were placed between the heat exchangers and kept there for a few hours. Evaluations of fouling were done visually and with a Fourier transform infrared analyser (FTIR) as well as with X-ray diffraction (XRD). The XRD diffractograms were recorded by a Siemens D5000 diffractometer employing nickel-filtered Cu Kα radiation (λ = 1.5406 Å, 40 kV, 30 mA) at 0.02° intervals in the range of 10° ≤ 2θ ≤ 75° directly from the metal plates and the catalyst foils. A FTIR (Perkin Elmer Spectrum One) equipped with an Attenuated Total Reflectance (ATR) unit was used to give information on the bonds on the solid surface. The measurements were carried out at room temperature directly from the metal plates and catalyst foils with the ATR unit. The spectra were measured in the range of 4000-650 cm\(^{-1}\). All XRD analysis as well as FTIR analysis was done in cooperation with the Central Ostrobothnia Polytechnic in Kokkola.

The possible corrosion of materials by sulphuric acid was also tested. In the laboratory experiments, Aluzinc and AISI 304 steel plates were placed on the upper part of a closed apparatus where at the bottom sulphuric acid with water was vaporized and the vapour was ducted to the metal plates. The experiments were carried out for 2 hours first with 50 w-% sulphuric acid and then for approximately 8 hours with 10 w-% sulphuric acid. In addition, the Aluzinc and AISI 304 steel plates were corroded in 93.5 w-% sulphuric acid solution over night. Evaluation of the corrosion was carried out visually and with an FTIR and XRD.

The material that formed inside the industrial-scale incinerator and caused fouling of the heat exchangers in SVOC oxidation was analysed with different methods of analysis. Thermo gravimetric analysis (TG) with gas analysis (MS) (NETZSCH STA 409 PC/PG) was carried out in the Laboratory of Metallurgy in the Department of Process and Environmental Engineering at Oulu University. The experiment was carried out in an air/helium atmosphere with a heating rate of 20°C/min from 25°C to 1000°C. A chemical analysis of the material itself and its ashes, a head-space MS-analysis and a nuclear magnetic resonance (NMR) analysis were carried out in the Department of Chemistry. The metal concentrations in the deposit were also measured by atomic absorption spectrometry (AAS) in the Department of Process and Environmental Engineering at Oulu University.

### 3.3 Results and discussion

#### 3.3.1 Thermal durability of Aluzinc

The thermal durability of Aluzinc was evaluated visually after the furnace tests described in Section 3.2.1. According to the manufacturer Aluzinc is stable up at least to a temperature of 315°C (Anon 2005a). This was also confirmed in the experiments (See Fig.13a). In the first three samples (temperatures 300°C, 400°C and 500°C), no significant changes were observed. After the experiment at 600°C, the surface of the
Aluzinc started to change colour. Furthermore, the samples at 700, 800 and 900°C were green soon after taking them out of the furnace, but after a while they turned to a grayish colour. The samples are presented in Figs 13 a and b.

The Aluzinc coating consisted of aluminum 55 w-%, zinc 43.4 w-% and silica 1.6 w-%. As pure compounds, the melting points of the above mentioned metals are 660°C, 420°C and 1410°C, respectively (Weast 1977). According to an Al-Zn alloy phase diagram (van Lancker 1967), with this mixing ratio, the melting point of the alloy is approximately ~560°C. (Si was not included into the diagram.) According to manufacturer (Anon 2002) the melting point for aluminised layer of Aluzinc is ~580°C.

![Fig. 13. Aluzinc samples a) after the experiments, b) sample 7 soon after being removed from the furnace.](image)

This study shows that Aluzinc should not be used at temperatures above 500°C, or more precisely, above 560°-580°C, where the protective coating of steel starts to degrade. Furthermore, the time spans used in this study were rather short, and most likely the time also contributes to the degradation to some extent. The temperature limits of Aluzinc should be taken into account especially in the case of SVOC oxidation due to higher oxidation temperatures needed. At least the heat exchangers close to the catalysts are exposed to elevated temperatures and should be made of more thermally durable material.

### 3.3.2 Effect of materials in oxidation of n-butyl acetate

The possible effect of the heat exchangers’ construction materials on the oxidation of n-butyl acetate was studied at the laboratory. The experimental arrangement is described
in Section 3.2.2. Fig. 14 illustrates the results of the laboratory-scale experiments. The addition of packing material into the reactor results in less $T_{50}$ (temperature of 50% conversion) of n-butyl acetate than in the thermal experiment. The effect of the metallic or inert glass material on the light-off temperature is not as significant as the effect of the catalyst. However, if the reactor bed consists of combinations of a catalyst and metallic or glass material, the $T_{50}$ temperature of n-butyl acetate is not further decreased.

There are at least four possible effects of the heat exchanger material on the n-butyl acetate oxidation. It is known that organic combustion reactions in the gas phase are sensitive to the size of the reactor vessel and the nature of its surface. Firstly, heat exchangers in the industrial-scale may act as a ‘third body’, which initiate oxidation reactions. (Laidler 1987) Secondly, the heat exchangers may improve the mixing of emission gases, and thus intensify the contact of oxygen molecules with VOC compounds and, ultimately enhance the oxidation reactions. A third possibility is that metal improves the heating of the gas and creates a larger heat exchange area. Finally, one explanation can be that the metallic construction material is catalytically active.

The effect of the surface area was tested with inert glass granules. The amounts of glass granules within the packings were 30 pieces, which corresponds to the outer surface
area of the metal packing, and 60 pieces. As Fig. 14 shows, no significant effect was observed when the surface area of glass granules was doubled. Moreover, the effect of better mixing when glass granules were used had a minor effect on the temperature of 50% conversion (T_{50}) of n-butyl acetate. It is worth mentioning that metal packing also suffers from bypassing and the effective surface area may be even smaller than the total external surface area listed in Table 5.

In the experiments with other packing materials it was observed that stainless steel (AISI 304) packing did not greatly enhance the oxidation reaction, whereas Aluzinc and copper significantly decreased the T_{50} temperature of n-butyl acetate. Aluzinc and copper packings gave a ~100°C and a ~200°C decrease, respectively, in the T_{90} temperature of n-butyl acetate. However, none of these packing materials was as effective as the catalyst, which gave a decrease of over 300°C in the T_{50} temperature. Some of the properties of the used materials and packings are presented in Table 5.

<table>
<thead>
<tr>
<th>Table 5. Single-bed descriptions and properties of the materials.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bed name</strong></td>
</tr>
<tr>
<td>----</td>
</tr>
<tr>
<td>Aluzinc</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>S.Steel</td>
</tr>
<tr>
<td>Glass</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
</tr>
</tbody>
</table>

* pieces, ** not known, *** Automation Creations Inc. (2005)

The greater enhancing effect of copper on the oxidation reaction, as compared to stainless steel, can be partly explained by its better heat conductivity properties. Compared to the uncoated stainless steel, Aluzinc decreases the T_{90} temperature. This might be due to other properties of the metal, such as its surface properties (Carlsson 2005). Furthermore, copper and Aluzinc surfaces are in more oxidized form than AISI304 steel (O. Forsén & A. Pehkonen, personal communication).

The oxidation of n-butyl acetate without the packing material can be considered to take place via homogeneous reactions with a free radical mechanism. Fig. 14 shows that, in catalytic reactions and in copper packing experiments the homogeneous gas phase reactions do not take place below their T_{50} temperature. The T_{50} temperature for the thermal experiment is 580°C. At the same level, it corresponds to over T_{90} for the copper and over T_{90} for the catalytic experiments. Therefore, the enhancing effect of the copper packing at lower temperatures may also partly be due to factors other than the heat conductivity of the metal. However, it is important to take into account the fact that the surface temperature of copper, which is probably higher than the gas-phase temperature at the inlet of packing, was not measured. These higher surface temperatures may enhance the initiation of the gas phase oxidation.
It is very difficult to distinguish between the possible effect of thermal properties and metal activity on the oxidation of n-butyl acetate. In general, copper oxide is a catalytically active material that is used in VOC oxidation, but zinc, used in Aluzinc coating, can act as a catalyst poison by forming harmful compounds that cover active surface sites of the catalyst (Moretti 2001, Engelman 2000, Jennings 1985). ZnO, however, is also used as a stabilizer and/or promoter in catalysts. Oxides of aluminium, too, have some catalytic effects and due to their large surface area, they are commonly used as a washcoat material of catalysts, especially γ-Al2O3, which has been observed from the surface of Aluzinc (Carlsson 2005).

Experiments with metal packings were repeated several times. During the repeated experiments with Aluzinc, the T50 temperature decreased by 80°C between the first and the last experiment. Conversely, with copper an 80°C increase in T50 was observed. However, the T100 temperatures were the same in all these experiments. The increase in T50 in the copper experiments may be due to mass/heat transfer limitations originating from the deposition of dark grey/black oxidation products of copper on the surface of the plates. Similarly, the enhancement of oxidation with Aluzinc may be due to further oxidation of the Aluzinc surface in repeated experiments.

Thermodynamically feasible oxides on copper surface in an n-butyl acetate-air mixture at different temperatures were calculated by HSC Chemistry® 5.1. program (Roine 2002). In these calculations air, n-butyl acetate/air mixtures and copper were considered bulk materials. According to calculations, the copper surface was probably in the form of CuO, which is also supported by the colour of the deposit. No clear phase change was observed at 380°C (T50 for copper packing experiment) neither in thermodynamic equilibrium calculations of copper-air, nor in calculations of copper-air-n-butyl acetate mixtures. XRD measurements on the deposit confirmed the presence of CuO on the surfaces of copper plates.

According to Birks and Meier (1983), the oxidation behaviour of metal coatings follows the principles of alloy oxidation i.e. they protect metal by selective oxidation to form Al2O3, Cr2O3 and SiO2 etc. scales. Thus, in this case, the Aluzinc surface may contain these oxides, of which the quantity of Al2O3 is the highest. The thermodynamic equilibrium calculations of Zn, Al, and Si in air (at 0°C-800°C) also showed the presence of other oxides, such as ZnO and ZnSiO3 (Ojala et al. 2005b). Fig. 14 indicates that some of these oxides could slightly enhance the n-butyl acetate oxidation reaction (observe the light-off curves for stainless steel and Aluzinc). However, further experiments with these oxides are needed to confirm the results. On the outer surface of the uncoated stainless steel at temperatures above 300°C, the oxides are mostly Cr oxides, even if the metal contains mostly Fe (Härkki & Heikkinen 2001). It seems, that in this case these oxides are less active than those on the Aluzinc surface.

### 3.3.3 Fouling of materials in SVOC oxidation

When a catalytic incinerator was tested in the oxidation of chip bin emissions, after certain amount of time, it was observed that the flow throughput within the incinerator started to decrease. When the incinerator was stopped and opened, an accumulation of black deposit on the heat exchanger surfaces was observed. Originally three hypotheses
on the origin of the deposit formation were suggested. Firstly, it was assumed to have formed due to the polymerization of terpenic compounds as a result of incomplete oxidation. Secondly, the probability of elementary sulphur formation according to the Claus reaction was considered. Third, the possible corrosion of construction materials due to sulphuric acid was deliberated.

At the beginning, the possibility of fouling by pinenes was tested. A short preliminary experiment of four hours at the laboratory with Aluzinc plates and a catalyst revealed that when Turpentine vapor in air was introduced into a reactor with a space velocity of 31,500 h⁻¹ a black deposit was formed on Aluzinc plates. The formation of the black deposit was not observed in the four-hour test with the lower space velocity of 15,000 h⁻¹. The deposit was formed on the plates after the catalyst, but not before. The deposit changed its color from black to light brown after the plates were taken off from the reactor and left in an open air. Figs 15a-c shows the results of these above-mentioned tests.

![Deposit formation in a) four hours with one catalyst, b) 13 hours with two catalysts and c) 13 hours where one test stick shows the formation of the deposit being decreased after ~1.5 times the catalyst bed.](image)

Earlier, Ramos et al. (1997) had studied the polymerisation of α- and β-pinenes and they discovered that the polymerization yield of α-pinene decreases as the temperature is increased, but the polymerisation yield of β-pinene increases at the same time. Encarnacão et al. (2003) found that the presence of light has an important role in the α-pinene polymerisation, which suggests that α-pinene polymerisation takes place via a radical mechanism. They also claimed that a catalyst (V₂O₅) seems to increase the radical initiator species. These results would suggest that the temperatures used in the incinerator are not high enough to oxidize terpenic compounds with a high space velocity.

Fig. 15c shows that the formation of the black deposit takes place close to the front edge of the catalyst bed, but it is not found at the end of the catalyst bed. In the pilot-scale incinerator, the formation of black deposit was more significant in the cooler part of heat exchangers. This may mean that the gas stream at the outlet of the catalyst probably includes reactive terpenic species that start to polymerize when the gas stream cools down at the lowest (and coldest) heat exchangers, and therefore blocks the coolest heat exchangers more predominantly.

Furthermore, the activity of a catalyst similar to an industrial-scale catalyst, was tested in order to determine the light-off (Tₚ₀) of the catalyst in the turpentine oxidation. The activity of the catalyst was also tested with different space velocities and with different turpentine concentrations close to the T₁₀₀ temperature (T₁₀₀ is defined as a
temperature of 100% conversion). This study was carried out in order to find a temperature where the oxidation of terpenic compounds is complete, and in order to study the parameters affecting the complete oxidation. The catalytic light-off curves for α- and β-pinene oxidation are presented in Fig. 16.

![Fig. 16. Light-off curves for α- and β-pinene oxidation over a Pt-catalyst with a space velocity of 31,500 h⁻¹ (Ojala et al. 2005a).](image)

The light-off temperature ($T_{50}$) for α-pinene is ~190°C and for β-pinene ~80°C (with precision of +/- 5°C) (Fig. 16). In general, β-pinene has a lower $T_{50}$ temperature than that of α-pinene. In these experiments, only the concentrations of α- and β-pinene were observed and quantified. Mass balances were not calculated and it is possible that the decrease in the concentration of pinenes may also be due to some reactions other than oxidation (e.g. polymerization). In addition, the effect of concentration and space velocity on catalytic oxidation of α- and β-pinene were studied (Figs 17 and 18).
Fig. 17. $T_{50}$, $T_{90}$ and $T_{95}$ temperatures for $\alpha$- and $\beta$-pinenes with different space velocities. The first two bars show the repeatability of the experiments (Ojala et al. 2005a).

In general, a decrease in space velocity clearly decreases the $T_x$ temperatures of both $\alpha$- and $\beta$-pinene oxidation. This would suggest that a more complete oxidation of those pinenes is also possible with smaller space velocities. This may decrease the formation of polymer deposits in industrial scale applications. However, this is not proved entirely, since the polymer formation cannot be analysed with the existing laboratory facility and the mass balances are not calculated since all the by-products are not quantified due to the complicated turpentine mixture.

Fig. 18 shows the effect of a turpentine concentration on the oxidation of pinenes close to the $T_{100}$ temperature (~300°C). In these experiments, a constant space velocity of ~15,000 h$^{-1}$ was used.
Fig. 18. Effect of turpentine concentration on end conversion in α- and β-pinene oxidation (Ojala et al. 2005a).

An increase in the concentration of pinenes does not significantly affect end conversions (Fig. 18). Based on these results it can be concluded that the space velocity has more a significant effect on these oxidation reactions than the concentration of pinenes.

According to the results of the laboratory experiments, the operation temperature of the industrial-scale incinerator was increased, first from ~470°C to 500°C and then to ~520°C. The formation of the black deposit was followed by the test sticks being placed into the incinerator. Fig. 19 shows the formation of the black deposit at different operation temperatures.

a) ~470°C b) ~500°C c) ~520°C

Fig. 19. Test sticks after a one hour test run at the incinerator’s operation temperatures of a) ~470°C, b) ~500°C and c) ~520°C (Ojala et al. 2005a).

The sticks were placed between the heat exchangers. The temperature between the heat exchangers fluctuated according to the process operation. Fig. 19 shows that the black deposit formation changed with the change in temperature. The formation of the black
deposit slightly decreased close to the catalyst bed at higher temperatures compared to the deposit formation between the lower and thus the colder heat exchangers. When the incinerator’s operation temperature was increased the formation of deposit was also decreased (Figs 19a-c). However, it is possible that the heat exchangers were already blocked again at the end of the experiment and the decrease in the deposit formation was due to the decreased flow through the system. Furthermore, after the addition of a double catalyst, the formation of the black deposit was not avoided. Based on this, it was concluded that the polymerization of terpenic compounds is not the major cause behind the fouling of heat exchangers.

The second possibility for deposit formation is the Claus process, in which hydrogen sulphide reacts with sulphur dioxide according to the following total reactions (Hase et al. 1998, Ertl et al. 1997b):

\[
\begin{align*}
H_2S + \frac{3}{2} O_2 & \rightarrow SO_2 + H_2O \quad (1) \\
SO_2 + 2H_2S & \rightarrow 3S + 2H_2O 
\end{align*}
\]

The latter reaction is partly non-catalytic and partly catalyzed by Al2O3. The emission gases from a chip bin include H2S, but they do not include SO2 according to measurements (Ojala et al. 2005a, Ojala et al. 2005e). However, at a particular moment, when the direction of flow in the incinerator is reversed, it is possible that H2S inside the emission flow comes into contact with SO2 in an oxidized gas flow. This may lead to the formation of elementary sulphur, which accumulates on the heat exchanger surface, which contains Al2O3, as described earlier. The possibility of a Claus reaction was studied with the aid of thermodynamic calculations (HSC Chemistry® 5.1.). It was observed that the formation of elementary sulphur is not thermodynamically significant when H2S and SO2 are present in diluted concentrations in air (500 mg H2S and 250 mg SO2 as function of O2 concentration). Furthermore, the formation of solid sulphur decreases as the temperature is increased (calculations were carried out at 200, 300 and 600°C).

If it is present, the formation of elementary sulphur via the Claus process may be avoided by e.g. using a pre-catalyst, in which H2S is oxidized prior to the actual catalytic incinerator. According to laboratory experiments the inlet temperatures needed for the pre-catalysts (the same used in the industrial-scale) with GHSV of 121,020 h⁻¹ is ~400°C and with GHSV of 60,530 h⁻¹ ~300°C in order to guarantee the total conversion of H2S. The values of GHSV were selected based on the dimensions of pipings in industrial-scale. In these experiments a possible mixture-effect was not considered.

The third possibility for the formation of a deposit is corrosion caused by sulphuric acid. It is possible that SO3 is formed in the oxidation reactions and reacts with water when cooled to form sulphuric acid according to the following reaction:

\[
SO_3 + H_2O \rightarrow H_2SO_4 
\]

Sulphuric acid condenses rapidly at ambient temperature to form a fine sulfuric acid aerosol that frequently appears as a blue fume near the stack outlet (Flagan & Seinfeld 1988). The sulphuric acid that forms may react with construction materials and form solid salts on the surfaces of heat exchangers. This may be avoided if the temperature is kept
above the sulphuric acid dew point throughout the incinerator (De Nevers 2000). The condensation of sulphuric acid was studied with thermodynamic calculations (HSC Chemistry ® 5.1.). In general, the sulphuric acid dew point depends on the concentration. The dew point temperature increases as the concentration of sulphuric acid is increased. Fig. 20 shows the acid dew point curve for sulphuric acid.

Experiments were also carried out at the laboratory to study the corrosive effect of sulphuric acid. The visual observations after the Aluzinc and steel plates were exposed to sulphuric acid vapour showed that no corrosion of plates took place. This result was the same with both 10 w-% and 50 w-% sulphuric acid–water solutions. However, after the plates were kept in a strong (93 wt-%) sulphuric acid solution overnight, corrosion was observed. The surface of steel turned green, and Aluzinc turned dark grey. The surfaces of these plates along with similar plates from industrial-scale tests were analyzed with FTIR and XRD. As Fig. 21 shows, the IR spectra of different plates deviated from each other. In addition, the IR spectrum for the black deposit is included in the figure. Surprisingly the spectrum for the deposit is similar to the spectra of Aluzinc and AISI304, which were kept in concentrated sulphuric acid. This would suggest that the deposit is formed due to sulphuric acid corrosion. Furthermore, the stretchings in IR spectra at ~3200-2900 cm⁻¹ and ~1630-1680 cm⁻¹ are most probably related to –OH bonds, and thus to water. Stretchings at ~1100 cm⁻¹ and ~680 cm⁻¹ are due to sulphates. An XRD analysis of the plates also supports this conclusion (Figs. 22a and b). For example, when XRD

---

**Fig. 20.** Acid dew point curve for flue gas containing 11.0 % water vapor at 1 atm (de Nevers 2000, Holmes 1985).
dифракограмм черного отложений, а также свежих, промышленно испытаных и 93% серной кислоты корродированных AISI304 и Aluzinc являются сравниваются, схожести между промышленно испытанной и кислотой корродированной пластинами AISI304 отмечены. Дифракограммы промышленно испытанной и кислотой корродированной AISI304 пластин имеют пики около 2\(\theta\) ~ 26\(^\circ\), который не наблюдается в дифракограмме свежей пластины. Сходно, пики при 2\(\theta\) < 30\(^\circ\) отмечены в случаях промышленно испытанной и кислотой серной кислоты корродированной Aluzinc пластин, которые не наблюдается в дифракограмме свежей пластины. Эти пики связаны с металлическими сульфатами.

Fig. 21. FTIR спектры черного отложений а также свежих, промышленно испытаных и 93% серной кислоты корродированных AISI304 и Aluzinc пластин.
As was mentioned earlier, the deposit was formed at the lowest heat exchangers where the temperatures are close to 100°C. The formation of deposit does not occur in the upper heat exchangers, where the temperatures are higher (close to catalyst operation temperature). Furthermore, studies showed that a wet deposit, collected from the bottom of the incinerator, is acidic and when it was contacted with water, after filtration, the solution contained sulphuric acid. Headspace analysis with GC-MS revealed the presence of SO₂, DMS, DMDS, dimethyl trisulphide (DMTS) and aromatic compounds. XRD-analysis confirmed that the deposit is amorphous. This deposit was soluble only to dimethylsulfoxide (DMSO).

Several analyses have been carried out on the composition of the black deposit. A thermogravimetric analysis (TG) (see Figure 23) showed a first decrease in the mass of the sample before a temperature of −200°C, a second decrease before −300°C and a third one before 800°C. At the end, (~1000°C) approximately 16% of the initial mass of the sample was left. The gas analysis (Figure 24) showed a release of H₂O in connection with the second decrease in mass, where the initial mass decreased approximately 50% from the initial value. After that, CO₂ was formed up to a temperature of approximately 700°C. At the same time SO₂ formation was observed, but it too formed at the end temperature (985°C).

Fig. 22. XRD analysis of fresh, industrially tested (Process) and 93% sulphuric acid-corroded (Acid) plates of a) AISI304 and b) Aluzinc.
Fig. 23. Thermogravimetric analysis of the deposit.

Fig. 24. MS analysis of the outlet gases of TG at different temperatures.
After the TG experiment, the ashes were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The ashes contained Fe and Zn as well as small amounts of Cu, Ni, Cr, Mn and Ba, which could be a sign of corrosion of the construction materials. The ash sample did not contain sulfur. Similar analysis was also carried out for a ‘fresh’ deposit. The results are presented in Table 6.

Table 6. Analysis of the deposit.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>Fe</th>
<th>Zn</th>
<th>Al</th>
<th>Cr</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>16%</td>
<td>3%</td>
<td>189 mg g⁻¹</td>
<td>45.9 mg g⁻¹</td>
<td>29.2 mg g⁻¹</td>
<td>17.1 mg g⁻¹</td>
<td>7.03 mg g⁻¹</td>
<td>478.23 mg g⁻¹</td>
</tr>
</tbody>
</table>
| **Note** | **160 mg g⁻¹**, **30 mg g⁻¹**

The sample was first dried at 80°C, which explains the missing half of the mass. This is also consistent with the results of the TG analysis, in which a significant release of water is connected to a decrease of ~50% of the initial mass of the sample. According to chemical analysis, the most dominant compounds of the sample are carbon and sulphur followed by iron.

The paramagnetic compounds included in the sample, e.g. Fe, affected the NMR analysis. However, it could show that polymers were present only in negligible amounts. Furthermore, the NMR confirmed that the sample contains water in significant amounts. The NMR also showed the presence of one or more organic acids and some aromatic compounds.

In addition to other findings it is worth mentioning that the blocking rate of the heat exchangers is rather high. The rate even increased when the operation temperature of the incinerator was increased, and furthermore, the addition of a double catalyst did not eliminate the blocking. After the heat exchangers were replaced, the blocked heat exchangers were stored outside in open air where they were in contact with air and moisture/water. During storing the deposit changed from a black amorphous form to a white, more crystalline form (see Figs 25 a and b).

![Fig. 25. The deposit a) soon after the blocking, b) after storing in moist conditions.](image-url)
According to XRD analysis, the white deposit is aluminium sulphate with the presence of some metal with an oxidation state of +II. AAS analysis of the sample showed also that zinc is present in the sample in significant amounts. This discrepancy is due to heterogeneous nature of the sample and thus, it is safe to conclude, that the white deposit contains both aluminium and zinc sulphates.

To conclude, if the formation was only due to the polymerisation of pinenes, the double catalysts would have eliminated it. On the contrary, if the formation was due to SO₂ over-oxidation on the catalysts, it would be worsened when double catalysts were installed and in fact, the heat exchangers were blocked very rapidly. Increasing the temperature at the level used and the addition of the double catalysts would not eliminate the Claus reaction. However, thermodynamic calculations showed that the Claus reaction is not likely due to the diluted concentrations. Furthermore, analyses from both of the forms of the deposit as well as analyses from the metallic test sticks strengthen the conclusion about sulphuric acid corrosion.

3.4 Conclusions

The experiments with the materials of construction showed that Aluzinc enhances the oxidation reactions compared to thermal oxidation. This is probably due to oxides formed on the Aluzinc surface under the conditions studied. However, Aluzinc should not be used at temperatures above 600°C due to thermal degradation of the coating.

In summation, the facts about the deposit formation in the chip bin emission abatement are:

- The deposit formation depends on temperature and the deposit is formed at lower heat exchangers having a temperature approximately 100°C
- The deposit consists mainly of carbon and sulphur as well as metals from the construction material
- The deposit is amorphous and mostly inorganic in nature, however it changes to crystalline aluminium and zinc sulphates upon contact with air and moisture
- The amorphous deposit contains ~50% water (of its mass)
- The amorphous deposit is acidic and contains sulphuric acid

Based on the findings, even though the exact formula for the amorphous deposit could not be determined, it is concluded that the deposit is formed mainly due to corrosion of the construction materials caused by sulphuric acid. However, this might not be the only reason, since the rate of blocking of the heat exchangers is rather high. Therefore, other mechanisms should be also taken into account, for example deposition of carbonaceous species. The corrosion reactions may be avoided by increasing the temperature throughout the catalytic incinerator above the sulphuric acid dew point, which is dependent on the concentration of sulphuric acid (see Fig. 20). In general, some precautionary temperature level should be used due to the fact that the concentration of sulphuric acid will not certainly remain constant in the process conditions. When these considerations are taken into account, the materials of the incinerator should be selected to be durable enough to withstand relatively high temperatures.
4 Catalyst research

The third part of process characterization concentrates on the most central matter of catalytic incineration: on the properties of different catalysts. There are three main features of the catalysts that determine the ‘goodness’ of a catalyst: activity, selectivity and durability. This chapter considers these three aspects and applies the obtained information to VOC and SVOC emission abatement.

4.1 Introduction

As mentioned in the Chapter 1, both fixed-bed and fluidized-bed systems are used in catalytic oxidation. Fixed-bed catalytic oxidizers may use a monolithic or a packed-bed catalyst of which the monolithic catalysts are more widely used, since they have certain advantages such as they offer a lower overall pressure drop (see Section 1.2) compared to packed-bed systems. (Moretti 2001, Hayes & Kolaczkowski 1997) The catalysts used for VOC abatement include metal oxides and precious metals such as platinum (Pt) and palladium (Pd). In general, precious metal catalysts have a longer lifetime and they are more resistant to poisoning and fouling than less expensive base metal catalysts. (Moretti 2001)

The selection of the catalyst should be based on knowledge of emissions that should be oxidized, since catalysts show different activities in the oxidation of different VOCs and SVOCs. Much research has been done in order to test and to develop suitable catalysts for the oxidation of selected VOCs. For example, the abatement of chlorinated hydrocarbons is studied over LaCoO$_3$, LaMnO$_{3+x}$ (Sinquin et al. 2000), over different chromia-based catalysts (Padilla et al. 1999), over Pt-based catalysts (Corella et al. 2000, Musalik-Piotrowska & Syczewska 2002) and over protonic zeolites (Lopez-Fonseca et al. 2003). The catalytic oxidation of benzene, butanol and ethyl acetate are studied over Group VIII metal catalysts on alumina (Papaefthimiaou et al. 1997) and n-butane and ethyl acetate are tested over transition metal oxides (Pradier et al. 2000). Catalytic oxidation may also be coupled with e.g. UV-light (Keller et al. 2003) or plasma (Demidiouk et al. 2003), which may enhance the oxidation efficiency and/or selectivity of the whole abatement system.
This chapter considers the activity, selectivity and durability of catalysts in both VOC and SVOC oxidation. The model compounds for laboratory tests were selected based on measurement results from solvent emission sources and from the pulp mill chip bin. The VOC model compounds are n-butyl acetate and methane, the latter of which was selected based on the fact that of the light hydrocarbons it is the most difficult to oxidize (Gélin & Primet 2002, Burch & Urbano 1995) and differences between the activities of the catalysts can be observed more clearly. The SVOC model compounds are methyl mercaptane (MM) and dimethyl disulphide (DMDS), which are among those malodorous compounds emitted from a chip bin.

4.2 Experimental

The activities of the fresh and aged catalysts were evaluated with the light-off tests. The experimental set-up for the light-off tests is described earlier in Section 3.2.2. The catalysts light-off is defined as the temperature of 50% conversion (T50) of the selected compounds and this information is used to compare different catalysts. In this case, temperatures close to complete oxidation (Tx) are also used, since in the emission abatement, total oxidation of emitted compounds is desired. During the light-off tests, information on catalysts' selectivity was also collected. The characterization of fresh and aged catalysts was done with physorption (BET) and chemisorption (CO) measurements, by a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS), by X-ray diffraction (XRD) and by infrared spectroscopy (FTIR).

The surface areas of the catalysts and CO-chemisorption measurements were usually carried out before and after the experiments. Specific surface areas (m²g⁻¹) were determined by a Coulter Omnisorp 360CX and later by a Micromeritics ASAP 2020 Surface area and porosity analyser according to the standard BET method. The experimental procedure was the same with both of the analysers. At first, the catalysts were outgassed in a vacuum at 140°C for 16 hours before the measurements. Surface areas were obtained from the N₂ adsorption isotherms at -196°C by assuming the cylindrical shape of the pores. Pore size distributions of catalysts SVOC6-8 were calculated from N₂ desorption isotherms by BJH (Barret-Joyner-Halenda) method. Chemisorption measurements (ASAP 2020) were carried out at 35°C in order to determine the dispersion of noble metal particles and the amount of active metal in the catalyst. CO was used as the adsorbate gas with the assumption of a stoichiometry of 1:1 regardless of the particle size.

A Jeol JSM-6400 scanning electron microscope equipped with an energy dispersive spectrometer (EDS) was used for high magnification imaging and elemental analysis. In the pre-treatment stage, flat pieces of fresh and aged catalysts were cut and potted in epoxy in order to obtain side views of the catalysts. Prior to analysis the samples were polished and coaled to avoid the accumulation of charge. The accelerating voltage and current in the measurements were usually 15 kV and 12 nA, respectively. SEM-EDS resources were used in the Institute of Electron Optics at the University of Oulu.

The aging of VOC catalysts (A-D) was carried out in the industrial conditions of solvent emission abatement. The industrial aging conditions are described in more detail later in connection with the results. In aging, four different catalysts, four of each, were placed inside a metal rack that had been installed into the catalytic incinerator in June.
2002. In Fig. 26 the sample catalysts are placed into the rack designed and manufactured at the University of Oulu. The rack was installed into the catalytic incinerator between the catalyst bed and the heat exchangers (see Fig. 47 in Section 5.2) which allows the raw emission gases to pass the sample catalyst in one flow direction and the once treated gas in the other flow direction (due to reverse flow operation).

![Sample catalysts inside a rack.](image)

The first catalyst samples were taken out after 3 months of aging, the second samples after approximately 9 months of aging, the third after 16 months and the last catalyst after 25 months of aging.

The durability of the SVOC5 catalyst (see coding in Section 4.2.2) was tested on a laboratory-scale. The experiment was carried out with ~1060 mg m\(^{-3}\) DMDS in air at a temperature of ~490°C and with GHSV of 31,500 h\(^{-1}\). The temperature was selected based on activity measurements to maintain a total oxidation of DMDS. The outlet gas composition was followed with GC-FPD. The catalyst was placed inside an oven and the DMDS-air mixture was fed continuously for 55 hours, after which the experiment was stopped during the night hours. At the end of the experiment, the total time for the durability testing was 70 hours. A more detailed description of the experiment can be found in connection with results in Section 4.5.2. Prior to the experiment the catalyst was pre-treated similar to other experiments, i.e. heated to 800°C in an airflow and cooled to a room temperature.

### 4.2.1 Catalysts and model compounds for VOC tests

The VOC-catalysts used in the activity tests were different in their chemical (active components, loadings etc.) and physical (size, shape, etc.) composition. Four of the catalysts (catalysts A-D) were metallic monoliths with a cell density of 500 cpsi, and the
other six (catalysts E-J) were granules. In Table 7, the characteristics of the catalysts are presented in more detail.

### Table 7. Characteristics of the catalysts used in the VOC experiments.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active compound</td>
<td>Pt</td>
<td>Pt-Pd</td>
<td>Pt</td>
<td>Pt-Pd</td>
<td>Cu-Mn-oxides</td>
</tr>
<tr>
<td>Loading (%)</td>
<td>0.21</td>
<td>0.11/</td>
<td>0.22</td>
<td>0.11/</td>
<td>11 - 17</td>
</tr>
<tr>
<td>Support</td>
<td>Al₂O₃-Ce</td>
<td>Al₂O₃-Ce</td>
<td>Al₂O₃-La</td>
<td>Al₂O₃-La</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Shape</td>
<td>Monolith</td>
<td>Monolith</td>
<td>Monolith</td>
<td>Monolith</td>
<td>Extrudate</td>
</tr>
<tr>
<td>Catalyst</td>
<td>F</td>
<td>G</td>
<td>H</td>
<td>I</td>
<td>J</td>
</tr>
<tr>
<td>Active compound</td>
<td>Pt</td>
<td>Pt</td>
<td>MnO₂-</td>
<td>CuₓMg(1-x)</td>
<td>CuₓCr₂O₄</td>
</tr>
<tr>
<td>Loading (%)</td>
<td>&gt;0.09</td>
<td>&gt;0.09</td>
<td>5 / 4.5</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Support</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Shape</td>
<td>Extrudate</td>
<td>Pellet</td>
<td>Pellet</td>
<td>Pellet</td>
<td>Pellet</td>
</tr>
</tbody>
</table>

Figs 27 and 28 enable the visual comparison of the different catalysts. The catalysts fixed into the reactor are presented in Fig. 27. Fig. 28 presents SEM images from some of the catalysts.

![Fig. 27. Different catalysts used in the screening tests.](image)

The catalysts were received from three catalyst producers. The monolith catalyst B (see Table 7) is used in industrial-scale VOC incinerators, but also in automotive exhaust gas catalysis. The other monoliths were selected to compare the effect of support and active metal. The catalysts E to G are also used commercially and designed for VOC abatement. Since the structure and purpose of these catalysts was originally different from the monolith catalysts, the functioning was compared. The catalysts H to J are model VOC catalysts prepared in a research institute.
Catalysts A-D are monolithic catalysts that are prepared on a thin Fe-Cr-Al metal foil. The washcoat consists mostly of Al₂O₃, but stabilizers and/or promoters (Ce, Zr, La) are also used. The active metals are Pt and Pd. Catalysts A-D are manufactured by an open coating technique, which enables the formation of a smoother and thicker washcoat layer than would a complete substrate coating technique. All of these catalysts were originally designed for automotive exhaust gas catalysis, where they have proved to be very stable in long-term use. (M. Louhelainen, personal communication)

Catalysts E-G are designed for VOC oxidation purposes. Catalyst E has, according to the manufacturer, the oxides of copper and manganese on an extrudate carrier. This is a cheaper oxidation catalyst that is especially good for the removal of oxygenates such as ethyl acetate. The dimensions of the catalyst E are: diameter 3 mm and length 3 mm-10 mm. Catalyst F is a sphere pellet-type catalyst with a diameter of 4.7 mm. The active component is platinum and it is located in an eggshell position. This is a very active catalyst with a low ignition temperature but it is relatively sensitive to poisoning, e.g. sulphur, which may deactivate it rapidly. This catalyst is used in applications where the composition of the exhaust gas is well defined, such as in the ECS (Emission Control
System) of formaldehyde plants, where HCHO, methanol, CO and DME are the only VOCs that need to be oxidized. Catalyst G is also a platinum catalyst but the carrier is an extrudate, with a diameter of 3 mm and a length of 3 mm-10 mm. This egg-white VOC catalyst can withstand poisons, e.g. compounds with silicon, better and is used in, for example, printing applications. (M. Hernelind, personal communication) Due to the dimensions of experimental apparatus, these catalysts had to be crushed, since without crushing the flow channeling inside the bed and between the bed and wall would have been too dominant. Crushing destroyed the designed structure of the catalysts and the results may differ from results achieved without crushing. Crushing did not significantly alter the measured BET surface area of the catalysts.

Catalysts H-J are granulated spherical catalysts designed for the VOC oxidation. In addition to the information presented in Table 7 and some physical data, no additional information is available.

The first model compound, n-butyl acetate, was selected for these oxidation tests, since it was one of the most dominant compounds in solvent emissions previously measured (Ojala et al. 2005d). The n-Butyl acetate is a transparent or yellow liquid, and it has very characteristic smell. Its boiling point is 126°C and a vapour pressure of 2 kPa (at 25°C). (WHO 2005) Another model compound, methane, was selected due to the fact that it is difficult to oxidize and the differences between the catalysts’ activities are thus easier to determine than with n-butyl acetate. It is also postulated that when methane in the VOC emission stream is oxidized completely, oxidation of all the other VOCs present in the emission stream are completed (Janbey et al. 2003).

### 4.2.2 Catalysts and model compounds for SVOC tests

The catalysts used in the SVOC tests are presented in Table 8. Four of the catalysts used in the VOC tests (A, B, H, I and J) were also selected for the SVOC tests. In addition to these, a metallic monolith containing Pt on pure Al₂O₃ and Pd on Ce-modified Al₂O₃ were tested. The catalysts E-G were not used in SVOC tests, since according to the manufacturer they may deactivate in the presence of sulphur compounds, especially catalyst F.

**Table 8. Characteristics of the catalysts used in the SVOC experiments.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SVOC1</th>
<th>SVOC2</th>
<th>SVOC3 (= A)</th>
<th>SVOC4 (= B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Act.comp.</td>
<td>Pd</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt-Pd</td>
</tr>
<tr>
<td>Loading [%]</td>
<td>0.22</td>
<td>0.23</td>
<td>0.21</td>
<td>0.11/0.11</td>
</tr>
<tr>
<td>Support</td>
<td>Al₂O₃-Ce</td>
<td>Al₂O₃</td>
<td>Al₂O₃-Ce</td>
<td>Al₂O₃-Ce</td>
</tr>
<tr>
<td>Shape</td>
<td>Monolith</td>
<td>Monolith</td>
<td>Monolith</td>
<td>Monolith</td>
</tr>
<tr>
<td>Catalyst</td>
<td>SVOC5 (= H)</td>
<td>SVOC6 (= I)</td>
<td>SVOC7 (= J)</td>
<td></td>
</tr>
<tr>
<td>Act.comp.</td>
<td>MnO₃-MgO</td>
<td>CuₓMg₁₋ₓCr₂O₄</td>
<td>CuₓCr₂O₄</td>
<td></td>
</tr>
<tr>
<td>Loading [%]</td>
<td>5/4.5</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Support</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>Shape</td>
<td>Pellet</td>
<td>Pellet</td>
<td>Pellet</td>
<td></td>
</tr>
</tbody>
</table>
Methyl mercaptane (MM) and dimethyldisulphide (DMDS) were used as model compounds. Both of those compounds are included in the chip bin emissions (Ojala et al. 2005a, Ojala et al. 2005e). Furthermore, DMDS is formed during incomplete oxidation of MM (Ojala et al. 2005a). DMDS is a liquid and has an irritating odour. Its boiling point is 199°C and its vapour pressure is ~3.8 kPa at 25°C. (WHO 2005)

4.3 Activity of catalysts

A good catalyst must possess a high level of activity. The activity of a catalyst is in general the measure of its goodness in operation. It can be considered the magnitude of a catalyst’s ability to lower the activation energy of a certain reaction, and in this case, to decrease the temperature required for the oxidation of VOC or SVOC emissions. However, as Ertl et al. (1997a) emphasise, it is not enough to say that when a catalyst is active, it is alive. According to Ertl et al. conversion alone, or conversion versus time, is useless as the measure of activity. Activity should be measured as a rate, and it may be defined e.g. by the number of the catalytic actions per unit time, or turnover rate, or turnover frequency (TOF). (Ertl et al. 1997a)

\[ \text{TOF} = \frac{\text{number of molecules of a given product}}{(\text{number of active sites}) \cdot (\text{time})} = \frac{1}{S \cdot \text{dt}} \], \hspace{1cm} (4)

where \( S \) is the number of active sites.

In heterogeneous catalysis it is often difficult to determine the number of active sites, and thus \( S \) is often replaced by the total area \( A \) of the exposed catalyst. This replacement sets a lower limit on the TOF. By now, it has become more and more common to use TOF as a measure of catalyst activity in heterogeneous catalysis due to the advanced analytical techniques, however it is still applied most profitably to single-crystal model catalysts. (Thomas & Thomas 1997)

The rate of heterogeneous catalytic reaction is a result of both the actual chemical reaction on the catalytic surface and the supply rate of reactants to the surface by diffusion (molecular or convective). At low temperatures the reaction rate is small compared to the rate of diffusion and thus the overall reaction rate is kinetically controlled. When temperature is increased, the reaction rate will increase according to Arrhenius equation. This exponential growth of reaction rate proceeds until it comes equal to the diffusion rate. Further increase in temperature does not increase the overall reaction rate significantly, since the reaction is controlled by diffusion. (Frank-Kamenetskii 1969) \( T_{50} \) is approximately in the middle of the transition regime between kinetically controlled and diffusion controlled regimes. Thus it is related to the light-off of a catalyst and can be used as a reasonable measure of catalytic activity. In this research, \( T_{50} \) was also used as a measure of activity of different metal plates in Section 3.3.2.

The selection of the catalyst is not straightforward, since it depends on the VOCs and SVOCs to be oxidized, for example. Furthermore, selectivity and durability may play a
more important role than activity. At best, a catalyst has high activity, high selectivity and high long-term stability.

In general, there are several factors that may affect catalyst activity to oxidize certain compounds. Examples of these are: the active compound, loading (Cullis & Willat 1983) and oxidation state of the active compound (Burch & Urbano 1995, Janbey 2003), washcoat material (Cullis & Willat 1983, Zwinkels et al. 1999), the surface area of the catalyst and the dispersion of the active material (Gélin & Primet 2002) as well as modifiers and promoters (Yang et al. 2002, Thevenin et al. 2002b), even precursor salts (Baldwin & Burch 1990, Marceau et al. 2001). Furthermore, variations in process operation conditions such as in temperature, in pressure and in gas mixture composition influence catalyst activity (Ciuparu et al. 2002).

A lot of research has been carried out to study the catalytic oxidation of methane. However, less specific information is available on n-butyl acetate, MM and DMDS oxidations. Next is a review of some of the earlier research on the catalytic oxidation of the model compounds, the catalysts used, and oxidation conditions.

Methane combustion catalysts include noble-metal based catalysts (e.g., Pt, Pd, Rh, Au), metal oxides (e.g., Co₃O₄, CuO, NiO, Mn₂O₃, Cr₂O₃) and mixed oxides (perovskites, doped metal oxides, hexa-aluminate materials) (Choudhary et al. 2002). According to many authors (e.g. Lee & Trimm 1995, Janssen & van Santen 1999) palladium oxide is the catalyst exhibiting the lowest light-off temperature in oxidation of methane. However, as Ciuparu et al. (2002) concluded, at higher temperatures metallic Pd can also be active for methane oxidation. The PdO phase in a catalyst is stable up to the temperature level of 700°C-850°C and the decomposition of PdO is strongly dependent on the support material. For PdO supported on Al₂O₃, the decomposition temperature has reported to be close to 800°C. (Ciuparu et al. 2002, Farrauto et al. 1992, Farrauto et al. 1995) Monometallic Pt catalysts have lower catalytic activity in the total oxidation of methane compared to Pd catalysts (Gélin & Primet, 2002). However, due to the better sulphur deactivation resistance of Pt over Pd, the bimetallic catalysts are attractive. Furthermore, Janbey et al. (2003) studied Pd, Pt and Pt-Pd catalysts supported on e.g. γ-Al₂O₃ and found out that a bimetallic Pt-Pd catalyst shows lower temperatures of T₁₀, T₅₀ and T₉₀ compared to monometallic catalysts. Similar results were found with the addition of Pt to PdO/α-Al₂O₃ catalysts, which was considered to arise from a higher dispersion of supported particles and suppressed particle growth (Narui et al. 1999).

The enhancement of the catalytic activity of Pt has also been studied. The addition of hydrogen (Deutschmann et al. 2000) and C₃H₈ (Corro et al. 2005) to the methane feed and oxidation of the mixture over a Pt/alumina catalyst has been observed to decrease the light-off temperature of methane. From the other catalysts, Ferrandon et al. (1999) studied the oxidation of e.g. methane over Mn and Cu oxide catalysts as well as over Pt and Pd catalysts. They found the following activity order between the fresh catalysts: CuOₓ = CuOₓ-Pd = CuOₓ-Pt > Pd = MnOₓ-Pd = MnOₓ-Pt = MnOₓ = Pt. MgO has been reported to have some activity towards methane oxidation, but more importantly it increases the thermal stability of γ-Al₂O₃ (Qi et al. 1996). Comparing the methane oxidation results of Zwinkels et al. (1999) concerning the Cr₂O₃ catalyst supported on γ-Al₂O₃ with the results achieved from other publications for noble metal catalysts, Cr₂O₃ gives higher light-off temperatures and thus seems to be less active than noble metal catalysts.
The oxidation of n-butyl acetate has been studied alone or in mixtures e.g. over perovskites (Musalik-Piotrowska & Syczewska 2000), U$_3$O$_8$ (Taylor et al. 1998, 2000) and over copper manganate (Linz & Wittstock 2001). Organic air pollutants in industrial exhaust gases are usually mixtures of several compounds with different characteristics. The possible ‘mixture-effect’, in which oxidation of certain compounds may be promoted or inhibited by the presence of other compounds, is very difficult to predict beforehand. For example, n-butyl acetate oxidation over bulk perovskite is strongly inhibited by n-hexane, and over monolithic perovskite by toluene and n-hexane (Musalik-Piotrowska & Syczewska 2000).

In addition to ‘conventional catalysis’, the catalytic oxidation of n-butyl acetate has been activated with the aid of UV-light and plasma. Keller et al. (2003) tested photocatalytic oxidation of n-butyl acetate in a vapor phase over a titanium oxide semiconductor, Pt/TiO$_2$ and WO$_3$/TiO$_2$. They postulated that photocatalysis on TiO$_2$ is advantageous because it takes place at room temperature, and thus no thermal activation is necessary and only low-intensity UV light is needed. The photocatalytic oxidation led to the complete oxidation of n-butyl acetate, however, conversions decreased after the initial 100% conversion to 20-50% on Pt/TiO$_2$ and to 70-90% on WO$_3$/TiO$_2$. (Keller et al. 2003) In the plasma-catalytic system, catalytic oxidation is enhanced by some excited species from non-thermal plasma (for instance ozone molecules, radicals or atoms), which have rather high reactivity. Demidiouk et al. (2003) discovered that with a Pt catalyst, no by-products were formed. In general, when comparing palladium and platinum, Pd is more active for the oxidation of short-chain hydrocarbons whereas Pt exhibits higher activity toward long-chain hydrocarbons and aromatics (Burch & Hayes 1995).

Catalytic oxidation of MM has been studied e.g. by Ross & Sood (1977), Dalai et al. (1997), Chu et al. (1998) and more recently by Kastner et al. (2002, 2003). Ross & Sood (1977) studied MM oxidation (1000 ppm) over a cobolt molybdate catalyst at a temperature range of 140°-420°C. They did not find significant changes in catalytic activity although the surface area of the catalyst was decreased during the experiments. Kastner et al. (2002, 2003) studied H$_2$S and MM oxidation over coal fly ash and wood ash. H$_2$S formed elemental sulfur and MM was oxidized to DMDS. Further oxidation of DMDS over coal fly ash and wood ash did not take place. Wang & Weng (1997) carried out a study on DMDS oxidation over eight different metal oxides (CuO, ZnO, Cr$_2$O$_3$, MoO$_3$, MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$ and NiO). They also tested nine possible promoters (oxides of Mo, Cr, Ni, Mn, La, Fe, Co, Sr and Zn). CuO supported on γ-Al$_2$O$_3$ with the MoO$_3$ promoter was found to be the most active one. They also compared their catalyst to a Pt/γ-Al$_2$O$_3$ catalyst and observed approximately a 70°C decrease in $T_{50}$ and ~100°C decrease in $T_{100}$ with the CuO-MoO$_3$ catalyst.

As was mentioned earlier, the activities of different catalysts may be compared with light-off tests, in which a catalyst is heated up in an oven at a certain rate and under using a fixed gas-flow. A proper analyser follows the oxidation of the selected compounds. As a result, the light-off curve, in which conversion is plotted versus temperature, is achieved. In order to compare different catalysts, the basis for comparison should also be considered. In this research, the comparison is mainly based on the volume of the catalyst packing; however, comparison based on mass of the catalyst or active compound is also presented in order to bring out the possible differences between rankings based on different features.
4.3.1 Results of VOC tests

The results of the light-off experiments concerning the oxidation of methane and n-butyl acetate are presented in this section. All the experiments have been repeated and it was observed that the catalysts’ light-off behaviour between the repetitions did not change significantly. Figs 29 a and b show the light-off curves for catalytic and non-catalytic (thermal) methane and n-butyl acetate oxidation, respectively. The comparison presented here is based on the volume of the catalysts.

Fig. 29. a) Light-off curves for catalytic oxidation of methane and b) Light-off curves for catalytic oxidation of n-butyl acetate (2000 ppm, 31,500 h⁻¹).
It can be seen from Fig. 29a that thermal (non-catalytic) oxidation of methane does not take place in this temperature range whereas the catalysts decrease the T50 significantly. It has been reported that the homogeneous gas phase oxidation of 1 vol-% methane starts at the temperature range of 800-825°C (Hayes & Kolaczkowski 1997, Pieck et al. 2002). The bond strength of C-H in methane is 104 kcal/mol, which needs to be broken in thermal oxidation. In contrast, the apparent activation energies of dissociative adsorption of methane on certain crystal faces of transition metals is only 7-10 kcal/mol. (Ciuparu et al. 2002)

When the catalysts are arranged on the basis of the T50 and T95 temperatures, the following order is observed for methane oxidation:

T50: J (450°C) > I > E > D > H > G > B > F > A > C (640°C)

T95: J (590°C) > I > E > G > F > A > D > H > B > C (780°C).

The similar order for n-butyl acetate oxidation is as follows:

T50: G (210°C) > E > C > B > F > A > D > I > J > H (300°C)

T95: G (290°C) = E > F > A = C > I > H > B > D > J (490°C).

As expected, oxidation of n-butyl acetate needs lower temperatures compared to methane oxidation. This is due to the compounds’ dissociation energies. Methane is a stable and highly symmetric molecule, thus it possesses the greatest C-H bond strength of all of the saturated hydrocarbons (Ciuparu et al. 2002).

The three catalysts that have the lowest T50 for methane oxidation (J, I and E), contain copper. All these catalysts are designed for VOC oxidation purposes. The fourth catalyst D (in T50) contains both platinum and palladium. These results are roughly consistent with the results of Ferrandon et al. (1999), who also observed that copper-containing catalysts are more active compared to the Pt, Pd or MnOx catalysts. The difference in light-off temperatures observed in this study, is about 200°C between the lowest and highest T50 temperature. The T95 temperature for methane in these conditions is achieved, again, first with copper-containing catalysts (J, I, E) but then with the Pt-only catalysts: G followed by catalysts F and A. The difference between the highest and lowest T95 is, again, about 200°C.

The effect of Pt and Pd can be compared with catalysts A-C. Results show that the Pt-Pd catalyst allows a slightly lower T50 for methane oxidation than the Pt-only catalyst. Many research groups e.g. Gélin & Primet (2002) have reported the superiority of Pd compared to other noble metal catalysts under methane lean burn conditions. This is due to the fact that Pd is in the form of PdO in the conditions of methane oxidation. Burch et al. (1999) suggested that the differences between Pt and Pd in methane oxidation are due to two reasons: the Pt surface in these conditions is fully covered with adsorbed oxygen, which cannot readily activate the almost non-polar C-H bonds in methane (homolytic mechanism) and the PdO surface contains Pd²⁺O²⁻ ions, which can easily activate C-H bonds by a heterolytic mechanism.

The differences between the catalysts’ activities are smaller in n-butyl acetate oxidation compared to methane oxidation (See Fig. 29b). Catalysts decrease the T50 of
n-butyl acetate compared to thermal experiment by up to more than 300°C. The difference between all the catalysts’ light-off is about 100°C. Within the first 50°C only one copper-containing catalyst (E) is included – the rest are noble metal catalysts. However the ‘ranking’ of the catalysts changes when comparing the T95 temperatures. When monolithic catalysts (A-D) are compared, the Pt-only catalysts seem to be more active. It has also been shown before (e.g., by Schwartz et al. 1971) that Pt catalyst is more active in oxidation of longer-chain hydrocarbons than Pd. Fig. 29b also shows that some of the catalysts may suffer from mass transfer limitations when near complete combustion is approaching, i.e. the T100 temperature is shifted to a higher temperature region.

The activities of different catalysts are also compared on the basis of their masses. Fig. 30 shows the concentration decrease of methane and n-butyl acetate at certain temperatures (600°C and 300°C for methane and n-butyl acetate, respectively) divided by the total mass of the catalyst (Equation 5). The light-off temperatures of methane or n-butyl acetate oxidation for different catalysts when the volume of the catalyst was selected to be constant are presented in brackets after the catalysts’ symbol.

\[
\Delta c_m^T = \frac{c(\text{inlet}) - c(T)}{m(\text{cat, total})}, \tag{5}
\]

where
- \(c(\text{inlet})\) is the inlet concentration
- \(c(T)\) is the concentration at a selected temperature (e.g. methane, n-butyl acetate)
- \(m(\text{cat, total})\) is the total mass of the catalyst
- \(\Delta c_m^T [\text{ppm g}^{-1}]\) is concentration decrease per mass of the catalyst.

Fig. 30. Mass-based comparison of the catalysts (Ojala et al. 2005c). The light-off temperature of a catalyst [°C] is presented in brackets after the catalyst symbol.
This kind of comparison reveals that the noble metal catalysts are the most active ones among all the catalysts tested. It also shows that Pt-Pd catalysts are more active than the monometallic Pt catalyst at these temperatures for both model VOC compounds. However, if the same comparison is made based on the mass of the active compound, Pt catalyst (G) is also among the most active catalysts (Ojala 2003, Ojala et al. 2005c). Table 9 summarizes the $T_{50}$, $T_{90}$ and $T_{95}$ temperatures as well as end conversions and corresponding temperatures of n-butyl acetate oxidation experiments.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{50}$</td>
<td>250</td>
<td>240</td>
<td>230</td>
<td>260</td>
<td>230</td>
</tr>
<tr>
<td>$T_{90}$</td>
<td>290</td>
<td>370</td>
<td>290</td>
<td>375</td>
<td>260</td>
</tr>
<tr>
<td>$T_{95}$</td>
<td>360</td>
<td>430</td>
<td>360</td>
<td>450</td>
<td>290</td>
</tr>
<tr>
<td>$X_{end}$</td>
<td>99.9</td>
<td>99.8</td>
<td>99.9</td>
<td>99.8</td>
<td>99.8</td>
</tr>
<tr>
<td>$T_{end}$</td>
<td>819</td>
<td>800</td>
<td>785</td>
<td>796</td>
<td>822</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{50}$</td>
<td>250</td>
<td>210</td>
<td>300</td>
<td>280</td>
<td>290</td>
</tr>
<tr>
<td>$T_{90}$</td>
<td>290</td>
<td>270</td>
<td>380</td>
<td>320</td>
<td>450</td>
</tr>
<tr>
<td>$T_{95}$</td>
<td>310</td>
<td>290</td>
<td>390</td>
<td>370</td>
<td>490</td>
</tr>
<tr>
<td>$X_{end}$</td>
<td>99.9</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
</tr>
<tr>
<td>$T_{end}$</td>
<td>806</td>
<td>811</td>
<td>805</td>
<td>691</td>
<td>774</td>
</tr>
</tbody>
</table>

Different VOCs require different kinds of catalysts for total oxidation. Real VOC emissions are usually mixtures of hydrocarbons, and in mixtures, the compound that is the most difficult to oxidize determines the rate of total oxidation (Janbey et al. 2003). Quite often that compound is methane. Precious metals, Pt or Pd, are usually preferred over base metals because precious metal catalysts allow lower operating temperatures and higher space velocities for a given destruction efficiency (Jennings 1985, Gélin & Primet 2002). However, volume-based comparisons show clearly the goodness of Cu-based catalysts in methane oxidation.

If a very high cleaning efficiency is required, a feature more important than the $T_{50}$ temperature is the temperature of complete oxidation. A lower $T_{50}$ temperature probably means, however, less formation of by-products. This is important if the catalyst’s temperature in the industrial incinerator is fluctuating periodically as in our case, where operation of the industrial catalytic incinerator is controlled by temperature, or if the incinerator operates below the complete combustion temperature. This matter is discussed in connection with the catalysts’ selectivity in Sections 4.4 and 5.3.2.

### 4.3.2 Results of SVOC tests

This Section presents the results of the methyl mercaptane (MM) and dimethyl disulphide (DMDS) oxidation experiments. All the experiments have been carried out at least twice
in order to ascertain the reliability of the results. The results of the thermal oxidation of MM and DMDS showed that the reaction temperature has to be around 500°C for the total oxidation of MM and close to 600°C for DMDS without a catalyst, although the temperatures for 100% conversions for MM and DMDS are ~350°C and ~500°C, respectively (Figs 31a and b). MM requires temperatures higher than 250°C and DMDS close to 400°C for the 50% conversion. The comparison presented in Fig. 31 is based on the catalyst’s volume.
Most of the catalysts decrease the $T_{100}$ (temperature of 100% conversion) of both MM and DMDS. In general, of all of the tested catalysts, metal oxide catalysts were more active than noble metal catalysts in both cases. For the most active catalyst, the $T_{50}$ temperature could not be determined due to its ability to adsorb MM before oxidation. The following order for the MM oxidation can be presented:

Fig. 31. Light-off curves for the oxidation of (a) MM and (b) DMDS.
T₅₀: SVOC₆ > SVOC₇ (80°C) > SVOC₅ > SVOC₄ = SVOC₁ > SVOC₃ > SVOC₂ (230°C)

The order is similar for T₁₀₀ except that the catalyst SVOC₇ is as active as SVOC₅. The corresponding orders for DMDS oxidation are as follows:

T₅₀: SVOC₆ (220°C) = SVOC₅ > SVOC₇ > SVOC₂ = SVOC₄ = SVOC₃ = SVOC₁ (320°C)
T₁₀₀: SVOC₅ (410°C) > SVOC₃ ~ SVOC₆ ~ SVOC₇ > SVOC₄ ~ SVOC₂ ~ SVOC₁ (530°C)

In MM oxidation the catalyst SVOC₆ decreased T₁₀₀ by approximately 270°C. This was over 100°C more than with the other metal oxide catalysts and over 150°C compared with the noble metal catalysts. This is consistent with the results of Wang & Weng (1997). All the metal oxide catalysts showed significant adsorption of MM at the beginning of the experiments; furthermore, part of MM was also oxidized to SO₂ with the most active catalysts SVOC₆ and SVOC₇. Later, when the temperature was increased to the level where 100% conversion of MM was achieved, significant production of SO₂ was observed.

No significant differences between the activities of metal oxide catalysts in DMDS oxidation were observed. Furthermore, in the DMDS oxidation experiments, some adsorption of DMDS was also observed, but it was less significant, and the formation of SO₂ was detected already around the 50% conversion. Adsorption and desorption will be discussed later in connection with the selectivity of the catalysts.

When the results of monolithic noble metal catalysts were compared, it was observed that for the MM oxidation, T₅₀ decreased by approximately 100°C with the catalysts supported on Ce-modified Al₂O₃. For the DMDS oxidation the decrease of T₅₀ was less than 100°C. With the best catalysts T₁₀₀ decreased by ~150°C and ~100°C for MM and DMDS, respectively. The Pt catalyst supported on pure Al₂O₃ showed less activity in the MM oxidation than other catalysts, but similar activity in the DMDS oxidation. This suggests that Ce (Zr) -modification of Al₂O₃ is needed especially in MM oxidation.

At the beginning of the DMDS experiments, DMDS was detected in larger quantities at the outlet of the reactor than was assumed by the feeding values. This was probably due to adsorption of DMDS either on the catalyst surface or on the inner walls of the experimental apparatus. When heating was started, DMDS started to desorb from the surfaces and its values at the outlet increased. This was not as significant with metal oxide catalysts as with noble metal monoliths. Furthermore, blank analyses with air prior to the experiments did not show desorption of any sulphurous compounds from the surfaces of experimental apparatus.

Temperatures at 50% (T₅₀) and 100% (T₁₀₀) conversions of MM and DMDS for all the tested catalysts are presented in Table 10.
Table 10. \(T_{50}\) and \(T_{100}\) [\(\degree C\)] of MM and DMDS for different catalysts.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(T_{50}) MM</th>
<th>(T_{50}) DMDS</th>
<th>(T_{100}) MM</th>
<th>(T_{100}) DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVOC0</td>
<td>270</td>
<td>400</td>
<td>360</td>
<td>530</td>
</tr>
<tr>
<td>SVOC1</td>
<td>170</td>
<td>320</td>
<td>230</td>
<td>~530</td>
</tr>
<tr>
<td>SVOC2</td>
<td>230</td>
<td>320</td>
<td>360</td>
<td>~530</td>
</tr>
<tr>
<td>SVOC3</td>
<td>200</td>
<td>320</td>
<td>300</td>
<td>430</td>
</tr>
<tr>
<td>SVOC4</td>
<td>170</td>
<td>320</td>
<td>230</td>
<td>~530</td>
</tr>
<tr>
<td>SVOC5</td>
<td>100</td>
<td>220</td>
<td>200</td>
<td>410</td>
</tr>
<tr>
<td>SVOC6</td>
<td>&lt;40</td>
<td>220</td>
<td>90</td>
<td>470</td>
</tr>
<tr>
<td>SVOC7</td>
<td>80</td>
<td>250</td>
<td>220</td>
<td>470</td>
</tr>
</tbody>
</table>

To conclude, according to our results Pd-containing catalysts (of the noble metal catalysts) are slightly more active in MM oxidation compared to monometallic Pt catalysts. This is consistent with the results of Burch & Hayes (1995). Similar observations have been done e.g. in methane oxidation (Ojala 2003). Furthermore, catalysts supported on Al\(_2\)O\(_3\)-Ce were better than the one supported on pure Al\(_2\)O\(_3\). No remarkable differences between catalytic activities of noble metals in the DMDS oxidation were found, except \(T_{100}\) for the SVOC3 catalyst was ~100\(\degree C\) less than with other noble metal catalysts.

During pre-treatment, the surface of the catalyst is oxidized and it seems that this is important especially in MM oxidation. The metal oxide catalysts tested have superior activity towards the oxidation of MM and DMDS compared to noble metal catalysts. This may be partly due to the fact, that catalysts SVOC5-7 are designed for VOC oxidation purposes whereas catalysts SVOC1-4 are not (see Chapter 4.2). Furthermore, due to the adsorption capacity of metal oxide catalysts, abatement of MM was actually realised already close to ambient temperatures.

### 4.4 Selectivity of catalysts

Selectivity is regarded, in many cases, as the most important property of a catalyst. The selectivity of a catalyst reflects to the catalyst’s ability to direct the conversion of reactants along one specified reaction pathway (Thomas & Thomas 1997). Catalyst selectivity can be calculated according to the following equation (Ertl et al. 1997a):

\[
S = \frac{\text{amount of desired product}}{\text{amount of all products}} = \frac{\text{amount of desired product}}{\text{amount of consumed reactant}}
\]

In the case of VOC and SVOC complete oxidation, the desired reaction products are CO\(_2\), H\(_2\)O and SO\(_2\). In addition, the oxidation of organic air pollutants, particularly oxy-derivatives such as n-butyl acetate, generally yields partially oxidized by-products (Haberhayer-Troyer et al. 1999). This is also the case with the MM and DMDS oxidation (e.g., Ross & Sood 1977). In addition, formation of SO\(_3\) in the catalytic oxidation of SVOCs is possible (Corro et al. 2001). In catalytic oxidation, due to lower temperatures,
the NO\textsubscript{x} does not form, since thermal NO\textsubscript{x} formation below 1027°C is thermodynamically improbable (Ciuparu et al. 2002, Thevenin et al. 2002a). The formation of intermediates or by-products depends for example on the catalyst used, the oxidized compound and temperature (Ojala 2003).

In catalytic oxidation reactions oxygen and VOC as well as SVOC migrate to the catalyst’s surface by diffusion from the gas stream and adsorb onto the active sites on the catalyst’s surface where the oxidation occurs. The reaction products are then desorbed from the surface and diffuse back into the surrounding gas phase. (Moretti 2001, Levenspiel 1972, Hayes & Kolaczkowski 1997) The oxidation reaction on the catalyst surface may include several mechanistic steps depending on the catalyst and reacting compound. Sometimes products that are only partially oxidized may escape into the gas phase. If the reactivity of the escaped by-product is less than that of the ‘parent compound’, higher temperatures are needed for total oxidation. (O’Malley & Hodnett 1999) If the temperature of incineration is high enough, the oxidation of organic compounds may also take place via gas-phase oxidation in addition to the catalytic route (Janssen & van Santen 1999, Quick & Kamitomai 1995), and it is possible that oxidation of by-products as well as ‘original’ unreacted emission compounds proceeds at the gas phase after a catalyst.

Investigation of partially oxidized by-products during light-off tests can give preliminary information on oxidation mechanisms over different catalysts. However, the formation of by-products in emission abatement applications is not desired, since some unwanted reactions might cause the formation of compounds that are even more harmful than the initial emissions. This is the case when the selectivity of the catalyst plays even a more important role. There are several possibilities to improve the selectivity of a catalyst including promoters, chiral adsorbates (stereoselective and enantioselective catalysis), selective poisons and solvents, without forgetting the shape selectivity of different zeolites (Ertl et al. 1997a). In general, it has been found that noble metal catalysts are more selective in the complete oxidation of VOCs than the metal oxides. This is most likely due to different oxidation mechanisms. The oxidation of VOCs over noble metal catalysts generally takes place via the Langmuir-Hinshelwood mechanism, where both hydrocarbon and oxygen are adsorbed on the active sites and react on the surface to form complete oxidation products. On the other hand, the oxidation mechanism over a metal oxide catalyst proceeds via the Mars-van-Krevelen mechanism, which is a redox mechanism involving both gas-phase and lattice oxygen. This mechanism promotes more likely partial oxidation. (Spivey 1987) Next, selectivity, or the formation of partially oxidized by-products in the oxidation of selected model VOCs and SVOCs, are shortly reviewed.

Research on the selectivity of catalysts in connection with the oxidation of methane usually concerns partial oxidation (e.g., CH\textsubscript{4} → CH\textsubscript{3}OH). It seems that in the case of total oxidation of methane, the more important features of the catalysts are activity and durability. Li et al. (2003) studied the oxidation mechanism of methane over Pd/Al\textsubscript{2}O\textsubscript{3} and Pd/Co\textsubscript{3}O\textsubscript{4} catalysts by the in situ IR technique. They reported the formation of HCOO\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} as adsorbed intermediates that form CO and CO\textsubscript{2}, respectively. They also found that if the ratio O\textsubscript{2}/CH\textsubscript{4} > 2, the adsorbed HCOO\textsuperscript{−} may be converted to CO\textsubscript{3}\textsuperscript{2−}, and CO formation is avoided. In this research, the oxidation conditions are lean, and thus, the formation of CO is not expected. Furthermore, as was mentioned, due to low
oxidation temperatures, composition of emission gases and model compounds, the formation of NOx is not likely to occur.

By-products of the n-butyl acetate catalytic oxidation have been studied e.g. over perovskites, over copper manganate and over uranium oxide. The results of these studies are summarized in Table 11.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Catalysts</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Musalik-Piotrowska &amp; Syczewska 2000)</td>
<td>Perovskites: LaMn₂O₃ (bulk)</td>
<td>Acetaldehyde, propionaldehyde, butyraldehyde</td>
</tr>
<tr>
<td></td>
<td>Ag/cordierite/LaMn₂O₃</td>
<td>Aldehydes, traces of butanol</td>
</tr>
<tr>
<td>(Taylor et al. 1998)</td>
<td>U₃O₈</td>
<td>No organic by-products detected</td>
</tr>
<tr>
<td>(Taylor et al. 2000)</td>
<td>U₃O₈</td>
<td>No organic by-products detected</td>
</tr>
<tr>
<td></td>
<td>U₃O₈/SiO₂</td>
<td></td>
</tr>
<tr>
<td>(Lintz &amp; Wittstock 2001)</td>
<td>Copper manganate</td>
<td>Acetaldehyde, acetic acid, butanol, butene, crotonaldehyde</td>
</tr>
</tbody>
</table>

For example, Lintz & Wittstock (2001) found the formation of the above-mentioned by-products at temperature of 350°C when the T₁₀₀ of n-butyl acetate was already achieved. In the experiments, the amounts of by-products started to decrease when the reactor length i.e. residence time was increased.

In MM oxidation over cobalt molybdate Ross & Sood (1977) detected the following reaction products at a temperature level of 300°C: DMDS and water (main reaction products), SO₂ (about 25% compared to fed MM) and traces of methanol, formaldehyde, ethyl methyl disulphide, ethyl mercaptan and CO₂. Methanol formation was enhanced when water was present, and the formation of ethyl methyl disulphide was increased at higher initial MM concentrations. However, at temperatures > 400°C mostly SO₂, CO₂ and H₂O were present. Dalai et al. (1997) found out that when MM was oxidized over activated carbon (50-175°C, 122-364 kPa, O₂:MM 1.1-1.33 times stoichiometric value) the main reaction products were DMDS and water, while CO₂ was produced in small amounts. CS₂ and (CH₃)₂S (dimethyl sulphide, DMS) were produced at 200°C in trace amounts. A 99.99% conversion of MM was achieved at temperatures >100°C. Unfortunately, catalyst deactivation was observed.

### 4.4.1 Results of VOC tests

This section concerns the catalytic oxidation of n-butyl acetate over different catalysts. In addition, the thermal oxidation of n-butyl acetate is also discussed as a comparison. As was expected, the formation of organic by-products was not observed during methane oxidation, and therefore, methane oxidation is not included in this discussion.

In order to discover the by-products and their concentrations, all the organic compounds formed during the light-off tests over different catalysts and in thermal
oxidation were analysed by the GC-FID (quantitative analysis). Identification of by-products with some of the catalysts has also been carried out by the GC-MS, since different compounds may have same retention time in GC-column and may be easily falsely detected as reported in Section 2.1.2. Some of the hydrocarbons formed during oxidation are detected but not identified and/or quantified due to their low concentrations and the detection limits of the GC-MS analysis. The quantification of those unidentified compounds is carried out with a representative compound that elutes with similar retention time (see Table 12; quantification compound). Furthermore, only the catalysts that produced by-products at larger concentrations were analysed with GC-MS. Therefore, the mechanism of the n-buty l acetate oxidation reaction over different catalysts is not fully understood and by-products are presented as numbers according to their retention time in a GC column. Table 12 presents the numbering of by-products, retention times, representative compounds that were used in quantification, and alternative compounds that were identified by GC-MS at a certain retention time during n-butyl acetate oxidation over some of the catalysts.

Table 12. Numbering, retention times, quantification compounds and some of the identified by-products of n-butyl acetate oxidation over selected catalysts.

<table>
<thead>
<tr>
<th>By-product Retention time [min]</th>
<th>Quantification compound of FID</th>
<th>Identified compound by GC-MS (Catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 3.824 Methane</td>
<td>Methane (H, I, J)</td>
<td></td>
</tr>
<tr>
<td>2 4.063 Methanol</td>
<td>2-methyl-1-propene (H), Butene (T)</td>
<td></td>
</tr>
<tr>
<td>3 4.124 Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 4.245 i-Propanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 4.275 Acetone</td>
<td>Acrylic aldehyde (H, I, J), Acetone (D)</td>
<td></td>
</tr>
<tr>
<td>6 4.319 n-Pentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 4.364 n-Propanol</td>
<td>Propionaldehyde (H), Acetic acid (D)</td>
<td></td>
</tr>
<tr>
<td>8 4.632 n-Hexane</td>
<td>n-Hexane (D)</td>
<td></td>
</tr>
<tr>
<td>9 4.680 Ethyl acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 4.745 i-Butanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 4.782 n-Heptane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 5.271 Methyl cyclohexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 6.156 Toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 6.263 n-Butyl acetate</td>
<td>n-Butyl acetate (T, D, H, I, J)</td>
<td></td>
</tr>
<tr>
<td>15 8.366 o-Xylene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As Table 12 indicates, the by-products eluted at a certain retention time differ depending on the catalyst. Therefore, all the by-products of n-butyl acetate with all the different catalysts should be identified separately by GC-MS. Table 13 lists the identified compounds formed in oxidation over four of the catalysts.
Table 13. Some of the by-products of n-butyl acetate oxidation over selected catalysts detected by GC-MS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (450°C)</td>
<td>Hexane, 2-Methyl-1-propene, Acetone, Butyraldehyde</td>
</tr>
<tr>
<td>H (350°C)</td>
<td>Methane, 2-Methyl-1-propene, Acetone, Butyraldehyde, 1-Butanol</td>
</tr>
<tr>
<td>I (350°C)</td>
<td>Methane, 2-Methyl-1-propene, Acetone, Butyraldehyde, 1-Butanol</td>
</tr>
<tr>
<td>J (400°C)</td>
<td>Methane, 2-Methyl-1-propene, Acetone, Acetic acid, Butyraldehyde, 1-Butanol</td>
</tr>
</tbody>
</table>

According to the literature, the earlier identified by-products of n-butyl acetate oxidation include acetaldehyde (etanal), propionaldehyde (propanal), butyraldehyde (butanal), butanol, acetic acid, butene and crotonaldehyde (2-butenal) (see Table 11 for references). Our identifications are quite well in agreement with the earlier findings.

The following Figs 32 a-f show some examples of the by-product formation during the oxidation of n-butyl acetate over selected catalysts.
Fig. 32. Examples of the by-product formation during the n-butyl acetate light-off tests, quantified by GC-FID: a) thermal experiment, b) catalyst C, c) catalyst D, d) catalyst E, e) catalyst H, and f) catalyst J.
In general, the formation of by-products starts to decrease after the T_{50} temperature. However, with catalysts C (Fig. 32b), D (Fig. 32c), H (Fig. 32e) and J (Fig. 32f) some secondary maxima are detected. The amount of by-product 2 starts to increase after the light-off temperature with catalyst C even it was not formed as significantly as before the light-off. The secondary maximum of by-product 2 is observed with catalysts D, H and J. This kind of behaviour is probably due to different active sites on the catalysts’ surface.

Sometimes the amount of by-product 1 (elutes with the same retention time as methane) increases when the temperature approaches the end temperature of the experiment. This phenomenon was observed with the catalysts A to D, which were noble metal catalysts on metallic monolith carriers. This kind of behaviour was not seen with granular-type catalysts (catalysts E-J). Table 14 presents four highest peaks of by-products as well as their relative amounts and the sum total concentration of all by-products divided by the number of experiments in which by-products were observed. The total concentrations of by-products are calculated from discrete analysis points and should only be considered suggestive.

Table 14. Maximum peak ranking of the by-products, their relative amounts and proportional cumulative total concentrations of by-products for the experiments.

<table>
<thead>
<tr>
<th>Peak ranking</th>
<th>Thermal (T)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2 (95.5)</td>
<td>7 (47.3)</td>
<td>7 (27.1)</td>
<td>7 (11.8)</td>
<td>2 (56.4)</td>
</tr>
<tr>
<td>2.</td>
<td>5 (1.2)</td>
<td>8 (22)</td>
<td>2 (30.8)</td>
<td>2 (37)</td>
<td>7 (10.6)</td>
</tr>
<tr>
<td>3.</td>
<td>7 (1.3)</td>
<td>5 (6.2)</td>
<td>8 (18.2)</td>
<td>5 (13)</td>
<td>3 (14.6)</td>
</tr>
<tr>
<td>4.</td>
<td>1 (0.7)</td>
<td>2 (15.2)</td>
<td>5 (10.1)</td>
<td>8 (15.2)</td>
<td>8 (9.3)</td>
</tr>
<tr>
<td>Additional*</td>
<td></td>
<td></td>
<td></td>
<td>1 (13.4)</td>
<td></td>
</tr>
<tr>
<td>Total/ppm**</td>
<td>1792</td>
<td>33</td>
<td>68</td>
<td>17</td>
<td>46</td>
</tr>
</tbody>
</table>

The maximum peak ranking of by-products does not necessarily correlate with the cumulative amount of the formation of a certain by-product. However, when the data of the highest peak and relative amount is combined, a small relative amount indicates a narrower temperature range, which the by-product is formed and, probably, in some cases more temperature-dependent reaction window compared to the formation of other by-products.

In the thermal experiment (T, without any catalyst) it was observed that by-product 2 (butene) comprised 95.5 vol-% of all the measured by-products. The total amount of detected by-products is almost 1800 ppm. The 99.8% conversion of n-butyl acetate was achieved at 795°C, and the total VOC concentration remaining at the end temperature...
was still 6.1 ppm. When catalysts are used, none of these compounds is as dominating as butene in the thermal experiment. However, the relative amount of by-product 2 with catalysts H-J (for H: 2-methyl-1-propene) are close to the corresponding value of the thermal experiment. In the experiments with catalysts A-G, the relative amounts of other detected by-products increase when compared with the thermal experiment. Dominating compounds and their concentrations change with different experiments, which indicates that the mechanism of the reaction for certain case has to deviate from each other. Based on intermediates, it seems that the mechanisms between noble metal catalysts have some similarity together (see relative amounts and peak ranking from Table 14) and the mechanisms of metal oxide catalysts have some similarity together, provided that the by-products are the same.

When the total amounts of by-products are compared, one can observe that catalysts in general decrease the total amount of the by-products formed. Platinum-containing catalysts seem to be more selective to form CO₂ than the corresponding Pt-Pd catalysts. However, slightly higher temperatures are needed for the 99.8% conversions than, for example, with copper-containing catalysts I and J. Catalyst C forms the minimum amount of by-products, but it is only just the third in T₅₀ and the fourth in T₉₅ rankings. However, the catalyst E (Cu-Mn oxide) too exhibits very good selectivity, i.e., formation of by-products is low and it is the second in both T₅₀ and T₉₅ rankings. The most active catalyst G in n-butyl acetate oxidation is fifth in selectivity.

When comparing metallic monoliths, it can be seen that less by-products are formed with the catalysts Pt/Al₂O₃-La and Pt-Pd/Al₂O₃-La than with the catalysts Pt/Al₂O₃-Ce and Pt-Pd/Al₂O₃-Ce. This may indicate that by using the Al₂O₃-La washcoat, less formation of by-products will occur. La stabilized Al₂O₃ seems to improve the selectivity of the total oxidation of n-butyl acetate more than Al₂O₃-Ce. However, the maximum amounts of by-products occurred in a narrower temperature range with the Al₂O₃-Ce catalysts, which may be more important in industrial-scale applications, since temperature-based controlling of the formation of by-products may be easier when by-products are formed in a narrow temperature range.

As was already mentioned in Section 3.1, the total concentrations of VOCs decrease further as the gas flows through heat exchangers after the catalysts. This indicates that the oxidation reactions in the industrial scale incinerator continue when the gas flow passes through the heat exchangers. This may be partly due to the gas-phase oxidation initiated at higher temperatures at the outlet of the catalysts maintained by the heat exchangers and partly due to the activity of heat exchanger construction material. The formation of by-products in laboratory experiments (Chapter 3) was stronger in thermal oxidation and in the case of metal packings than in studies conducted with a catalyst. As was observed, the selectivities of total oxidation with metal oxide catalysts were, with rough estimation, smaller than with noble metal catalysts. This is also consistent with the conclusions of Spivey (1987). If the surface of the heat exchanger is active, it is due to metal oxides (and probable Mars-van Krevelen mechanism), and then the larger formation of by-products cannot be only attributed to thermal oxidation mechanisms. However, this does not exclude the possibility of thermal oxidation, either, and it is quite reasonable to state that oxidation reactions in the industrial-scale incinerator occur both with catalytic and gas-phase oxidation mechanisms. This was also speculated by Janssen & van Santen (1999).
4.4.2 Results of SVOC tests

The formation of sulfur-containing by-products was followed by GC-FPD during MM and DMDS oxidation. These measurements also allowed for the calculation of sulfur balances at T₁₀₀ as well as selectivities to SO₂ during the experiments. The formation of sulphur-containing compounds (i.e. H₂S, DMS, DMDS) was observed in both model reactions, in MM and in DMDS oxidation. Since the detection of H₂S, DMS, DMDS was carried out only by GC-FPD, some caution should be taken into account in the interpretation of the results due to the fact that the by-products were not confirmed by GC-MS. Furthermore, possible organic by-products formed during the reaction (mentioned in earlier research by Ross & Sood 1977) could not be detected by the FPD-detector.

The sulphur balances of MM and DMDS oxidation to SO₂ are presented in the following table, Table 15. The general oxidation reactions of MM and DMDS, which were used in calculations, are as follows:

\[
\text{CH}_3\text{SH} + 3 \text{O}_2 \rightarrow \text{CO}_2 + \text{SO}_2 + 2 \text{H}_2\text{O} \quad (6)
\]

\[
2 \text{CH}_3\text{SSCH}_3 + 11 \text{O}_2 \rightarrow 4 \text{CO}_2 + 4 \text{SO}_2 + 6 \text{H}_2\text{O} \quad (7)
\]

Table 15. Theoretical and measured yields for SO₂ in the oxidation of MM and DMDS as well as the corresponding T₁₀₀ °C temperatures.

| Catalyst | MM | | | | | | DMDS | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Theoretical SO₂ yield [mg m⁻³] | SO₂ yield at T₁₀₀ [mg m⁻³] | T₁₀₀ [°C] | Theoretical SO₂ yield [mg m⁻³] | SO₂ yield at T₁₀₀ [mg m⁻³] | T₁₀₀ [°C] |
| SVOC0 | 1385 | 666 | 360 | 1341 | 3234 | 530 |
| SVOC1 | 1631 | 256 | 230 | 1546 | 1715 | ~530 |
| SVOC2 | 2002 | 1182 | 360 | 1587 | 1364 | ~530 |
| SVOC3 | 1818 | 708 | 300 | 1602 | 442 | 430 |
| SVOC4 | 1880 | 233 | 230 | 1827 | 939 | ~530 |
| SVOC5 | 1483 | 356 | 200 | 1340 | 3579 | 410 |
| SVOC6 | 1845 | 0 | 90 | 1674 | 2917 | 470 |
| SVOC7 | 1859 | 964 | 220 | 1662 | 2971 | 470 |

* Note: T₁₀₀ temperatures are the lowest temperatures where feed compound was not observed.

Table 15 shows that in MM oxidation at the temperature of 100% conversion, sulphur balance is not fulfilled in any of the cases. This is partly due to the formation of sulphur-containing by-products and partly due to adsorption. This is especially significant with catalyst SVOC6, which adsorbs all MM at 90°C without the formation of SO₂. In the thermal experiment (SVOC0) the formation of H₂S was observed at T₁₀₀. It is important to note that in MM experiments with catalyst SVOC1 and SVOC4-7 the additional formation of H₂S was observed above the T₁₀₀ temperature. This temperature was usually
around 300°C, except with catalyst 7 it was higher than 600°C. Similarly, H₂S was observed momentarily in DMDS oxidation in all of the experiments at roughly above temperature of 300°C.

The SO₂ yields measured in DMDS oxidation at T₁₀₀ are over the respective theoretical values, except with noble metal catalysts 2, 3 and 4. The formation of H₂S at T₁₀₀ was observed in the thermal experiment (SVOC0) and with metal oxide catalysts 5, 6 and 7. As was mentioned, the formation of H₂S sometimes started before DMDS achieved the T₁₀₀ temperature, starting at around 300°C. This is quite unexpected, since H₂S formation is usually connected to reducing atmospheres and, for example, the H₂ reduction of sulphates formed on surface of the catalyst (Bazin et al. 1997, Luo et al. 2002). Probably H₂S is not a by-product of oxidation reaction, but a by-product caused by e.g. experimental apparatus.

To give a more complete view of these results, the SO₂ selectivity for MM and DMDS oxidation at different temperatures during the light-off tests were calculated. The selectivity of MM and DMDS oxidation to SO₂ was calculated according to Equations 8 and 9. The selectivities are calculated based on the exact feeding concentrations of MM and DMDS with an assumption that the reactant is totally consumed. Thus the unreacted DMDS below T₁₀₀ is considered to be an unwanted ‘product’.

\[
S_{MM} = \frac{c(SO_2)}{c(MM)} \cdot 100\% \quad (8)
\]

\[
S_{DMDS} = \frac{c(SO_2)}{2 \cdot c(DMDS)} \cdot 100\% \quad (9)
\]

Figs. 33 a and b present the selectivity of MM and DMDS oxidation to SO₂, respectively.
Fig. 33. Selectivities to SO$_2$ for the oxidation of a) MM and b) DMDS.

Fig. 33 shows a general trend in SO$_2$ selectivity. First, SO$_2$ selectivity starts to increase and roughly between the temperatures of 300-400°C in MM oxidation (SVOC0 and SVOC5), and between 280-400°C in DMDS oxidation (in all the experiments), SO$_2$ selectivity exceeds the theoretical maximum. In addition, above ~650°C in MM oxidation and above ~600°C in DMDS oxidation, the selectivity of SO$_2$ is over 100% again. Several researchers have observed a similar kind of trend in SO$_2$ adsorption, in SO$_2$ + O$_2$ reaction or in SO$_2$ TPD experiments. For example Corro et al. (2001) studied SO$_2$ reactions over pure γ-Al$_2$O$_3$ and Pt, Sn and Pt-Sn supported on γ-Al$_2$O$_3$. They found that the adsorption of SO$_2$ begins at 25°C. The maximum uptake of SO$_2$ is at around 150°C and then it starts to decrease. This is consistent with our results, where the SO$_2$
concentration at the outlet of the reactor starts to increase above a temperature of ~150°C. Corro et al. (2001) did not find additional adsorption above temperatures of 150°C.

In SO2 TPO experiments Corro et al. (2001) found a second uptake of SO2 at 400°C on γ-Al2O3 and proposed that it is related to the oxidation of SO2 to SO3. They also found out that Sn added into a Pt/γ-Al2O3 catalyst decreases the SO3 formation. (Corro et al. 2001) In our experiments, the oxidation of SO2 is a possible explanation for the decrease in SO2 concentrations roughly at above 300°-400°C in MM oxidation and above 350°C in DMDS oxidation. The oxidation of SO2 to SO3 over the Pt/Al2O3 catalyst has been reported to occur at temperatures over 300°C (Corro et al. 2001). Limousy et al. (2003) have studied SO2 sorption on different SOx traps, and found out that the SO3 formation was thermodynamically restricted at 600°C and above. The formation of SO3 may cause the formation of sulphides and sulphates e.g. with the alumina washcoat. They found out that the decomposition of aluminium sulphite starts at 450°C and aluminium sulphate at 860°C.

When the total oxidation temperatures, where only SO2 formation was observed at first (See Table 16), are compared with selectivities, it can be seen that in both cases, the formation of SO2 is close to its second minimum (at T_{total ox.}) or decreases from the first maximum when the temperature is further increased. First the formation and then the decomposition of sulphates, sulphites or both would explain the decrease in SO2 selectivity and the following increase after T_{total ox.} in our case, too. Unfortunately we are not able to prove this explicitly.

It is very important to take into account the results of the thermal experiment. The thermal experiments (VOC0) show that the phenomenon described above and in Fig. 32 is not only due to catalysts, but it is also probably partly caused by the adsorption of sulphur compounds on the surfaces of the experimental apparatus. Therefore, SO2 yields and selectivities do not give accurate information in this case, and only trends can be observed. However, when the results of thermal experiment are compared to the result of the experiments with catalysts, the decrease in SO2 selectivity above a temperature of ~400°C is not as significant as with catalysts. Furthermore, the initial formation of SO2 starts at higher temperatures than with catalytic experiments. Thermal T_{SO} for MM and DMDS are 270°C and 400°C, respectively. This should be equivalent to ~50% selectivity, in the ideal case. However, in MM oxidation corresponding selectivity is less, and it may mean the formation of SO3, which is slowly decreased up to temperatures of ~400°C after when SO2 is more preferred form. In the thermal case, the first ‘over production’ of SO2 may also be related to adsorption on the surfaces of experimental apparatus and following desorption. The following decrease ends close to the value of 100% selectivity (~600°C), which may indicate complete oxidation without the formation of by-products (compare T_{tot ox.} Values in Table 16). In addition, it does not decrease below 100%, and starts to increase again close to 700°C. It has been reported that the formation of SO3 from SO2 is thermodynamically restricted at higher temperatures and favored at lower temperatures (Turpeinen & Maunula 1993). Also, possible decomposition of sulphates starts at higher temperature, which may contribute to increase in SO2 formation at the end of the experiment. This supports the opinion that in thermal experiments sulphur may be in the form of SO3 at least up to the temperature of 400°C, and when the temperature is further increased, the formation of SO3 is more favored. In general, the limiting temperature is, however, dependent on the oxygen concentration as well as the presence of noble metals and different supports in the case of catalytic experiments.
Table 16. Temperatures for total oxidation of MM and DMDS and cumulative amounts
(proportional to experimental points) as well as identifications of by-products during the
experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(T_{\text{total ox.}}^{*}[^\circ\text{C}])</th>
<th>Concentration [mg m(^{-3})]</th>
<th>By-products (proportions to experimental points)</th>
<th>Concentration [mg m(^{-3})]</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVOC0</td>
<td>~550</td>
<td>~600</td>
<td>DMDS</td>
<td>150</td>
<td>H(_2)S</td>
</tr>
<tr>
<td>SVOC1</td>
<td>~370</td>
<td>~540</td>
<td>DMDS, H(_2)S</td>
<td>64</td>
<td>H(_2)S, DMS</td>
</tr>
<tr>
<td>SVOC2</td>
<td>450</td>
<td>~530</td>
<td>DMDS</td>
<td>105</td>
<td>H(_2)S, DMS</td>
</tr>
<tr>
<td>SVOC3</td>
<td>~550</td>
<td>~430</td>
<td>DMDS, DMS</td>
<td>116</td>
<td>H(_2)S, DMS</td>
</tr>
<tr>
<td>SVOC4</td>
<td>~400</td>
<td>540</td>
<td>DMDS, H(_2)S</td>
<td>164</td>
<td>H(_2)S</td>
</tr>
<tr>
<td>SVOC5</td>
<td>~408</td>
<td>~488</td>
<td>DMDS, DMS, H(_2)S</td>
<td>125</td>
<td>H(_2)S, DMS</td>
</tr>
<tr>
<td>SVOC6</td>
<td>~559</td>
<td>~541</td>
<td>DMDS, DMS, H(_2)S</td>
<td>135</td>
<td>H(_2)S</td>
</tr>
<tr>
<td>SVOC7</td>
<td>~469</td>
<td>~551</td>
<td>DMDS, DMS, H(_2)S</td>
<td>223</td>
<td>H(_2)S</td>
</tr>
</tbody>
</table>

* Temperatures for the total oxidation should be considered maximum temperatures (i.e. due to the fact that the analysis was not continuous, this was the first temperature when any of the by-products were not detected by GC-FPD).

Further investigation of Fig. 33 reveals that metal oxide catalysts (5-7) seem to be slightly more selective in DMDS oxidation at lower temperatures compared to noble metal catalysts (1-4). However, this may be attributed to their adsorption capacity. The differences between the selectivities of metal oxide catalysts and noble metal catalysts in DMDS oxidation are related to their light-off temperatures: the \(T_{50}\) temperatures deviate by \(~100[^\circ\text{C}]\), but at those temperatures selectivities are roughly the same i.e. 75% selectivity is achieved at \(220[^\circ\text{C}]\) and at \(320[^\circ\text{C}]\) with metal oxide and noble metal catalysts, respectively. Similar trends cannot be observed in MM oxidation as clearly as in DMDS oxidation.

When this result, discussed above, is compared to the results presented in Table 16, one can see that in the case of MM oxidation, the noble metal catalyst SVOC4 (Pt-Pd/Al\(_2\)O\(_3\)-Ce) produces more by-products than the other catalysts. In DMDS oxidation the metal oxide catalyst SVOC7 (Cu\(_x\)Cr\(_y\)O\(_z\)/Al\(_2\)O\(_3\)) produces the most significant amounts of by-products. Less by-products in MM oxidation are formed with noble metal catalyst SVOC2 (Pt/Al\(_2\)O\(_3\)) and in DMDS oxidation with noble metal catalyst SVOC1 (Pd/Al\(_2\)O\(_3\)-Ce). In general, slightly more sulphur-containing by-products are formed in MM oxidation than in DMDS oxidation. When the formation of by-products in catalytic oxidations is compared with the results of thermal oxidation, no great differences can be observed between these two cases. Interestingly, it seems that in our case it is not enough to calculate selectivities to SO\(_2\) or sulphur balances, but the amount of formed by-products should also be taken into account when the catalysts are compared.

In summation, the oxidation of MM and DMDS leads first of all to the formation of oxidation products: CO\(_2\), H\(_2\)O and SO\(_2\). However, in the case of MM oxidation, the significant formation of DMDS as a by-product is also observed. The total catalytic oxidation of MM requires, depending on the catalyst, temperatures of 370-560[^\circ\text{C}] and that of DMDS 430-550[^\circ\text{C}] until all the by-products, which may be detected by GC-FPD, are oxidized. The same temperatures for thermal oxidation are \(~550[^\circ\text{C}]\) and \(~600[^\circ\text{C}]\) for MM and DMDS, respectively.
The formation of DMDS was also observed in pilot experiments carried out earlier (Ojala et al. 2005a). In general, the formation of DMDS as a by-product is consistent with the measurements of Kastner et al. (2003), Martinez et al. (2002) and Dalai et al. (1997). At around 350°C MM and DMDS are not fully oxidized, and it is suggested (Martinez et al. 2002) that the mechanism of oxidation includes the formation of methylthiyl radicals (CH₃S), which further react to form DMDS. Kastner et al. (2003) have proposed a potential mechanism for the oxidation of MM: They believe that if the R group is a methyl group, oxygen is not capable of reacting with R-SS-R or R-S-R. Therefore, there is no further reaction for that, and this thus leads to the formation of DMDS from MM. This could be avoided when the temperature is increased.

4.5 Durability of catalysts

The previous two sections have demonstrated the importance of a catalyst’s activity and selectivity in the catalyst’s operation. As the comparisons of T₁₀₀ and T₅₅₅ temperatures show, it is not enough to follow only the oxidation of emission compounds; rather the formation of by-products should be avoided, too. In industrial scale incinerators, it is quite typical to increase the operation temperature in order to improve catalyst activity and selectivity, and thus decrease the formation of by-products. Increasing the temperature is very practical in one sense, but it may affect the stability or durability of a catalyst. This section presents the durability of selected catalysts in VOC and SVOC emission abatement.

A catalyst is not consumed during the reaction, and by this definition it should last forever. In real life, a catalyst loses its activity during the time of the usage i.e. it deactivates. Deactivation is a result of the removal of the active sites from a catalyst surface, which can occur through a number of different mechanisms, both physical and chemical (Butt & Petersen 1988). Table 17 summarizes the different mechanisms of catalyst aging.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Thermal</th>
<th>Fouling</th>
<th>Mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Poisoning: irreversible</td>
<td>- Sintering (redispersion)</td>
<td>- Carbonaceous deposits</td>
<td>- Thermal shock</td>
</tr>
<tr>
<td>adsorption or reaction on/with</td>
<td>- Alloying</td>
<td>(coking)</td>
<td>- Attrition</td>
</tr>
<tr>
<td>the surface</td>
<td>- Support changes</td>
<td>- Small particulate deposits (masking)</td>
<td>- Mechanical breakage</td>
</tr>
<tr>
<td>- Inhibition: competitive</td>
<td>- Noble metal-base metal interactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reversible adsorption of poison precursor(s)</td>
<td>- Metal/metal oxide-support interactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Poison induced reconstruction of catalytic surfaces</td>
<td>- Oxidation (alloy formation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Physical/chemical blockage of support pore structure</td>
<td>- Noble metal surface orientation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Metal volatilization</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A catalyst with good stability will only change very slowly over the course of time under conditions of use. Some of the things that lead to a progressive loss of activity or selectivity or mechanical strength are as follows (Ertl et al. 1997a):

- Coke forms on some catalysts through the involvement of unwanted reactions of hydrogenolysis, polymerization, cyclization, and hydrogen transfer
- Reactants, products or poisons may attack active agents or the support
- Volatile agents, such as chlorine, may be lost during reactions such as reforming
- The crystals of a deposited metal may become enlarged and regrouped. A change in the crystalline structure of the support can cause a loss of mechanical strength
- Progressive adsorption of trace poisons in the feed or products may reduce activity.

In the catalytic oxidation of VOCs, probably the most important deactivation mechanisms are fouling and chemical deactivation, although thermal shocks (mechanical deactivation) may occur if the organic waste stream is not evenly distributed or perfectly mixed before the catalyst. Also, abrasion may occur if the waste gas contains particulates. Thermal deactivation mechanisms may occur if the VOC concentration is momentarily increased, but in normal operation conditions, the temperature does not exceed the critical values for thermal deactivation. In an industrial scale operation, it is also important to realize that the deposition of rust and scale on the catalyst surface originating from the other parts of the process is not uncommon (Trimm 2001, Jennings 1985).

Sulphur is known to be a catalyst poison. However, the poisoning can be reversible (Jennings 1985) and it is dependent on temperature (e.g., Chu et al. 2003). The oxidation of SVOCs may cause the deactivation of the catalyst during the time of usage. There are a number of possible deactivation mechanisms due to sulphurous compounds. For example, DMDS may adsorb on catalytic surfaces, but as discussed before, the possible formation of SO$_3$ during the oxidation reactions (of e.g., H$_2$S, MM and DMDS), too, may cause e.g., the sulphating of the support. (Dalai et al. 1997, Bashkova et al. 2005, Jones et al. 2003, Chang et al. 1997, Meyoo et al. 1998) It is reported that Pt in particular is very active in catalyzing the SO$_2$ reaction to SO$_3$ and probably thereby sensitive to the sulphation of the support (Jones et al. 2003, Mahzoul et al. 2000). In addition, H$_2$S observed in the oxidation of MM and DMDS (see Section 4.4.2) may bond very strongly to the active sites and form stable surface metal sulphites (Jones et al. 2003).

Chu et al. (2003) studied the poisoning of an MnO/Fe$_2$O$_3$ catalyst e.g. in DMDS oxidation and found out that sulphur-poisoning was dependent on the reaction temperature. The deactivation was not significant when the temperature exceeded 350°C. Jones et al. (2003) studied methane oxidation over Pt, Pd and Rh catalysts supported on Al$_2$O$_3$ in the presence of reduced sulphur compounds (e.g. MM). They observed the deactivation of all the tested catalysts, of which the Pd catalyst was less deactivated. The regeneration in reducing conditions recovered, at least partly, the activity of Pd and Rh catalysts, but with the Pt catalyst agglomeration was observed and the regeneration was seen as very difficult. Lee & Rhee (1998) found out that Pt-Pd bimetallic interaction (supported on beta zeolite) could improve resistance to irreversible sulphur adsorption and sulphur-induced coke formation during isomerization of n-hexane. A lot of research has been carried out concerning the deactivation of different catalysts with SO$_2$ (e.g., Ferrandon et al. 1999). Interestingly, SO$_2$ sometimes also has beneficial effects. For example Corro et al. (2002) have reported on the promoting effect of SO$_2$ on propane oxidation over Pt/Al$_2$O$_3$ catalyst at temperatures higher than 300°C. Skoglundh et al.
(2001) too have reported on the promoting effect of SO$_2$ in the oxidation of ethyl acetate, ethanol and propane over a Pt/γ-Al$_2$O$_3$ catalyst, and Meyoo et al. (1998) in methane oxidation.

The simulation of real deactivation is difficult on a laboratory scale, since it is not an easy task to exactly reproduce the same operation conditions to the laboratory to imitate the real process conditions. To create fast and reliable aging in the laboratory, knowledge of the real aging conditions is needed. According to Lassi (2003), the usage of multiple surface characterization techniques when studying real aging, gives a reliable basis for the selection of proper laboratory scale aging procedures.

The aging of the catalysts in VOC oxidation processes is also a slow phenomenon. The expected time of usage in normal process conditions for the monolithic catalysts should be approximately 20 years. This argument is partially based on the experience gained from the catalytic oxidizer, which was installed some 10 years ago in Tikkurila, Finland (Lylekangas 1996). However, in the case of SVOC oxidation, the deactivation of a catalyst is expected to be more pronounced than in solvent-VOC oxidation.

The following sections present the results of catalyst aging, or durability tests. The durability of four noble metal catalysts (A-D) in solvent VOC oxidation conditions was followed in industrial scale, whereas the durability of one SVOC catalyst (SVOC5) was traced at a laboratory scale in the oxidation of DMDS.

### 4.5.1 Results of VOC tests

The durability of four VOC catalysts (A-D) was monitored on an industrial scale. The set-up for aging and the catalysts’ characteristics are presented in Experimental Section 4.2. The test catalysts (Pt, Pt-Pd) were installed in an industrial-scale catalytic incinerator, close to a painting shop that uses solvent-based coating agents, the emissions of which are treated catalytically. The emission gases mostly contain n-butyl acetate, but some alcohols and other organic compounds are also found (Ojala 2004b). The pigments used in paints include e.g., magnesium silicate, titanium dioxide, iron oxide and tin oxide (information given by the suppliers), which may be potential catalyst poisons or more likely, cause masking of the catalytic surfaces. The incinerator operates with flow-reversal at close to 350°C and if the temperature exceeds 520°C the incinerator will be shut down automatically. The temperature of the gas at the inlet of the incinerator fluctuates according to the concentration and phase of the process. However, the temperature above the catalyst remains roughly constant, ~400°C, regardless of the process phase (Ojala 2004b). Due to low temperatures, thermal deactivation of the catalysts was not expected.

Characterization of fresh and aged catalysts has been carried out by activity experiments (light-off measurements) and by different characterization methods (e.g., BET, chemisorption, SEM, XRD and FTIR), presented in Sections 3.2.2 and 4.2.

The light-off curves for the fresh catalysts in methane oxidation, presented in Fig. 34, show that bimetallic Pt-Pd catalysts (B and D) are slightly more active than similar monometallic Pt catalysts (A and C). Temperatures close to 800°C are needed for the 100% conversion of methane. In n-butyl acetate oxidation, monometallic Pt catalysts were somewhat more active. However, 100% conversions were achieved at around 500°C with all the catalysts.
Fig. 34. Light-off curves for the fresh catalysts in methane oxidation.

Figures 35 a and b show the T\textsubscript{50} temperatures (temperature of 50% conversion) and the conversions at 750°C for methane oxidation over the catalysts with different ages. The temperature of 750°C was selected as the reference temperature, since it has been reported (Pieck et al. 2002) that the mean temperature needed for the combustion of methane without a catalyst is about 825°C and the possible effect of gas phase oxidation when comparing the results is thus avoided.

Fig. 35. a) T\textsubscript{50} temperatures of methane oxidation and b) conversions at 750°C for fresh and aged catalysts.
The $T_{50}$ values of methane for the catalysts aged 25 months are increased by ~50°C (Fig. 35a). Similarly, conversions at 750°C are decreased from the initial values (see Fig. 35b). The variation in both $T_{50}$ and conversions at 750°C between the catalysts with different ages may be partly due to reversible poisoning. For example, Vigneron et al. (1996) have reported similar variations in the aging of VOC catalysts operating in the oxidation of coil-coating emissions, which were assumed to originate from reversible poisoning. Concentrations of the emissions after the industrial scale incinerator were also measured when the catalyst samples were taken out from the incinerator. The calculated conversions were 96.9% (initial), 98.7% (9 months), 85.5% (16 months) and 87% (25 months) (Ojala 2004b). These values are affected by the duration of the measurement and the operation phase of the incinerator, and thus the changes may not indicate reversible poisoning. Without continuous monitoring of the outlet concentrations in an industrial-scale incinerator, the possibility of reversible poisoning cannot be assured.

In general, catalysts C and D supported on $\gamma$-Al$_2$O$_3$-La seemed to be more active at 750°C after 25 months of aging. A similar trend cannot be observed in $T_{50}$. No clear trend in activities can be observed between conversions at 750°C for similarly supported Pt and Pt-Pd catalysts; however, Pt-Pd catalysts aged 25 months have a slightly lower $T_{50}$ in methane oxidation. In this case, when the question is the abatement of solvent emissions, the more important feature is the end conversion or total oxidation temperature, rather than the $T_{50}$ and it seems that La stabilization of a catalyst is more effective than Ce regardless of the noble metal used (Pt, Pt-Pd).

The specific surface areas (BET) of the catalysts for fresh and aged samples are presented in Fig. 36. In general, the surface areas decrease during aging after the first increase in the surface area. The increase in the surface area is probably related to the slight increase in the activities of the catalysts, which is observed when the light-off curves for different catalysts in methane and in n-butyl acetate oxidation (not shown here) are compared. The BET surface areas for catalysts C and D ($\gamma$-Al$_2$O$_3$-La washcoat) were slightly higher than for catalysts A and B after 25 months of aging.

Fig. 36. Specific surface areas (BET) of fresh and aged catalysts.
The chemisorption measurements of the catalysts show an increase in metal dispersion after 3 months of aging except with catalyst C. This increase is consistent with the observations of BET measurements. It has also been noticed that with these certain catalysts the activity increases after certain time of usage as well. These phenomena are probably due to further calcination of the catalysts. The values of metal dispersion and metallic surface area generally decrease when further aging takes place. The metal dispersions as well as metallic surface areas of catalyst D remain quite unchanged during the whole aging period. As a rule, they are smaller for catalyst C and D (supported on $\gamma$-Al$_2$O$_3$-La). However, the conversions at 750°C for those catalysts are higher than for catalysts A and D. With catalysts 25 months old, the metal dispersions as well as metallic surface areas of catalysts A and B (supported on $\gamma$-Al$_2$O$_3$-Ce) are decreased close to the values of catalysts C and D ($\gamma$-Al$_2$O$_3$-La). In general, $\gamma$-Al$_2$O$_3$-La seems to be a more stable washcoat than $\gamma$-Al$_2$O$_3$-Ce. Fig. 37 a and b show the changes in metallic dispersions and the metallic surface areas of the catalysts with different ages.

**Fig. 37.** Changes in (a) metal dispersions and (b) metallic surface areas of the catalysts with different ages.

The SEM-EDS imaging of the catalysts did not show visual differences between the catalysts of different ages (see Fig. 38). This is also consistent with the XRD measurements, where no differences were observed between the fresh and aged catalysts (see Fig. 39). In SEM-EDS imaging, Si was observed in one sample aged 25 months, which may indicate the possibility of poisoning due to the pigment compounds in the coating agents, since Si was not added into the washcoat material in the preparation stage of the catalysts. However, Si was not found in greater amounts, and does not affect the catalyst activity significantly, as proved in light-off experiments.
The sintering of Pd is reported to be significant on these types of catalysts even below 800°C in an air atmosphere in the presence of water vapour (Lassi 2003, Lassi et al. 2004). Furthermore, Hüttig temperatures for Pt (608°C) and Pd (548°C) as well as PdO (307°C) may be momentarily exceeded on the surface of the catalyst during the operation of the incinerator, indicating the possible mobility of atoms (Moulijin et al. 2001). However, the sintering or phase changes of a γ-Al₂O₃-based washcoat is not that likely to occur at these temperatures (Hayes & Kolaczkowski 1997). In this case, the thermal deactivation of catalysts during 25 months of industrial aging is not significant if the process operates normally, which is supported by the XRD results (see Figure 39).

FTIR measurements of fresh catalysts and catalysts aged 25 months also did not show significant differences between the catalysts (Fig. 40). A small stretching was observed with catalysts B and D at around 1047 cm⁻¹, which may contribute to Si-O-Si bond (at 1040-1070 cm⁻¹) or Si-OR bond (1100-1000 cm⁻¹) vibrations. This would support our
proposal about the possibility of slight Si-based poisoning of the catalysts. These catalysts are bimetallic, containing both Pt and Pd. Similar stretching was not observed with monometallic Pt-catalysts.

Fig. 40. IR spectra of a) catalyst B and b) catalyst D as fresh and aged.

4.5.2 Results of SVOC tests

The catalyst (SVOC5, MnO$_2$-MgO/Al$_2$O$_3$) for the short durability test or time-on-stream test with DMDS was selected among the tested catalysts due to its good activity. The catalyst was first used in DMDS oxidation at its total oxidation temperature (494°C) continuously for 55 hours. After this period, the experiment was stopped during the night hours. The effect of water vapour was also tested during the experiments. Water vapor was introduced into the reaction mixture altogether for 4 hours. In addition, the temperature of the experiment was decreased to 399°C at the end of the experiment for 3 hours. The total aging time was 70 hours.

Catalyst SVOC5 showed excellent stability during the whole aging period. The activity remained virtually unchanged (conversion was 100%) from the beginning almost to the end of the experiment, regardless of the addition of moisture in the reaction mixture. The conversion was decreased to ~96% when the reaction temperature was decreased to 399°C, 10°C below the T$_{100}$ temperature. This finding is similar to the results of Chu et al. (2003). The results prove that also for this catalyst, industrial aging tests are needed in order to study the aging properly. Examination of the catalyst SVOC5 by XRD after the time-on-stream test showed the presence of sulphates on the catalyst surface.

The characteristics of catalysts in DMDS oxidation was also followed by chemisorption (for catalysts SVOC1-4) and BET surface area (for all catalysts) as well as pore size distribution measurements (for catalysts SVOC5-7) before and after the light-off tests. Chemisorption measurements reveal that the metal dispersions as well as metallic surface areas of the noble metal catalysts (SVOC1-4) decrease markedly during
the light-off experiments in spite of the fact that the activities did not change significantly between the repeated experiments (see Table 18).

Table 18. Specific surface areas, decrease in dispersion and metallic surface areas of the catalysts before and after the light-off tests.

<table>
<thead>
<tr>
<th></th>
<th>BET [m² g⁻¹]</th>
<th>Decrease in dispersion [%]</th>
<th>Metallic surface area [m² g⁻¹ metal]</th>
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<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td>before</td>
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<tr>
<td>SVOC1</td>
<td>72</td>
<td>40</td>
<td>87.7</td>
</tr>
<tr>
<td>SVOC2</td>
<td>143</td>
<td>130</td>
<td>100.0</td>
</tr>
<tr>
<td>SVOC3</td>
<td>65</td>
<td>40</td>
<td>98.0</td>
</tr>
<tr>
<td>SVOC4</td>
<td>47</td>
<td>25</td>
<td>96.7</td>
</tr>
<tr>
<td>SVOC5</td>
<td>171</td>
<td>94</td>
<td>n.d.</td>
</tr>
<tr>
<td>SVOC6</td>
<td>105</td>
<td>85</td>
<td>n.d.</td>
</tr>
<tr>
<td>SVOC7</td>
<td>102</td>
<td>119</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Dispersions and metallic surface areas of Pt-containing catalysts decrease more than that of Pd-catalysts, which is consistent with the results of Jones et al. (2003). Specific surface areas also decreased, except with catalyst SVOC7. The average pore sizes of catalysts SVOC5-7 increased during the DMDS oxidation. The increase was most significant with catalyst SVOC5. This may indicate blocking of smaller sizes of pores and be the first sign of possible catalyst deactivation even if the activities of the catalysts between the experiments do not decrease significantly. (The possible effect of inhibition in repeated experiments due to adsorption of sulfuric compounds was minimized with the pre-treatment of the catalysts prior to every experiment.)

Dalai et al. (1997) have reported the deactivation of activated carbon catalysts in MM oxidation due to the adsorption of DMDS. This might be the case in this study, too. In addition, it has been reported (Bashkova et al. 2005) that DMDS adsorption at room temperature is much stronger than that of MM, which could explain the behavior of DMDS at the beginning of the light-off experiments, in which conversions achieved negative values (see Fig. 33). It is possible that this is not only characteristic of catalysts but also of the experimental apparatus, since it was also observed in thermal experiments. It is also known (see e.g., Lee & Rhee 1998) that in some cases e.g. in isomerization of n-hexane, Pd-Pt bimetallic interaction inhibits irreversible sulphur adsorption, which could partly explain the differences between chemisorption experiment with catalysts SVOC1-4. In addition to DMDS or MM adsorption, another explanation for chemisorption results is the SO₂ oxidation to SO₃ and the following sulphate formation with the washcoat. Sulphates were observed on SVOC5 surface after the time-on-stream experiment by XRD.

4.6 Conclusions and application

When comparing the different catalysts, three important features should be taken into account: activity, selectivity and durability. These three factors are sometimes in connection with each other, and it is not enough to evaluate only one feature. For
example, a catalyst might be very active, which means in industrial application less need for heating the emissions before the catalyst. If the catalyst is not so active, its activity may in practice be enhanced by increasing temperature, which at the same time affects selectivity. Temperature increase may improve selectivity or in some cases cause the formation of intermediates or by-products, which should be avoided (e.g., formation of SO$_3$ from SO$_2$). If activity and selectivity are improved by increasing the temperature, it may mean that the durability or lifetime of the catalyst is shortened. These cases illustrate very well that catalyst selection should be done case by case, and the best combination of activity, selectivity and durability should also be optimized according to process operation. (These things will also be discussed later, in the next chapter.)

According to the laboratory scale activity testing of the catalysts (based on volume), the most active catalyst in methane oxidation is catalyst J ($T_{50} \sim 450^\circ C$, $T_{95} \sim 590^\circ C$) and in n-butyl acetate oxidation catalyst G ($T_{50} \sim 210^\circ C$, $T_{95} \sim 290^\circ C$). Catalyst J is a metal oxide catalyst: $Cu_xCr_2O_4$ and catalyst G contains platinum. Both of these catalysts are designed for oxidation purposes, and it seems that metal oxide catalysts are more active than e.g. a Pt catalyst in the case of methane oxidation. In general, the differences between the activities of the catalysts in n-butyl acetate oxidation were not very significant.

In the case of SVOCs, the best catalyst in MM oxidation was catalyst SVOC6 ($Cu_xMg_{1-x}Cr_2O_4$) due to its good adsorption capacity entailing the $T_{50} < 40^\circ C$ and $T_{100} \sim 90^\circ C$. In DMDS oxidation, the selection is not as evident. Catalyst SVOC6 gives the lowest $T_{50}$ (90$^\circ C$) whereas the lowest $T_{100}$ (410$^\circ C$) is achieved with catalyst SVOC5. Due to the application (i.e. total oxidation is desired), the catalyst SVOC5 (MnO$_2$-MgO) would be the best choice in DMDS oxidation based on the volume of the catalyst.

On an industrial scale, catalyst selectivity is important due to environmental as well as operational reasons. First of all, the catalyst should not promote the formation of by-products that may be even more harmful to the environment than the initial compounds. Secondly, the formation of by-products that may have a harmful effect on the catalyst or construction materials of the incinerator should be avoided (e.g., SO$_3$). The formation of by-products depends on the active material (metal/metal oxide), the washcoat, washcoat additives, the temperature and water content (e.g., with chlorinated hydrocarbons, the formation of harmful by-products may be decreased in moist conditions). Several by-products were detected during the n-butyl acetate light-off experiments with all of the tested catalysts, which were for example methane, 2-methyl-1-propene, butene, acrolein, acetone and acetic acid to name few. In MM and DMDS oxidation, the by-products observed were DMDS, DMS and H$_2$S. The possible formation of by-products other than sulphur-containing by-products was not monitored.

In general, the formation of by-products in catalytic VOC oxidation decreased compared to thermal oxidation, which occurs by gas-phase radical mechanisms. When compared to the catalytic experiments, the amount of by-products at the end of the experiment was also higher when the oxidation of n-butyl acetate was tested over metallic packings (reported in Chapter 3). However, the amount of by-products decreased when the catalyst was added into the packing with metallic materials. Ultimately, this proves that catalytic reactions are dominant when both catalyst and metallic packings are used together, and that the by-product formation can be decreased by catalysis.

According to this research, among the tested catalysts, the most selective catalyst in n-butyl acetate oxidation is catalyst C (Pt/Al$_2$O$_3$-La) followed by catalyst E (Cu-Mn
oxides) and F (Pt). In volume-based activity comparisons these catalysts are all among
the best ones. However, in methane oxidation, catalyst C is the last one, whereas catalyst
E is one of the best catalysts.

In MM and DMDS oxidation, based on the information from cumulative
concentrations of the by-products, the most selective catalysts are SVOC2 (Pt/Al2O3) and
SVOC1 (Pd/Al2O3-Ce), respectively. It appears that independent of the model VOC or
SVOC, the noble metal catalysts seem to be most selective of the tested catalysts. These
results differ from the activity test results. Both catalyst SVOC1 and SVOC2 are among
the last ones in the activity comparisons. It seems, that by-product formation is decreased,
not only due to an active compound, but probably also due to the fact that the catalyst
starts to operate at a higher temperature level.

The durability of the catalyst is important on an industrial scale due to the fact that the
costs of the catalyst varies depending on the incinerator size from 3.1% to 19.1% of the
price of the whole incinerator (R. Silvonen, personal communication) and replacing it can
be quite expensive and sometimes complex. Fortunately, the catalysts tested seem to
exhibit excellent durability in the case of VOC oxidation (in normal industrial conditions
without an upset in a process) and in addition, the catalyst tested in SVOC oxidation
appears to be very potential for SVOC oxidation. If one has to select the best catalyst
among those tested in VOC oxidation, it seems that the catalysts supported on Al2O3-La
(C and D) are slightly more active after 25 months of aging. In industrial solvent VOC
oxidation conditions the most probable deactivation arises from the possibility that the
compounds included in the coating pigments drift with the flow to the catalytic surfaces.
In SVOC oxidation, deactivation occurs most probably due to sulphurous compounds.
Furthermore, due to higher oxidation temperatures compared to VOC oxidation, the
overheating of the catalyst is more possible.

In conclusion, with all the information obtained from the different features of
catalysts: activity, selectivity and durability in the cases of VOC and SVOC oxidation,
some conclusions about the selection of catalysts can be drawn. First, in solvent VOC
oxidation, the proposed order of importance for catalyst features is: selectivity, activity
and durability. It has been shown that durability is not a problem in solvent VOC
emission treatment over the catalysts tested. High selectivity gives more freedom to
operate with the incinerator temperature, while high activity keeps the temperatures of
oxidation low, and diminishes the need for the preheating of emission gas. Based on this,
catalyst E (Cu-Mn oxides) would be the best choice, however, information about the
durability of E is not available. Among the aged noble metal catalysts, catalyst C
(Pt/Al2O3-La) would be the best choice in solvent VOC oxidation, since it has good
durability combined with good selectivity, even the activity in methane oxidation is not as
good as with other noble metal catalysts.

Second, in SVOC oxidation the proposed order of catalyst features is: selectivity,
durability and activity. Selectivity and durability are important to avoid SO3 formation
and sulphur-induced deactivation of catalysts as well as corrosion reported in Chapter 3.
Activity is not considered so important. However, SVOC5 (MnO2-MgO) seems to be the
most potential selection among the tested catalysts due to its relatively good activity
(Ttot.ox.), due to its relatively high production of SO2 (if it means less production of SO3)
and due to the information obtained from time-on-stream tests.
5 Process parameters and application

This chapter concentrates on the operation of catalytic incineration more deeply. The effects of the industrial operation parameters, \emph{i.e.} GHSV (gas hourly space velocity), concentration and temperature, and in addition, the moisture content of the feed-gas are studied and the results are applied to industrial operation. Furthermore, transient operation of the reverse-flow process is considered, and the results obtained from catalyst laboratory testing are discussed from the industrial operation point of view. At the end, other aspects related to industrial abatement of VOCs and SVOCs, \emph{e.g.} the further processing of reaction products or other potential hybrid systems are considered.

5.1 Effects of process parameters

As was mentioned, the concentration (c), gas hourly space velocity (GHSV), temperature (T) and moisture content (Moist.) of the emission gas were selected as the experimental factors of the laboratory experiments for both VOC and SVOC. It has been reported, that water, CO and CO$_2$ formed in the VOC oxidation affect the activity of Pd and Pt catalysts, for example in the case of methane oxidation (Ciuparu \emph{et al.} 2002, Gélis \emph{et al.} 2003). The influence of water on catalyst activity is also affected by the type of support. For example, high oxygen mobility supports can accelerate hydroxyl desorption (Ciuparu \emph{et al.} 2002). Furthermore, catalysts do not respond instantaneously to changes in water concentration (Ciuparu \emph{et al.} 2002, Burch \emph{et al.} 1999). It has also been reported that water affects SVOC oxidation. Bashkova \emph{et al.} (2005) suggested that the presence of water in the MM adsorption/oxidation process facilitates MM dissociation and the following formation of DMDS over certain types of iron/activated carbon catalyst. Therefore, moisture was included in the experimental factors in order to find out its possible effects on the oxidation of selected VOCs and SVOCs.

On the industrial-scale, the catalytic incinerator related to this work is operated based on temperature. The operator can give the setting values \emph{e.g.} for minimum and maximum temperatures as well as for the flow reversal temperature. Furthermore, GHSV may be adjusted by changing the fan speed. The concentration of inlet gas is controlled based on the temperature of the oxidation reactions. If the temperature exceeds the value selected
by the operator, extra dilution air is introduced into the system. The moisture content of
the emission gas is not controlled; it depends on the application and may be reduced with
a water separator or dryer prior to the incinerator inlet if it has an adverse effect on the
oxidation results.

The following chapters present the results of the laboratory experiments of VOC and
SVOC oxidations. In both cases, the MODDE 6.0 program (Umetric AB) has been used
as a tool in statistical experimental design and in the evaluation of the effects of the
selected factors (temperature, GHSV, concentration and moisture) affecting the catalytic
oxidation of n-butyl acetate. Furthermore, in the case of VOCs, the effect of aging of the
catalyst was considered i.e. does aging change the effects of selected factors or does it
even change the significance order of them.

A set of experiments was done with a full two-level factorial design. The effect of a
single factor was evaluated at all the levels of the other factors, which enabled the study
of the effects of the interaction of selected factors. The measured response was the
conversion of the model compound over the fresh and aged catalysts. The validity of the
empirical models fitted with multiple linear regression (MLR) was tested with analysis of
variance (ANOVA). The confidence level used was 95%. Table 19 shows the array of
experiments where higher and lower parameter values are indicated with (+) and (−)
signs, respectively.

Table 19. Array of VOC and SVOC experiments (Ojala et al. 2005f).

<table>
<thead>
<tr>
<th>Number of experiment</th>
<th>Moisture [%]</th>
<th>Concentration [ppm]</th>
<th>GHSV [h⁻¹]</th>
<th>Temperature [°C]</th>
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<tbody>
<tr>
<td>1</td>
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<td>-</td>
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<td>-</td>
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<tr>
<td>2</td>
<td>+</td>
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<td>16</td>
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5.1.1 Results of VOC tests

The same laboratory set-up was used in ‘factorial experiments’ as before (see
Experimental Section 3.2.2). The levels of the factors were based on the earlier results
achieved from industrial measurements, from solvent emission sources and from the catalytic incinerator used in the solvent emission abatement. N-butyl acetate was selected as the model VOC compound. The metal-supported Pt/Al$_2$O$_3$ catalyst (A) was selected for these experiments based on the catalyst screening tests (see Section 4.3.1), where it was one of the best noble-metal catalysts in n-butyl acetate oxidation (Ojala 2003, Ojala et al. 2005c). The experiments were carried out with fresh Pt/Al$_2$O$_3$ catalysts and Pt/Al$_2$O$_3$ catalysts industrially aged 25 months (aging described in Section 4.2). Prior to the experiments the fresh catalyst was heated up to 600°C and cooled to room temperature in air. This procedure was not carried out for the aged catalyst, since it may have changed the state of the catalyst surface and even regenerated it. In addition, the activity of each catalyst was tested before and after the experiments. BET surface areas were also measured (Coulter Omnisorp 360CX) before and after the experiments.

The temperatures of the experiments were selected to be higher than the catalysts light-off ($T_{50}$), of which the lower temperature 300°C is close to a normal industrial operation temperature of an incinerator, and the higher temperature level, 500°C, is above it (close to $T_{100}$). The levels for the GHSV were 31,500 h$^{-1}$ and 63,000 h$^{-1}$, and they were adjusted by changing the total flow while the catalyst bed height (30 mm) was kept constant. The lower level of concentration (2000 ppm) was close to the maximum concentration of n-butyl acetate in the total solvent emissions measured (Ojala et al. 2005d), the higher level was 4000 ppm. The higher level for moisture was 2.5 vol-% and at the lower level water was not introduced into the system (i.e. zero level moisture). Fig. 41 shows calculated responses (n-butyl acetate conversions) over the fresh and aged catalysts.

![Fig. 41. Conversions of n-butyl acetate over the fresh (◊) and aged (●) catalysts (Ojala et al. 2005f).](image-url)
The fitting of responses (conversion of n-butyl acetate with fresh and aged catalysts) showed that the factors studied had similar effects on the conversion of n-butyl acetate in both cases. The calculated effects of factors for fresh and aged catalysts are presented in Figs 42 a and b, respectively. Furthermore, all single effects as well as interaction terms are included in Fig. 42, even if the effects of all these terms are not significant.

![Diagram](image)

Fig. 42. Calculated effects of GHSV, moisture (Moist), concentration (c) and temperature (T) on n-butyl acetate conversion over (a) fresh and (b) aged catalysts (Ojala et al. 2005f).
Fig. 41 as well as Figs 42 a and b show that GHSV has the largest and negative main effect on conversion, i.e. when GHSV is increased, conversion is decreased. Furthermore, the effect of GHSV is more significant at low temperatures and slightly more significant over the aged catalyst than over the fresh catalyst. Temperature has the second largest but positive effect on conversion, thus when temperature is increased conversion is increased as well. The third significant term is the interaction effect between temperature and GHSV followed by the effect of concentration. The concentration has a more significant effect on conversion when the GHSV is high than in the lower GHSV level. According to these results, moisture has only a negligible effect on conversion over both the fresh and aged catalysts. As can be seen in Figs 42 a and b, the aging of the catalyst did not change the significance order of the parameters. When the results of the study on turpentine oxidation presented in Section 3.3.3 are compared to these results, similar conclusions may be drawn concerning the effects of GHSV, concentration and temperature.

When the validity of the fitted model was evaluated with ANOVA, the results showed that the model was statistically significant with a 95% confidence level. The square of the multiple correlation coefficient of the model i.e. the response variation percentage explained by the model, $R^2$, for fresh and aged catalysts were 0.976 and 0.986, respectively. The response variation percentage predicted by the model, $Q^2$, were 0.945 for the fresh and 0.968 for the aged catalyst. In spite of good $R^2$ and $Q^2$, one has to remember that the model is valid only in the range of factors used (see Section 5.1).

During the experiments, the BET surface area of the fresh catalyst decreased slightly from its initial value (65.2 m$^2$g$^{-1}$). However, the activity of the catalyst was improved probably due to further calcination of the catalyst (Lassi 2003). The BET and light-off temperature of the aged catalyst did not change significantly from the initial values during these experiments; only the end conversions were improved after the experiments. It is possible that a higher reaction temperature has slightly regenerated the aged catalyst. (See Fig. 43)
In summation, the results show that increasing the operation temperature and inlet concentration, and decreasing the GHSV improves the conversion of n-butyl acetate. Moisture has only a minor effect, which is decreased further when temperature is increased. These are also illustrated in Fig. 44.

Fig. 44. Contour-plots for parameters. Left column shows temperature vs. other parameters for the fresh catalyst and right column for the aged catalyst. The other parameters are in the mid-level i.e. GHSV = 47 250 h⁻¹, c = 3000 ppm and moisture = 1.2 vol-% when they are constants (Ojala et al. 2005f).
Many authors (Matros et al. 1993, Salomons et al. 2003, Cimino et al. 2001) have reported that if the catalytic incinerator is operated auto-thermally with a flow reversal, some changes, for example in the flow rate, inlet temperature and concentration, may not affect the end conversion. This is due to a quasi-steady state operation where the temperature profile in a tubular reactor has a maximum value near the center of the reactor and it slowly oscillates towards the outlets of the reactor when the flow direction is changed. This effect is called a heat trap and it can be used to achieve and maintain higher reaction temperatures compared to a once-through reactor.

The positive effect of a higher concentration at the range of these experiments with a once-through system can be explained with the increased surface temperature. When there is more n-butyl acetate available, more reaction heat is generated and surface reactions are enhanced as long as there is enough oxygen available. The experiments in this study are carried out in lean conditions, and thus surplus oxygen is always available. An increase in surface temperature due to higher concentration may occur regardless of the operation mode of the reactor. In a once-through system this temperature maximum is close to the outlet of the catalyst (Sheintuch 2005).

The effects of the other factors are enhanced by a higher GHSV value. However, the higher temperature balances this effect. The reaction temperatures used in this study are more likely in the mass-transfer restricted area than in the kinetically-controlled area since the oxidation reactions have lit-off and conversions are high. If we consider the light-off curve presented in Fig. 43, an increase in GHSV moves the light-off curve towards a higher temperature region. If the reaction temperature is kept the same, the conversion of n-butyl acetate decreases. Then, when the temperature is increased, the conversion of n-butyl acetate is enhanced again. This may be due to the fact that a higher flow rate cools down the catalyst surface, which slows down the reactions if external heating is not enhanced and the compounds do not have enough time to react on the catalytic surface. In the temperature range used in this study, non-catalytic (i.e. gas phase) conversion of n-butyl acetate is less than 30% and it may only have a minor effect on the end conversion (Ojala 2003). It is also reported for flow-reversal systems that too high a GHSV will probably extinct the reactions due to too short a contact time at certain temperature (Ben-Tullilah et al. 2003).

Methane oxidation in the presence of water has been studied quite considerably. It has been observed that water has an inhibiting effect on the Pd/Al₂O₃ catalysts (van Giezen 1999) as well as Pt-Pd/Al₂O₃ catalysts (Pieck et al. 2002). On the contrary, Li et al. (2003) reported that water vapor might have a promoting effect on the methane catalytic oxidation over Co-Mn mixed oxides. In the case of n-butyl acetate oxidation, 2.5 vol-% water did not show any significant effect on the conversion of n-butyl acetate, in general. However, the very slight decreasing effect of water on the end conversions seemed to depend on the values of GHSV, concentration and temperature.

In previous laboratory experiments (Ojala 2003, Section 4.4.1), it was noticed that close to the catalyst light-off temperature some by-product compounds are formed. The formation of by-products is decreased when the temperature is increased further and the conversion of n-butyl acetate proceeds 100%. When the conversion of n-butyl acetate is not complete, as in these experiments, it is worthwhile to also consider possible by-product formation i.e. the selectivity of the catalyst. By-product formation was also monitored during these experiments, and the results showed that some by-products are formed in these experimental conditions. The formation of by-products is slightly more
significant when GHSV is at the higher level. Furthermore, at higher levels of GHSV and temperature, the moisture somewhat decreases the by-product formation. Aging, in this case, did not change the formation of by-products significantly. Only a slight increase in by-product formation is observed when the GHSV is at the higher level and the temperature is at the lower level.

### 5.1.2 Results of SVOC tests

The experiments with the model SVOC compound were very similar to the experiments carried out with the model VOC compound explained in the previous section. The model SVOC compound was selected to be DMDS, with concentration levels of ~1060 mg m$^{-3}$ and 530 mg m$^{-3}$. The catalyst used was selected based on the activity experiments, which showed that one of the most active catalysts in DMDS oxidation is SVOC5 (MnO$_2$-MgO/Al$_2$O$_3$). Only a fresh catalyst was used in the test. The catalyst had constant packing size (2.6 mm), and the GHSVs used were similar to VOC tests, i.e. 31,500 h$^{-1}$ and 63,000 h$^{-1}$. The temperatures of the experiments were selected based on the activity measurements, and they were also similar to those in the VOC tests (300°C and 500°C).

The results showed that when the temperature is at its higher level, the other factors do not affect the conversion values. More pronounced effects could be seen when the temperature was at its lower level. At a glance, it seems that at the lower level of temperature, the water vapour enhances the oxidation of DMDS. At the higher levels of concentration and GHSV the conversion values are decreased compared to the conversions at lower levels of concentration and GHSV. The fitting of the responses is presented in Fig. 45. All the single effects and interaction terms are included in the figure again; even they did not have significant effects.

![Fig. 45. The calculated effects of gas hourly space velocity (GHSV), concentration (c), temperature (T) and moisture (Moist) on the DMDS conversion over the catalyst SVOC8.](image-url)
Fig. 45 shows that temperature has the largest and positive main effect on DMDS conversion. The effect of concentration seems to be negligible. GHSV has a rather small, but negative effect on DMDS conversion. The negative effect of GHSV was also observed in VOC experiments. In contrast to the VOC experiments, moisture seems to have a positive effect on DMDS conversion. This observation can also be seen from the conversions presented in Fig. 46. Earlier, Li et al. (2003) have reported the promoting effect of water vapor on the catalytic oxidation of methane over cobalt/manganese-mixed oxides at low reaction temperatures. However, the promoting effect was not observed with single oxides. As in the VOC experiments, a higher oxidation temperature again balances the effects of other experimental factors – in fact, 100% conversion is achieved regardless of the levels of other factors. It is good to note, that thermal oxidation of DMDS (1060 mg m$^{-3}$) is also possible at temperature of 500°C (see Section 4.3.2). In addition, Chu et al. (2003) have reported that the homogeneous oxidation of 100 ppm DMDS starts as early as 300°C. Therefore thermal oxidation mechanisms are also rather likely present at 500°C.

ANOVA showed that the model was statistically significant with a 95% confidence level. The square of the multiple correlation coefficient of the model \( R^2 \), i.e. the response variation percentage explained by the model, and the response variation percentage predicted by the model, \( Q^2 \), were 0.992 and 0.997, respectively. Again, the model is valid only in the range of parameters used.

In summation, Fig. 46 shows the formation of by-products, the conversion of DMDS and selectivity to SO$_2$ in different experiments. The selectivities are calculated based on the exact feeding concentrations of DMDS with an assumption that all DMDS reacts. Thus the unreacted DMDS below T$_{100}$ is considered an unwanted 'product'. The concentrations of by-products are the averages of the by-products observed in repeated experiments.

Fig. 46. Concentrations of by-products, selectivities to SO$_2$ and conversion of DMDS in different experiments.
It can be seen that at higher temperature level, when the GHSV too is higher, the formation of H₂S occurs. As was mentioned, the formation of H₂S is usually related to operation in fuel-rich conditions (e.g., Neyestanaki et al. 2004), which is not likely in this case. Formation of H₂S at higher GHSV level indicates that the GHSV has some effect on the reaction even if the conversion values do not show it. At higher temperatures, the selectivities to SO₂, again, are over 100%, indicating probable desorption of SO₂ (see Section 4.4.2). In addition, the decomposition of possible sulphates formed with alumina washcoat is thermodynamically favored at temperatures above 500°C (Trimm 1995), which may also contribute to SO₂ formation.

Moisture does not have a significant effect on by-product formation even though it increases conversions when the temperature is at the lower level. Concentration may have a slight effect on by-product formation at the lower level of temperature. Furthermore, concentration seems to affect the selectivities on higher level of temperature.

5.2 Transient operation

The industrial scale catalytic incinerator operates in transient conditions. Catalyst temperatures decrease and increase according to process operation. Furthermore, the flow direction within the catalyst changes periodically. When the flow is reversed, the hot gas contacts the catalyst and raises the temperature of the catalyst. When the flow continues in the same direction, the heat exchangers prior to the catalyst are cooled, which also happens to the gas flow as well and, as a consequence, the catalyst inlet temperature decreases. When the temperature reaches a certain limit temperature, flow is reversed, and another catalyst contacts with the hot gas flow. Therefore the catalyst inlet temperature decreases as the gas flows through it. However, it has been measured (Ojala 2004b) that the temperature between the two catalyst beds remains relatively constant, and is not dependent on the direction of the gas flow. (see Fig. 47 for measurement sites of the incinerator)
Operating in transient conditions may have beneficial effects on catalyst operation. It may improve both the activity and selectivity of a catalyst. The catalyst properties, surface structure and chemical composition change according to the reaction gas mixture. If the time to reach a steady state under a reaction mixture is greater than the duration of the catalytic action, the reaction can proceed for a certain time under an unstationary state of a catalyst, which may be beneficial. The unstationary state may be maintained by flow reversal but also e.g. by changing inlet concentrations. (Matros 1990)

As a consequence, the effect of changing the temperature in VOC oxidation (methane and n-butyl acetate) was decided to be tested over catalyst B (Pt-Pd/Al₂O₃-Ce). First, the catalyst was heated up to 350°C and the temperature was kept constant for four hours in methane oxidation and for three hours in n-butyl acetate oxidation. After the constant temperature experiment, the temperature was fluctuated between 300-400°C. Temperatures were selected based on normal operation temperatures of an industrial-scale catalytic incinerator operating in solvent emission abatement. The concentration of the model compounds and GHSV were 2000 ppm and 31,500 h⁻¹, respectively. The concentration of CH₄ was followed by GC-FID at the outlet of the reactor. In the n-butyl acetate experiment, concentration was also followed by continuous PID in addition to GC-FID.

At a constant temperature the average conversions of methane and n-butyl acetate were 47% and 99.8%, respectively. The initial conversion of methane (~60%) decreased to ~40% during the experiment. In contrast, n-butyl acetate concentration increased
slightly from the initial value of 99.7% to 99.8%. Figs 48 a and b present conversions of methane and n-butyl acetate during heating and cooling.

Fig. 48. Conversions of a) methane, b) n-butyl acetate during heating and cooling of the reactor.

Figs 48 a and b show that conversions during the cooling phase are slightly enhanced compared to the heating phase in both cases. In methane oxidation the calculated average conversion in temperature cycling tests is ~40%, which is the same as the end
temperature in constant temperature oxidation. In n-butyl acetate oxidation, the average conversion was ~99%. Therefore, no significant differences could be observed between the constant temperature experiments and experiments where the temperature was changed between 300°-400°C. In a reverse flow operation, the untreated emission gas is fed to the catalyst during the cooling phase. This seems to be slightly beneficial compared to the case where catalyst would be heated during the reaction.

5.3 Industrial operation and application of laboratory results

5.3.1 Activity

In this research, the activities of the catalysts are compared based on light-off tests, where certain parameters are kept constant between the experiments to enable reliable comparison. Also, the catalyst volume is kept constant due to the very ‘mixed’ selection of the catalysts. On an industrial scale the space for the catalyst may be limited, which also supports the comparison of the catalysts based on volume. The most active catalysts according to laboratory experiments were catalyst J (Cu,Cr2O4) for methane oxidation, catalyst G (Pt) for n-butyl acetate oxidation and catalyst SVOC6 (Cu,Mg(1-x)Cr2O4) as well as SVOC5 (MnO-MgO) for MM and DMDS oxidation, respectively.

As was evident, emission gas that should be treated must be at a certain temperature in order to maintain T_{tot.ox} in the catalyst. As the light-off temperature is also dependent on the reactor characteristics, it cannot be determined exactly and direct use from laboratory to industrial scale design is not reasonable. Furthermore, these experiments are carried out in a once-through system at a laboratory whereas the industrial incinerator operates with flow-reversal. In has been shown in many studies (Salomons et al. 2004) that a flow-reversal reactor maintains higher catalyst temperatures than expected based on a calculated adiabatic temperature rise of emission compounds. Temperatures reached with a once-through reactor can be considered as inlet temperatures where T_{tot.ox} is certainly reached in a flow-reversal system.

In general, it can be postulated that an increase in temperature increases catalyst activity, which is even more pronounced in DMDS oxidation than in n-butyl acetate oxidation, since DMDS is more difficult to oxidize. Increasing GHSV in both cases (VOC and SVOC oxidation) decreases activity. In the case of n-butyl acetate oxidation, concentration increases conversion to some extent, while in the case of DMDS oxidation conversion decreases with increased concentration. A small amount of moisture has no significant effect on n-butyl acetate oxidation, but it enhances DMDS oxidation at lower temperature levels. On an industrial scale this means that removal of a low level of moisture is not needed, at least if only the activity of the catalysts tested is considered.

The factor experiments in both cases were carried out close to the optimum, and thus the clear limited optimum area for the factors was not found. However, in practice temperature, for example has a limit value due to heating costs and the durability of the construction materials of the incinerator (see Section 3.3.1). Furthermore, this sets a limit on maximum GHSV when the total oxidation of model compounds is desired. The maximum concentration in industrial operation is limited by flammability limits and
regulations. For example in Finland the maximum limit allowed for the VOC concentration in emission oxidation is 20% of lower explosive limit (TUKES 1993).

5.3.2 Selectivity

According to the laboratory experiments, in n-butyl acetate oxidation, higher GHSV values cause the formation of by-products in spite of what the levels of temperature and concentration are. Moisture seems to decrease the amount of by-products formed. In DMDS oxidation a higher concentration at the lower temperature level as well as higher GHSV at the upper temperature level cause the formation of by-products. Water has no significant effect on by-product formation.

On an industrial scale, too, low operation temperatures may cause the formation of by-products. The formation of by-products depends on the $T_{50}$ of the catalyst as presented in Section 4.4, and thus, the incinerator should be operated above the catalyst $T_{50}$. Table 20 shows the maximum concentration of quantified by-products formed during n-butyl acetate oxidation at laboratory over different catalysts at normal operation temperatures of an industrial-scale catalytic incinerator operating at the solvent emission abatement, i.e. $T = 300\degree-350\degree$C, and the conversion range of n-butyl acetate in those conditions according to the laboratory experiments.

Table 20. Formation of by-products and conversion range at 300\degree-350\degree C. Results achieved with a once-through system.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Maximum concentration of quantified by-products [ppm] (by-product)</th>
<th>Conversion of n-butyl acetate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>&lt; 10 (2; butene)</td>
<td>1 - 3</td>
</tr>
<tr>
<td>A</td>
<td>&lt; 10 (2)</td>
<td>93 - 95</td>
</tr>
<tr>
<td>B</td>
<td>&lt; 30 (2)</td>
<td>83 – 88</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 10 (2)</td>
<td>92 – 95</td>
</tr>
<tr>
<td>D</td>
<td>&lt; 55 (2)</td>
<td>76 – 86</td>
</tr>
<tr>
<td>E</td>
<td>&lt; 20 (2)</td>
<td>98 – 99</td>
</tr>
<tr>
<td>F</td>
<td>&lt; 35 (5)</td>
<td>95 – 99</td>
</tr>
<tr>
<td>G</td>
<td>&lt; 15 (7)</td>
<td>98 – 99</td>
</tr>
<tr>
<td>H</td>
<td>&lt; 2,000 (2; 2-methyl-1-propene)</td>
<td>55 – 87</td>
</tr>
<tr>
<td>I</td>
<td>&lt; 1,610 (2)</td>
<td>80 – 95</td>
</tr>
<tr>
<td>J</td>
<td>&lt; 2,520 (2)</td>
<td>57 – 82</td>
</tr>
</tbody>
</table>

Usually the maximum concentrations in the temperature range of 300\degree-350\degree C are observed with the by-product 2. In general, less formation of by-products was achieved over catalysts A (Pt/Al$_2$O$_3$-Ce) and C (Pt/Al$_2$O$_3$-La), but with catalysts E (Cu-Mn oxides/Al$_2$O$_3$) and G (Pt/Al$_2$O$_3$) maximum conversions were achieved. When monolithic catalysts are compared, monometallic Pt catalysts in this temperature range achieved better conversions and less formation of by-products took place.

The formation of CO as an incomplete oxidation product of solvent VOCs was monitored on an industrial scale. Fig. 49 shows concentrations of SO$_2$ and CO at the
outlet of the incinerator. During the measurements, the inlet VOC concentration was \( \sim220 \text{ ppm} \) and the conversion about 87%.

**Fig. 49.** \( \text{CO}_2 \) and CO concentrations at the outlet of the catalytic incinerator working in solvent VOC emission abatement.

Fig. 49 shows that CO is formed, but less than 5 ppms. The flow-reversal occurs when the \( \text{CO}_2 \) concentration reaches minimum values. It can also be seen that CO production is higher soon after the flow reversal and starts to decrease until the end of the flow-phase. When the flow is reversed, CO production is momentarily increased again. These results show that some incomplete oxidation occurs during the measurement period. In addition, conversion is rather low, due to a low inlet VOC concentration. At low concentrations electric heaters are used to maintain adequate oxidation temperature. It has also been noticed that at higher VOC concentrations the conversions are also enhanced on an industrial scale (Ojala 2004b).

Earlier bench-scale tests in a pulp mill (Ojala *et al.* 2005a) have shown that over the Pt catalyst, temperatures over 400\(^\circ\)C are needed for the catalytic oxidation of chip bin emissions. If temperatures are not high enough, DMDS is formed in significant amounts as a by-product in the MM oxidation, which was also the case in laboratory experiments, with all the tested catalysts (See Section 4.4.2). Laboratory experiments on SVOC catalysts have shown that the most selective catalysts in MM and DMDS oxidation are noble metal catalyst SVOC3 (Pt/Al\(_2\)O\(_3\)) and SVOC1 (Pd/Al\(_2\)O\(_3\)-Ce), respectively. These catalysts should be operated according to once-through experiments at 540\(^\circ\)C to achieve total oxidation of emissions (provided that DMDS is the most difficult compound to oxidize from all emission compounds). At higher operation temperatures the formation of \( \text{SO}_3 \), too, is thermodynamically less favored and thus corrosion caused by sulphuric acid is more likely avoided.
If the operating temperature of the industrial scale incinerator is above the $T_{50}$ of a catalyst, the narrow temperature range for the formation of by-products may be more easily avoided. If the temperature in the industrial scale incinerator fluctuates markedly, the best catalyst will be the one in which less by-products are formed in the whole temperature range of operation.

In addition to selecting the most selective catalyst and increasing the temperature, the other possibility to decrease by-products formation is to decrease the space velocity either by increasing the amount of the catalyst or by adjusting the fan speed. This creates more active surface for oxidation reactions and enables a more complete oxidation of VOC compounds. In addition, when the space velocity is decreased, there is more time for the reactants to be oxidized, and thus to react more completely in the catalyst.

5.3.3 Durability

This section includes a discussion on the durability of catalysts as well as construction materials in industrial VOC and SVOC operation. As shown by aging, the durability of tested catalysts in solvent VOC emission abatement is excellent. Furthermore, a rather short (altogether 70 hours) time-on-stream test with catalyst SVOC5 in DMDS oxidation did not show any decrease in catalyst activity. This attracts interest in conducting longer-term aging tests with this catalyst. The effects of selected experimental factors on catalyst durability can therefore be speculated based only on the literature.

The effect of temperature, especially a high temperature, on catalysts’ durability is well studied, however, as shown in Section 4.5.1, significant thermal deactivation was not observed in the aging of catalysts in VOC solvent abatement conditions. The effect of moisture at higher temperatures is likely more significant than at lower temperatures. In a SVOC aging test, water did not show any instant effect on catalyst activity in DMDS oxidation. It is important to remember that water may not have an instant effect on oxidation results (Burch et al. 1999) and maybe the aging times used in SVOC experiment were not long enough. The effect of moisture in the aging of VOC catalysts was not studied.

In VOC oxidation, a high concentration may cause coking of the catalytic surface, but in the normal operation of a catalytic incinerator, the concentration of inlet VOC is kept well below explosive limits and thereby the incinerator operates at lean conditions. In the solvent emission abatement, it has been noticed that slightly higher VOC concentrations may allow higher conversions (Ojala 2004b). This was also seen in experiments presented in Section 5.1.1.

Instant fluctuations in the inlet concentrations may cause momentary overheating of the catalyst before the incinerator is shut down automatically. This is more likely to occur in chip bin emission abatement applications than in solvent emission abatement. The emissions of the coating processes included in this study are dependent on the coating speed, which is limited, and instantaneous high concentrations of emissions are not very likely. In the case of the chip bin, the wood chips are pretreated with water vapour and dilute malodorous gases prior to the cooking phase of a pulping process. If the height of the chip bed inside the bin is low, it is possible that malodorous gases escape to the outlet stack, and concentration of SVOCs at the inlet of a catalytic incinerator increases
instantaneously by as much as 1000 times the level of normal concentrations. In addition to a possible safety risk, this may cause the rapid deactivation of a catalyst. These kinds of situations may be avoided with control systems.

The effect of high GHSV on the durability of catalysts is related to, for example, possible abrasion of the catalysts. Furthermore, in the case of monolith catalysts, the VOC stream should be quite well mixed prior to entering the catalyst. Very high GHSV may result in a situation where the flow is not evenly distributed to the inlet of the catalyst and all the channels of monolithic catalysts are not used. This causes temperature differences inside the catalyst that may cause abrasion of a catalyst due to thermal expansion and contraction. In this case, the actual GHSV, too, may become much higher than the theoretical GHSV calculated from the dimensions of the incinerator.

The selection of suitable construction materials in VOC oxidation may sometimes enhance the oxidation results. However, in SVOC oxidation, the durability of construction materials sets limits on the selection. The materials must exhibit rather high thermal durability as well as corrosion resistance. The selection of a catalyst that does not catalyze SO₂ oxidation may ease the demands for construction materials, but the corrosion will not likely be avoided entirely this way. From the tested operation parameters, the largest demands to construction materials probably arises first from concentration and moisture (in SVOC emission abatement) and then from rather high temperatures used e.g. to avoid the effect of concentration and moisture. In solvent VOC oxidation, the durability of construction materials is not very problematic.

5.3.4 Other aspects related to industrial operation

In industrial operation, the emission abatement cases are different: the concentrations, compositions and amounts of emissions change. Therefore, it is sometimes reasonable to use so-called hybrid systems, i.e. in this case, include other abatement technologies in series with catalytic incineration. The incinerator related to this work can already be considered as a hybrid system, since it includes a filtering system for the removal of particulates prior the incinerator. However, sometimes combining other units to VOC and SVOC incineration may be beneficial or even necessary to achieve the most optimal emission abatement result.

In VOC (as well as in SVOC) oxidation, the emissions may contain compounds that can deactivate the catalyst. Removal of these compounds prior to the catalytic incineration will enhance the operation of the catalysts and sometimes even make the application of catalytic incineration possible. The most suitable way for the abatement of catalyst poisons depends on the poison compound. For example, adsorption and absorption are possible. Sometimes concentration of emissions prior to catalytic incineration may make the process more profitable. In this case, the possibility to dilute gases that are too concentrated is also available. Neither should the safety of the process be forgotten, since VOCs form flammable mixtures with air in certain conditions. For example, Purwono et al. (1999) have studied the dynamics of a runaway in reverse flow reactors operating in propene oxidation over a Pt/α-Al₂O₃ catalyst. They found out two types of runaways: a slow runaway over several cycles and a fast increase of the peak temperatures soon after the start-up. Switching flow directions retarded the slow
runaway. A runaway may arise e.g. from an upset in the feeding concentration or inlet temperature.

In SVOC abatement, the first consideration related to the hybrid systems is probably the further processing of SO₂ that is formed in oxidation. This can be carried out in several ways e.g., by scrubbing with H₂O containing finely ground limestone or by NaOH (De Nevers 2000).

### 5.4 Conclusions

According to the study, the GHSV has the largest and negative effect on the n-butyl acetate conversion over the Pt/Al₂O₃ catalyst. Increasing temperature and concentration and decreasing GHSV enhance the oxidation. Moisture had only a minor impact on the n-butyl acetate conversion. However, it somewhat decreases the formation of by-products. In general, similar results were achieved with fresh and aged catalysts, except the aged catalyst was slightly more affected by changes in GHSV than the fresh one.

In DMDS oxidation, temperature has the largest and positive effect on conversion. The interaction of GHSV and moisture also has a positive effect, but the single effect of GHSV is negative. Moisture seems to enhance the oxidation slightly. Concentration has almost no effect on conversion in the tested levels of factors. Moisture did not have, however, any significant effect on by-product formation. At the lower temperature level, higher concentration seems to cause slightly more formation of by-products.

Transient operation has been speculated to have a beneficial effect on catalytic oxidation, among other things. According to laboratory studies, oxidation of methane and n-butyl acetate at a constant temperature and a temperature that is changed between 300°-400°C did not show significant differences in total conversions.

The effects of the tested process parameters on catalytic activity, the selectivity of a catalyst and the durability of a catalyst as well as construction materials were speculated on Section 5.3. In conclusion, the highest temperature is limited by the durability of materials and operational setting values, the highest concentration is limited by flammability limits and authorities, and the highest GHSV is limited by the fan speed to the level of optimal oxidation results. Moisture content can be regulated by pretreatment, if needed. All these factors have an effect on the performance of an industrial incinerator and the effects depend largely on the application case.
6 Concluding remarks

In Chapters 2-5 different aspects of the process characterization (i.e. measurements, construction materials, catalyst research and process parameters) of catalytic incineration are described and studied. In this chapter, the following conclusions are drawn based on the information from all four parts of process characterization. In general, the existing incinerator concept operates excellently in solvent VOC emission abatement. However, successful application in chip bin SVOC emission abatement requires improvements, which are listed at the end of this chapter.

At the beginning of this thesis it is shown that systematization of the actual measurements and the combining of quantitative continuous measurements with qualitative analysis of gas samples will give a realistic view of emissions while maintaining low costs and being less work-intensive. At the same time, combining several different measurement techniques will generate information if some of the techniques used are not feasible for a certain application.

Second, the selection of construction materials is crucial in catalytic incineration. In solvent emission abatement the oxidation results can even be improved by selecting suitable construction materials. In chip bin emission abatement, the corrosion resistance of materials will become the most significant issue due to possible condensation of sulphuric acid. In addition to information on compounds, the selection of construction materials should be based on process operation conditions.

Third, the selection of a catalyst should be done based on the application. Good selection criteria are activity, selectivity and durability of the catalyst, the importance order of which depends on the application case. In solvent VOC abatement, the tested noble metal catalysts proved to be very durable, and therefore the main selection criteria are selectivity and activity. Based on the laboratory results, catalyst E (Cu-Mn oxides) or C (Pt/Al₂O₃-La) is the best choice. In chip bin emission abatement, the most important selection criteria are selectivity and durability. In the laboratory experiments, the best catalyst was shown to be SVOC5 (MnO₂-MgO). The selection of catalysts is based on catalyst volume.

Of the tested operation parameters, i.e. GHSV, temperature and concentration, VOC oxidation was mostly affected by GHSV by decreasing the conversion of n-butyl acetate. In the case of DMDS oxidation, temperature had the main and positive effect on the end
conversion. These results are valid only at the tested region of factor levels. The fourth factor (moisture) slightly decreased the formation of by-products in n-butyl acetate oxidation and slightly increased the DMDS conversion at lower temperature levels.

In general, solvent-VOC oxidation conditions are easier for the application of catalytic oxidation than chip the bin-SVOC oxidation conditions. The selection of materials and catalysts can be done more freely in the case of solvent-VOC abatement, and there are no high requirements for e.g. the thermal stability of construction materials or the deactivation resistance of catalysts. In the case of SVOC oxidation it is opposite. Compared to the existing incinerator and its operation, the temperatures at the inner surfaces of the incinerator should be kept above the sulphuric acid dew point temperature. This can be carried out e.g. by improving the heating or decreasing the heat recovery capacity. If the operation temperature is increased, the temperature durability of the construction material should be higher at the hottest part of the incinerator (*i.e.* close to the catalysts). Sulphuric acid corrosion resistant materials should be preferred at least at the coldest parts of the incinerator (*i.e.* in lower heat exchangers and at the outlet parts of the incinerator). When considering the operation of the incinerator, the most critical phases of operation are start-up and shutdown. In these phases it should be verified that sulphurous compounds are flushed out from the incinerator before it cools down or the inlet valve is not opened before the incinerator has reached the required operation temperature. When it comes to catalyst selection, one should prefer catalysts, which maintain the best selectivities to SO$_2$ over the high activity of a catalyst, which may mean the formation of SO$_3$ followed by sulphuric acid formation.

In this thesis, it has been proved that scientific methods and information gathered from the overall process characterization may be used to improve and widen the applicability of catalytic incineration in novel or unusual areas of emission abatement. The methods and practices described in the characterization of the incineration process may also be applied to other catalytic processes, application areas or emission measurements.
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