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Influence of the heat exchangers' construction material on catalytic incineration

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Abstract

In industrial scale catalytic volatile organic compounds (VOCs) incineration it is sometimes observed that the VOC conversions are higher than expected, based on the laboratory scale experiments at the same temperatures. One reason for this is that the construction material of the industrial scale catalytic incinerator may have an effect on the total VOC conversion. In this study, the effect of construction material on VOC removal activity is studied through laboratory experiments, by thermodynamic calculations and by flow modelling. The results showed that copper and Aluzinc decreased the light-off temperature (T_{50}) of *n*-butyl acetate compared to thermal experiments. Copper and Aluzinc did not, however, further decrease the T_{50} when they were introduced into the reactor packed with the catalyst. The higher total VOC conversion observed in the industrial scale incinerator is presumably due to the higher temperatures at the outlet of the catalyst, which is maintained by the heat exchangers.

Keywords: VOC abatement; Thermodynamic calculations; Flow modelling

1. Background

An evidence of the effect of construction material on VOC (*n*-butyl acetate) conversion was observed when 'mixing honeycombs', presumed to be inert, were installed in the laboratory scale reactor before the catalyst. The honeycombs were used to simulate the industrial set-up with higher precision and to make the contact between VOC compounds and air more efficient. The T_{50} temperatures (temperature of 50% conversion) achieved were somewhat lower than those observed in our earlier experiments [1]. The industrial scale catalytic incinerator consists of two honeycomb systems that include catalysts and heat exchangers (Fig. 1). The heat exchangers are considered to be regenerative. A regenerative heat exchanger temporarily stores energy from a hot gas stream produced during exothermic oxidation reactions in the catalyst bed. The hot stream is introduced into the bed until temperature of the bed nearly reaches the temperature of the hot stream. Then, the direction of streams is changed and a cold gas stream is passed through the hot bed. When the bed cools down, directions of streams are reversed again, repeating the cycle.

The measured total VOC conversion in the industrial scale incinerator was about 97% when the observed maximum temperatures before and after the catalysts were 400 and 420 °C, respectively. The inlet VOC concentration in this case was about 0.3 g/m^3, which is less than the incinerator's autothermal point (0.65 g/m^3). Due to this, extra heating was used to maintain the required oxidation temperature. The emission gases to be oxidized in this VOC incinerator contained mostly *n*-butyl acetate [2]. In order to achieve the 97% conversion for 2000 ppm (~10 g/m^3) of *n*-butyl acetate in the reactor inlet over the same catalyst, a reaction temperature of 450 °C is required in the laboratory scale. Generally, an increase in concentration requires higher oxidation temperatures. In this case, however, the reason for higher oxidation temperature in the laboratory scale might not be due to the higher concentration, as the difference in the concentrations between these two scales

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(0.3 and 10 g/m^3) is not significant. The concentration of VOC does not affect the catalytic oxidation to the same extent as the space velocity (GHSV) [2]. In the industrial scale incinerator, the flow is not likely distributed evenly at the catalyst inlet, which means that the real space velocity is different than the theoretical space velocity (31 500 h^{-1}). The space velocity is calculated from the catalyst volume and from the gas flow. The real space velocity is difficult to determine. Due to the difference in space velocities, it is possible that, in the industrial scale, the amount of catalyst needed for the same conversion is greater than that used in the laboratory scale experiments. It can be argued that the difference in the T_{97} temperatures might also originate from the discrepancies in the space velocity.

In addition to concentration measurements at the inlet and outlet of the industrial scale incinerator, the concentrations of total VOCs were measured before and after the heat exchangers, and some differences in concentrations were observed. The total VOC concentration before the heat exchangers was about 60 mg/m^3 and after the heat exchangers about 8 mg/m^3 [2]. However, this was observed only when the flow was directed downwards in that half of incinerator, where the measurements were carried out. See Fig. 1 for the location of measurement points in the incinerator. In this flow direction, it seems that the VOC oxidation proceeds after the gas flow exits the catalysts. This would indicate that, in an industrial scale incinerator, both heterogeneous catalytic reactions and homogeneous gas phase oxidation reactions take place.

There are several other explanations for the higher total VOC conversions observed in an industrial scale catalytic incinerator, such as inaccuracies or errors in industrial sampling and laboratory scale experiments. The total VOC concentration also fluctuates in industrial scale. Some VOC mixtures are easier to oxidize than pure VOC compounds, while usually one compound inhibits the oxidation of another compound, such as *n*-hexane and toluene inhibits *n*-butyl acetate oxidation over certain catalysts [3]. This study is performed to ascertain whether the construction material affects the industrial scale catalytic VOC oxidation. The study consists of laboratory experiments, thermodynamic equilibrium calculations, and flow modelling.

2. Experimental

The industrial scale measurements were performed in a catalytic incinerator, which was designed for the abatement of solvent emissions originating from a painting shop. The most dominant compound in painting shop emissions is *n*-butyl acetate [2], which was selected as a model VOC compound (2000 ppm, ~10 g/m^3) for the laboratory experiments. The laboratory experiments were carried out in a quartz reactor (see Fig. 1), which was heated up from room temperature to ~800 °C. The *n*-butyl acetate was fed by a calibrator, in which a syringe pump was injecting the liquid phase compound to the heater, to be vaporized and mixed with air. The air was fed through a mass flow controller. The outlet gas flow was analysed by using a GC/FID (Agilent Technologies, Model 6890N).

Laboratory experiments were carried out with and without a catalyst, with different metal plates, with inert glass granules and without any packing material, the latter called as thermal experiment. The experiment with glass

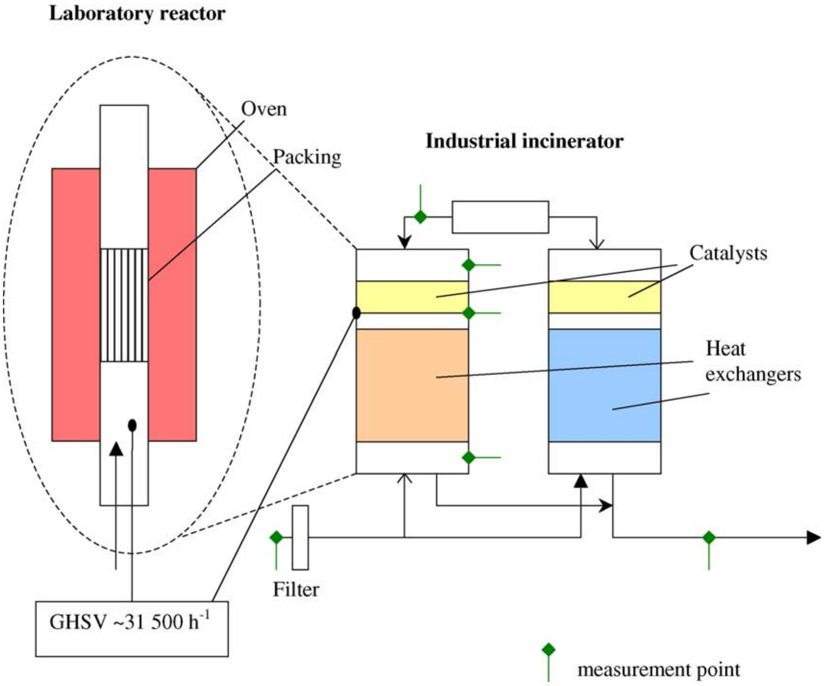

Fig. 1. Schematic of the industrial scale incinerator, the laboratory scale reactor and the measurement points in the industrial scale incinerator.

Table 1
Description of the bed materials

Bed name	Material	Mass (g)	External surface area (cm^2)	Specific heat capacity, c_p (kJ/kg K)	Heat conductivity, k_w (W/mK)
Thermal	–	–	–		
Aluzinc	Al/Zn/Si coated steel plate	5.2	∼24		
Copper	Cu-plate	8.0	∼24	0.39	400
Stainless steel	Stainless steel-plate	5.8	∼24	0.46	45
Glass	Glass granules	2.6	∼47 (60 pieces)		
		1.3	∼24 (30 pieces)		
Catalyst	Pt/Pd	–	–		

Experiments were carried out with single beds and with the combinations of a catalyst and other bed materials [4].

granules was performed with two different packing sizes. In the first case, the glass packing had the same volume than that of metal packing (60 pieces of granules) and, in the second case (30 pieces of granules), the external surface area of the glass granules was the same as the external surface area of the metal packing. The temperature in the glass granule test was limited to temperature of ∼600 °C due to the softening of the granules at 600 °C. The softening temperature was determined by oven tests before the experiments. While the different materials were inserted into the reactor, thus by changing the packing volume, the catalyst volume and gas flow (1 dm^3/min) were kept constant, in order to maintain the same space velocity (31 500 h^{-1}) within the catalyst honeycomb. The GHSV of 31 500 h^{-1} is the same than that of the theoretical industrial scale GHSV. Details of different experiments and some thermal data are presented in Table 1.

3. Results and discussion

Fig. 2 illustrates the results of the laboratory scale experiments. The addition of packing material into the reactor decreases the T_{50} of *n*-butyl acetate compared to the thermal experiment. The effect of the metallic or inert glass material on the light-off temperature is not as significant as the catalyst's effect. However, if the reactor bed consists of combinations of a catalyst and metallic/glass material, the T_{50} temperature of *n*-butyl acetate is not further decreased.

One might ask, why could the heat exchangers have an effect on the cleaning efficiency? 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. It might be the case that the heat exchangers act as a 'third body', which initiate branching oxidation reactions [5]. It is also possible that, the heat exchangers improve the mixing of emission gases, and thus intensify the contact of oxygen molecules with VOC compounds and, ultimately enhance the oxidation reactions. Another possibility is that metal improves the heating of the gas and creates more heat exchange area. A further explanation can be that the metallic construction material may be 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. 2 shows, no

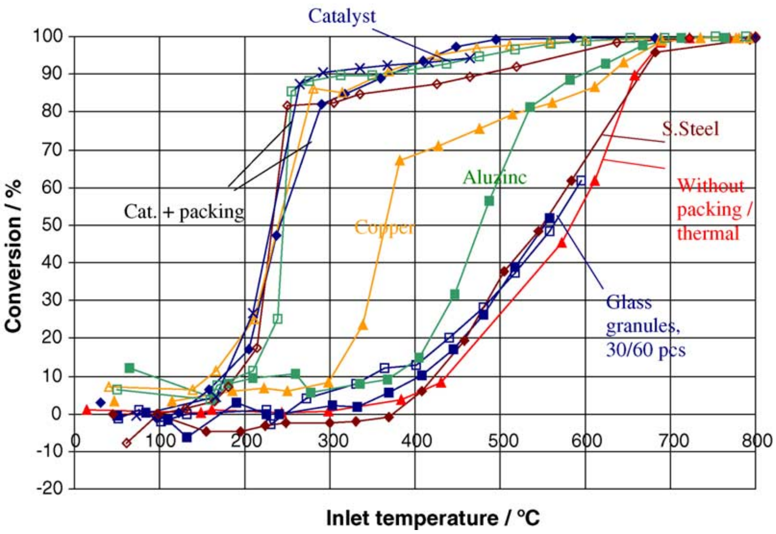

Fig. 2. Light-off curves of *n*-butyl acetate with different packing materials. Experiments were carried out with Aluzinc, copper and stainless steel plates; with glass granules (30 and 60 pieces); with the Pt/Pd catalyst and with combinations of the catalyst and other packing materials. The 'thermal' experiment was carried out without any packing material.

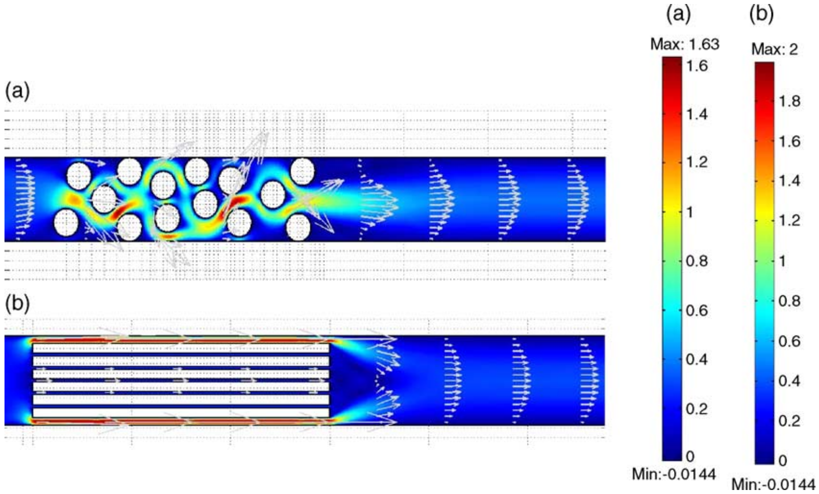

Fig. 3. Mixing in the laboratory reactor, modeled with Femlab 2.3: (a) mixing of gas in glass granule packing; (b) mixing of gas in metal plate packing (flow velocity (v) at the inlet 0.26 m/s, temperature (T) 402 °C).

significant effect was observed when the surface area was doubled. Moreover, the effect of better mixing when glass granules were used had minor effect on the T_{50} of *n*-butyl acetate. Fig. 3, modelled by Femlab, shows that the mixing in the glass granule packing is better than in the metal plate packing. Furthermore, the metal packing suffers from bypassing and thus the effective surface area may be smaller than the total external surface area listed in Table 1. Due to the relatively small Reynolds number, the flow was modelled with the incompressible Navier Stokes equation. In the modelling, the reaction and the heat transfer were not included. Since the actual VOC mixture used in the laboratory experiments is very lean, constants for the air were used. In the flow model, the gas velocity at the inlet (0.26 m/s) was the same as the inlet velocity in the laboratory scale reactor, and the boundary conditions on all the reactor and packing surfaces except at the inlet and the outlet, were considered to be 'no-slip'. The temperature used (402 °C), was the same as the temperature near the catalyst in the industrial scale incinerator. The average temperature in the laboratory experiments was also on the same level (400 °C). In the model, the effect of temperature was included in the parameter values.

In the experiments with other packing materials it was observed that stainless steel packing did not greatly enhance the oxidation reaction, whereas Aluzinc and copper decreased the T_{50} temperature of *n*-butyl acetate significantly. Aluzinc and copper packings give a ~100 and ~200 °C decrease, respectively, in the T_{50} temperature of *n*-butyl acetate. However, none of these packing materials is as effective as the catalyst, which gives a decrease of over 300 °C in the T_{50} temperature.

One possible explanation for the differences between the metal packings is that the surface of stainless steel was polished, which was not the case with copper and Aluzinc. The non-polished surface of Aluzinc and copper plates may allow a better contact between the gas molecules and the metal surfaces. The sizes of the packings were the same, thus the external surface areas were also the same. The only difference between these packings was that the weight of copper was a few grams greater than the weight of other metal packings. Some of the heat properties of copper and stainless steel are presented in Table 1.

Larger enhancing effect of copper on the oxidation reaction, as compared with stainless steel and Aluzinc, can be partly explained by its better heat conductivity properties. However, compared to the uncoated stainless steel, Aluzinc steel with an Al/Zn/Si (55 vol.%/43.4 vol.%/1.6 vol.%) coating, decreases the T_{50} temperature. This might be due to other properties of the metal, such as its surface properties.

The oxidation of *n*-butyl acetate without the packing material can be considered to take place via homogeneous reactions. Fig. 2 shows that, in catalytic reactions and in copper packing experiments the homogeneous gas phase reactions do not occur below the T_{50} temperature. The T_{50} temperature for the thermal experiment is 580 °C. At the same level, it corresponds to over T_{80} 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 other factors than the heat conductivity of the metal. However, it is important to take into account 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 covering active surface sites of the catalyst [6,7]. ZnO, however, is also used as a stabilizer and/or promoter in catalysts. Oxides of aluminium

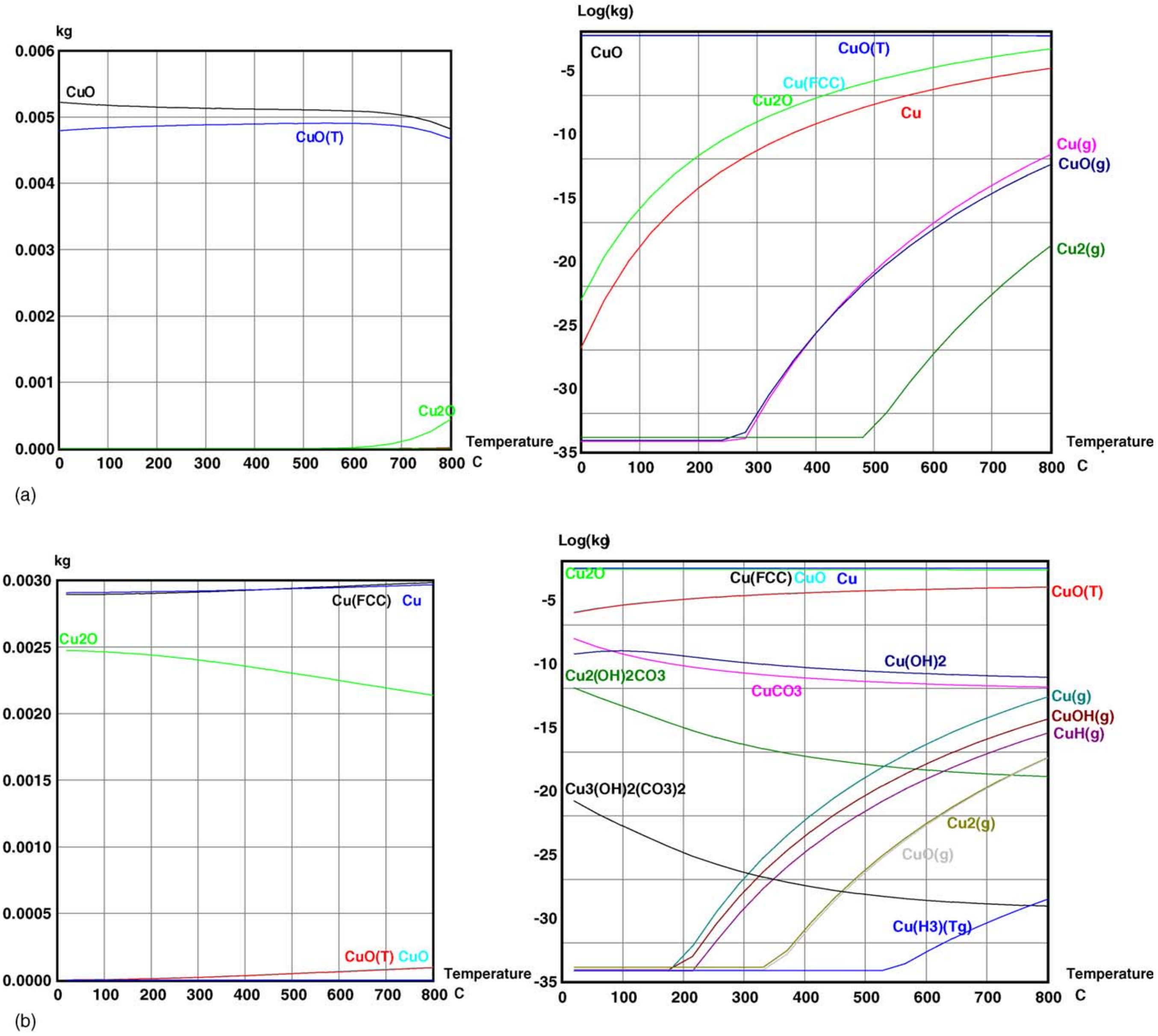

Fig. 4. Calculated thermodynamic phase diagrams for copper (a) in air (79% N_2 + 21% O_2) (b) in 2000 ppm *n*-butyl acetate and air mixture. Calculations were done in 1 bar as a function of temperature. Cu(FCC) = FCC copper, CuO(T) = tenorite, $Cu(H_3)(Tg)$ = copper tritium.

also have some catalytic effects and due to their large surface area, they are commonly used as washcoat material of catalysts.

Experiments with metal packings were repeated several times. During the repeated experiments with Aluzinc, the T_{50} temperature decreased 80 °C between the first and the last experiment. Conversely, with copper, an 80 °C increase in T_{50} was observed. However, the T_{100} temperatures were the same in all these experiments. The increase in T_{50} in copper experiments may be due to mass transfer limitations originating from the oxidation of the copper surface.

Fig. 4 shows the thermodynamic phase diagrams for air and for *n*-butyl acetate/air mixtures in the presence of copper, calculated by HSC Chemistry® 5.1 program. HSC Chemistry® 5.1 [8] is generally used for calculating chemical equilibriums between pure compounds in ideal solutions. In these calculations, enthalpies, entropies and heat capacities of compounds are needed. The HSC Chemistry® 5.1 program includes a thermochemical database that contains the values of enthalpies, entropies and heat capacities. The program does not consider any kinetic phenomena, but thermodynamically possible reactions can usually be proven by thermochemical calculations. Air, *n*-butyl acetate/air mixtures and copper were considered as bulk materials. Calculations were done in 1 bar. Gas mixtures included air (21 vol.% oxygen + 79 vol.% nitrogen) and, air + 2000 ppm *n*-ButAc. These conditions were selected based on earlier laboratory experiments, in which *n*-

butyl acetate was used as a model compound. Results from calculations are presented in Fig. 4, which shows the amount of different copper and copper oxide species, as a function of temperature in the temperature range of 0–800 °C. According to these calculations, the copper surface was probably in the form of CuO. No clear phase change was observed at 380 °C (T_{50} for copper packing experiment) neither in thermodynamic equilibrium calculations of copper–air, nor in calculations of copper–air–*n*-butyl acetate mixture.

According to Birks and Meier [9], the oxidation behaviour of metal coatings follows the principles of alloy oxidation that is they protect metal by selective oxidation to form Al_2O_3, Cr_2O_3 and SiO_2, etc. scales. Thus, in this case, the Aluzinc surface may contain these oxides, of which the quantity of Al_2O_3 was the highest. The thermodynamic equilibrium calculations of Zn, Al, and Si in air showed the presence of other oxides, such as ZnO and $ZnSiO_3$. Fig. 2 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, oxides are mostly Cr and Mn oxides, even if the metal contains mostly Fe [10]. It seems, that in this case these oxides are less active than those on the Aluzinc surface (i.e. Al_2O_3, SiO_2, ZnO, $ZnSiO_3$).

In the thermal experiment, which happens via homogeneous gas phase oxidation, a great deal of intermediates were observed even at the temperature level of ~800 °C, which is not the case with the catalytic reaction. These intermediates are organic compounds that usually have smaller molecular weight than *n*-butyl acetate i.e. butene, acetic acid, butyraldehyde, methane, etc. In addition, the amount of intermediates formed was larger in the thermal experiments. When compared to the catalytic experiments, the amount of intermediates at the end of the experiment is also higher when metallic packings were used. However, the amount of intermediates 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 intermediate formation can be decreased by catalysis.

4. Conclusions

Based on our experiments, we can conclude that addition of packing materials did not significantly enhance catalytic reactions. However, compared to the thermal experiments, copper and Aluzinc packing decreased the T_{50} temperature of *n*-butyl acetate. It is more likely that the heat exchangers maintain the temperatures needed for homogeneous gas phase oxidations. Consequently, within the industrial scale incinerator both catalytic surface and homogeneous gas phase oxidation reactions take place.

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