

Research Article

Effect of Process Parameters on Catalytic Incineration of Solvent Emissions

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Received 8 January 2008; Accepted 29 April 2008

Recommended by Peter Stockwell

Catalytic oxidation is a feasible and affordable technology for solvent emission abatement. However, finding optimal operation conditions is important, since they are strongly dependent on the application area of VOC incineration. This paper presents the results of the laboratory experiments concerning four most central parameters, that is, effects of concentration, gas hourly space velocity (GHSV), temperature, and moisture on the oxidation of n-butyl acetate. Both fresh and industrially aged commercial Pt/Al₂O₃ catalysts were tested to determine optimal process conditions and the significance order and level of selected parameters. The effects of these parameters were evaluated by computer-aided statistical experimental design. According to the results, GHSV was the most dominant parameter in the oxidation of n-butyl acetate. Decreasing GHSV and increasing temperature increased the conversion of n-butyl acetate. The interaction effect of GHSV and temperature was more significant than the effect of concentration. Both of these affected the reaction by increasing the conversion of n-butyl acetate. Moisture had only a minor decreasing effect on the conversion, but it also decreased slightly the formation of by products. Ageing did not change the significance order of the above-mentioned parameters, however, the effects of individual parameters increased slightly as a function of ageing.

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1. INTRODUCTION

Volatile organic compounds (VOCs) together with nitrogen oxides are the major contributors to the formation of photochemical ozone. In 1999, the EU adopted the VOC solvent emissions directive [1], the goals of which should be implemented by the year 2007. The wood-coating processes are among those that have to follow the VOC solvent emission directive. According to our experience, the solvent emissions from wood-coating processes include usually ethanol and n-butyl acetate [2] of which n-butyl acetate has the typical solvent odor.

The most feasible abatement technologies for emissions that are mixtures of different VOCs are destruction-based, that is, thermal and catalytic oxidation or biodegradation. If the total VOC concentrations are not very high, catalytic incineration with heat recovery is the most cost-effective alternative [3, 4]. The normal operation temperature of

an industrial scale catalytic VOC incinerator in solvent emissions abatement is about 350°C, but it varies depending on the VOC compound to be oxidized [5]. For example, minimum reactor inlet temperatures reported by Hayes and Kolaczowski [6] vary from 190°C to 350°C. The economy of catalytic incineration may be further improved by employing a heat recovery system and, furthermore, the operation of the incinerator may be autothermal, which means that no additional heating of emission gases are needed to maintain oxidation reactions. The autothermal operation may be achieved in practice, for example, with the aid of flow-reversal and regenerative heat exchangers [3, 4, 7].

In general, there are several process or operation parameters that may have an effect on the total oxidation of VOCs. These involve, for example, concentration of emission gases, gas hourly space velocity (GHSV), temperature, and moisture content of the emission gas. In this study, the effects of different process parameters on the oxidation of

n-butyl acetate are investigated at a laboratory-scale. Similar studies are carried out over both fresh and industrially aged Pt/Al₂O₃ catalysts. The objective of this study is to determine the optimal process conditions for the catalytic incineration of n-butyl acetate as well as to find out how significant the effects of these parameters are in practice. Computer-aided statistical experimental design is used as a tool in experimental design, and in evaluation of the results. The results are discussed "in the light of flow-reversal process," since the industrial process associated to this research is operated by flow-reversal. In addition, industrial ageing of Pt/Al₂O₃ catalyst was carried out in a flow-reversal incinerator.

2. EXPERIMENTAL

2.1. Laboratory experiments

Laboratory experiments have been carried out in a continuous-flow tubular quartz reactor with a diameter of 9 mm. Liquid-phase n-butyl acetate, which was selected as the model compound based on industrial measurements, was first vaporized and fed with air to the reactor by the aid of a calibrator (Temet Instruments Inc. Type Ø0009). Water in the moisture containing experiments was fed with a separate syringe pump, vaporized, and mixed with the reaction mixture prior to the reactor inlet. The reactor was heated up to the reaction temperature in a tubular furnace. The continuous gas flow was analyzed at the outlet of the reactor by GC/FID (flame ionization detector) and by GC/TCD (thermal conductivity detector) (Agilent Technologies model 6892N). The catalyst bed height (30 mm, giving a volume of ~1.9 cm³) was kept constant during the experiments. Temperature was measured at the catalyst inlet with a K-type thermo element.

The experiments were carried out over fresh and industrially aged Pt/Al₂O₃ metallic monoliths. The Pt/Al₂O₃ catalyst was aged in an industrial solvent-emission abatement process for 25 months. Sample catalysts were installed in an industrial-scale incinerator between a catalyst bed and regenerative heat exchangers in such a way that they were exposed to either once treated or untreated emission flow depending on the operation of the reverse-flow process. During the ageing period, the industrial incinerator was working in solvent emission abatement application, where the most dominant emission compound was n-butyl acetate. Total concentration of emission gases was fluctuating according to solvent-using process operation. The temperature of the catalytic incinerator during the ageing period was varying roughly between 350–400°C. More detailed description of industrial ageing is presented in [8].

Prior to the laboratory experiments, a 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 change the state of the catalyst surface and even regenerate it. The activity of each catalyst was tested by light-off tests before and after the factorial experiments. In the light-off experiments, the n-butyl acetate concentration was 2000 ppm, GHSV was 31 500 h⁻¹, and heating rate

5°C min⁻¹ from room temperature to about 700°C. BET surface areas were also measured (Coulter Omnisorp 360CX) before and after the laboratory experiments.

2.2. Experimental design

MODDE 6.0 program (Umetric AB) was used as a tool in the statistical experimental design and in evaluation of the effects of the selected parameters (temperature, GHSV, concentration, and moisture) affecting the catalytic oxidation of n-butyl acetate. Further, the effect of ageing of the catalyst was considered, that is, does ageing affect process parameters 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 levels of other factors, which enabled study of the effects of the interaction of selected parameters. The used response was conversion of n-butyl acetate over the fresh and aged catalysts, which was calculated from the measured concentrations. The validity of the empirical models fitted with the multiple linear regression (MLR) was tested with the analysis of variance (ANOVA). The used confidence level was 95%.

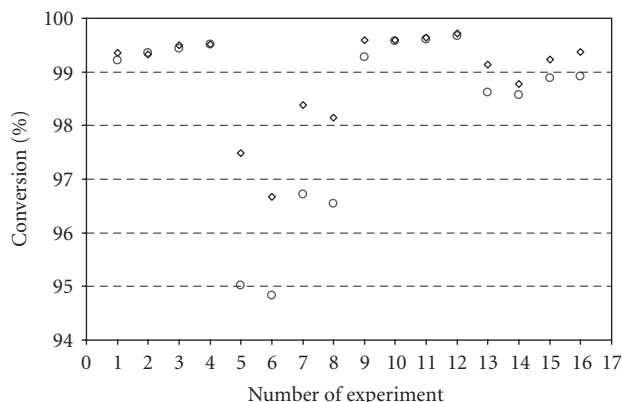
The parameters and the used levels were based on the earlier results achieved from industrial measurements, from solvent emission sources, and from catalytic incinerator used in the solvent emission abatement. The metal-supported Pt/Al₂O₃ catalyst was selected to these experiments based on catalyst screening tests, where it showed the highest activity in n-butyl acetate oxidation [3, 9]. As mentioned, the selected operation parameters were temperature, GHSV, concentration, and moisture content. Temperatures of the experiments were selected to be higher than the catalysts light-off, that is, above the temperature of 50% conversion, of which the lower temperature, 300°C, is close to a normal industrial operation temperature of the incinerator, and the higher temperature level, 500°C, is above it. The basis of the selection of GHSV levels, that is, 31 500 h⁻¹ and 63 000 h⁻¹, was similar to the selection of temperature levels. In the experiments, the GHSV levels were set by adjusting the total flow of the reacting gas mixture. The lower level of concentration (2000 ppm) was close to the concentration of n-butyl acetate in the solvent emission measured [2], 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).

3. RESULTS AND DISCUSSION

Objectives of this study were to determine the optimal process conditions for the catalytic incineration of n-butyl acetate and to find out significance levels of the selected parameters. The experimental data was analyzed with a statistical design software in order to have also a new insight into the simultaneous effects of several process parameters. Table 1 shows the array of experiments where higher and lower parameter values are indicated. Figure 1 shows responses (n-butyl acetate conversions) over the fresh and aged monoliths. In general, the conversions achieved are

TABLE 1: Array of experiments.

Number of experiment	Moisture [%]	Concentration [ppm]	GHSV [h^{-1}]	Temperature [$^{\circ}\text{C}$]
1	—	2000	31500	300
2	2.5	2000	31500	300
3	—	4000	31500	300
4	2.5	4000	31500	300
5	—	2000	63000	300
6	2.5	2000	63000	300
7	—	4000	63000	300
8	2.5	4000	63000	300
9	—	2000	31500	500
10	2.5	2000	31500	500
11	—	4000	31500	500
12	2.5	4000	31500	500
13	—	2000	63000	500
14	2.5	2000	63000	500
15	—	4000	63000	500
16	2.5	4000	63000	500

FIGURE 1: Conversions of n-butyl acetate over the fresh (\diamond) and aged (\circ) catalysts.

rather high (over 94%) in all experiments. The aged catalyst seems to give slightly smaller conversion values than the fresh one, which implies that the catalyst has actually lost its activity slightly during the 25 months of ageing. This is especially observed at higher GHSV values (experiments 5–8 and 13–16). It can also be clearly seen from Figure 1, that lower GHSV gives higher conversion values, as expected, but GHSV seems to have the largest main effect on the conversion of n-butyl acetate compared to the effects of other parameters as well.

To get more detailed information, the responses were fitted with the aid of MODDE program. In general, the fitting of responses showed that the parameters studied here had similar effects on the conversion of n-butyl acetate independent whether the catalyst was fresh or aged—the significance order of the parameters was not changed. The calculated effects of parameters for fresh and aged catalysts are presented in Figures 2(a) and 2(b), respectively. In more

detail, all single effects as well as interaction terms are included in Figure 2, even if the effects of all these terms are not significant. The error is indicated in each effect-indicating bar separately. If the error is greater than the calculated effect, the effect can be removed from the final model.

When the validity of the fitted model (MLR) was evaluated with ANOVA, the results showed that the model was statistically significant with a 95% confidence level. Square of the multiple correlation coefficient of the model, that is, the response variation percentage explained by the model, R^2 , for fresh and aged catalysts were 0.976 and 0.986, respectively. Response variation percentages predicted by the model, Q^2 , were 0.945 for the fresh and 0.968 for the aged catalyst. However, one has to remember that the model is valid only in the used range of parameters.

Figures 1, 2(a), and 2(b) show that GHSV has the largest and negative main effect on conversion, that is, when GHSV is increased, the conversion is decreased. Furthermore, the effect of GHSV is more significant at low temperatures and it is slightly more important over the aged catalyst than over the fresh catalyst. Due to the selected temperature levels, the model reaction occurs in the mass transfer limited area (See Figure 3). Increasing of GHSV moves reaction slightly closer to the transition phase where reaction switches from kinetic to mass transfer controlled region. At a mass transfer restricted area, the reaction rate is first affected by pore diffusion (at lower temperature level) and later by bulk diffusion. This affects the apparent reaction rate, and in more detail, bulk mass transfer phase of catalytic reaction. This step of reaction has smaller relative temperature dependence than other steps of reaction (i.e., pore diffusion, sorptions, and surface reaction), but it is more affected by flow conditions. The conversion is also affected by the fact that the residence time of reactants inside a catalyst at a higher GHSV level is also smaller than at a lower GHSV level.

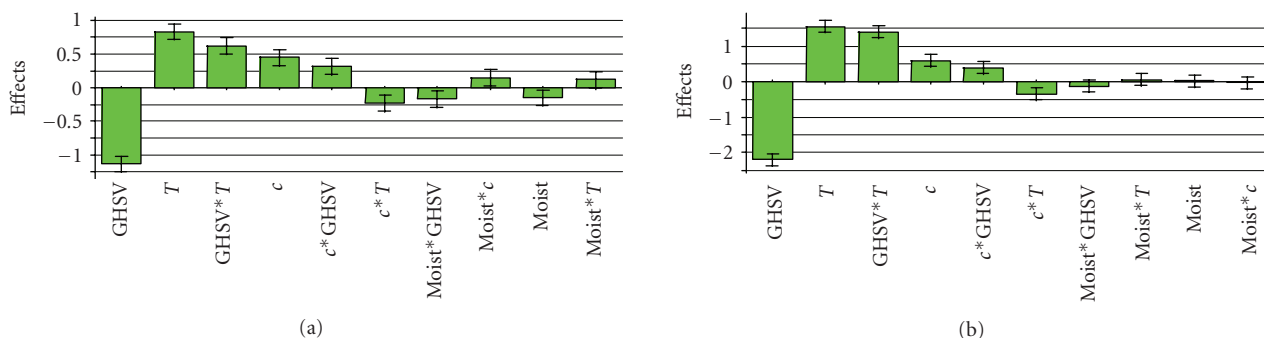


FIGURE 2: Calculated effects of GHSV, moisture (Moist), concentration (c), and temperature (T) on n-butyl acetate conversion over (a) fresh and (b) aged catalysts.

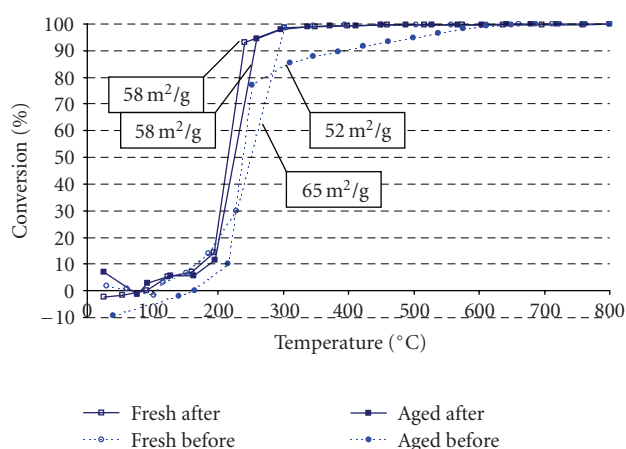


FIGURE 3: Light-off curves and BET surface areas for fresh and aged Pt/Al₂O₃ catalysts before and after the experiments. ($c_{n\text{-butyl acetate}} = 2000$ ppm, GHSV = 31 500 h⁻¹, heating rate 5°C min⁻¹.)

Temperature has the second largest but positive effect on conversion, thus when temperature is increased the conversion is increased as well. As the experiments have been carried out at mass transfer limited area, increasing temperature increases the apparent reaction rate less than decreasing the GHSV. For example, bulk molecular diffusion rates vary approximately by $T^{3/2}$ while surface reactions depend on temperature according to exponential Arrhenius law. Several authors [7, 10, 11] have reported that if the catalytic incinerator is operated autothermally with a flow reversal, small changes, for example, in the flow rate, inlet temperature, and concentration may not affect the end conversion at all. This is due to a quasisteady state operation where the temperature profile in a tubular reactor has a maximum value near the center of the reactor and it slowly oscillates toward 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. Higher catalyst surface temperature compared to bulk gas temperature may be formed also in a once-through system due to exothermic reactions. In a once-through system, this

temperature maximum is close to the outlet of the catalyst [12].

Third significant term is the interaction effect between temperature and GHSV. It can be observed from Figure 2, that the interaction effect is positive and increases the end conversion of n-butyl acetate. In general, the effects of other parameters are enhanced with a higher GHSV value. However, higher temperature is balancing this effect. If we consider the light-off curve presented in Figure 3, an increase in GHSV moves the light-off curve toward a higher temperature region. If the reaction temperature is kept the same, the conversion of n-butyl acetate decreases. Then when temperature is increased, the conversion of n-butyl acetate is enhanced again. At a higher flow rates, the compounds have not as much time to react on the catalytic surface as at lower flow rates, and therefore, higher temperature is needed to enhance surface reactions so that a similar oxidation efficiency of n-butyl acetate can be maintained in both levels of GHSV. In the temperature range used in this study, thermal (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 [3]. If considering GHSV values in practice, it is also reported for flow-reversal systems that too high GHSV will probably extinct the reactions due to too short contact time at a certain reaction temperature [13].

The effect of concentration is the fourth important effect in this evaluation. The concentration has a more significant effect on conversion when GHSV is high than at lower GHSV level. The positive effect of higher concentration can be explained, for example, with the increased temperature. This effect is most pronounced at the lower temperature level and high GHSV level, when the reaction phase is moved away from bulk mass transfer controlled phase of reaction. 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. These experiments are carried out in lean conditions, and surplus oxygen is available. In addition to surface reaction, chemisorption and desorption phases may be enhanced, as they are more temperature dependent than pore and bulk mass transfer phases. It is good to notice that in industrial flow-reversal applications, oxidation of 2000 ppm of n-butyl acetate is enough to allow autothermal operation. The “thermal effect,” however, is

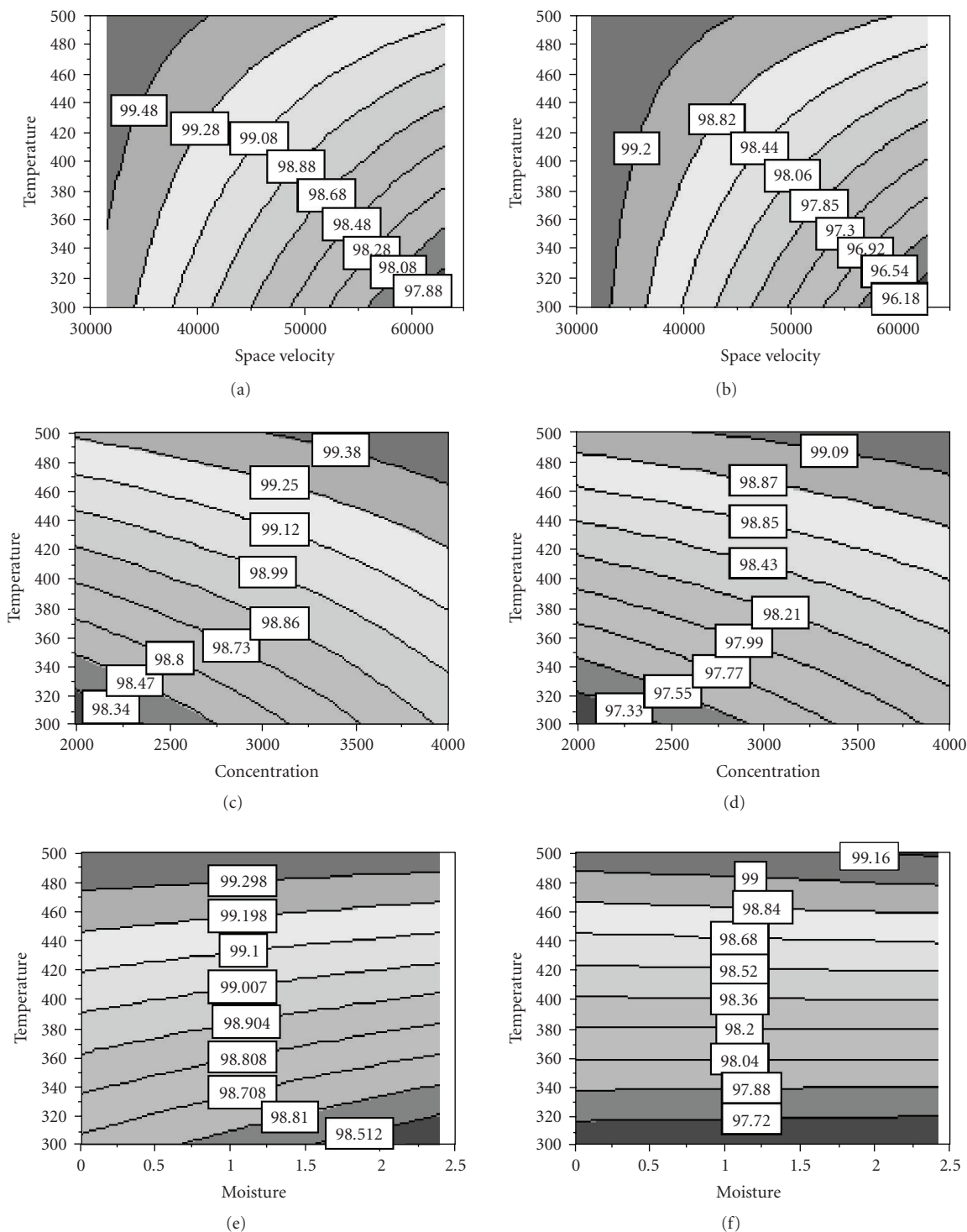


FIGURE 4: Contour-plots for parameters. Left column shows other parameters versus temperature for the fresh catalyst and right column for the aged catalyst. The other parameters are in the mid-level, that is, $GHSV = 47\ 250\ h^{-1}$, $c = 3000\ ppm$, and moisture = 1.2 if they are not presented in the figure.

probably not the only explanation to enhanced conversions at the higher concentration level, but also probability of reactions at the catalytic surface increases when more reacting molecules exist in the reacting mixture. This is especially a more pronounced effect at laboratory-scale experiments,

where autothermal operation or even adiabatic conditions were not present.

Despite the lack of previous information on oxidation of solvent compounds in the presence of water, 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 [14] as well as Pt-Pd/Al₂O₃ catalysts [15]. On contrary, Li et al. [16] reported that water vapor might have a promoting effect on the catalytic oxidation of methane over Co/Mn mixed oxides. Keeping in mind that the oxidation mechanism for methane and n-butyl acetate is different, it was found out that in the case of n-butyl acetate oxidation 2.5 vol-% of water did not show any significant effect on the conversion of n-butyl acetate, in general (See Figures 2(a) and 2(b)). However, the slight decreasing effect of water on the end conversions seemed to depend on the values of GHSV, concentration, and temperature.

In our previous study [3], it has been observed that close to the catalyst light-off temperature some by products are formed. These by products are normally partially oxidized compounds that escape from the catalyst surface before the total oxidation. Most of these organic compounds have smaller molecular weight than n-butyl acetate and the quality as well as quantity of these compounds depends strongly on the used catalysts. The formation of by products is decreased when 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 noteworthy to consider also the possible by product formation, that is, the selectivity of the catalyst. The by product formation was followed also during these experiments, and the results showed that some organic by products are formed in these experimental conditions. Total concentration of detected by products was always less than 20 ppm, even in the worst case. The formation of by products is slightly more significant when GHSV is at the higher level. This can be explained by the shorter residence time of reactants inside the reactor. Interestingly, at higher levels of GHSV and temperature, the moisture somewhat decreases the formation of organic by products. However, at the same time end conversion is very slightly decreased. Perhaps water molecules occupy sites where n-butyl acetate is adsorbed and as conversion of n-butyl acetate is suppressed, also the formation and escape of by products is suppressed as well. Confirmation of this would, however, require much deeper studies on the mechanism of n-butyl acetate oxidation in the presence of moisture than studies carried out in this case. Ageing, in this case, did not change the formation of by products significantly. Only a slight increase in the by product formation is observed when the GHSV is at the higher level and temperature is at the lower level.

During the experimental procedure, the BET surface area of the fresh catalyst decreased slightly from its initial value (65.2 m²g⁻¹). However, the activity of the catalyst was improved probably due to further calcination of the catalyst [17]. The BET value 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 significantly after the experiments (see Figure 3). It seems that the aged catalyst has been regenerated during the experimental procedure, which shows that the slight deactivation is reversible. The shape of the light-off curve (in Figure 3) for the aged catalyst before the factorial

experiments indicates the pore blockage as being one of the possible deactivation mechanisms. Pore blocking might be due to coke formation in the oxidation of carbon-containing compounds and the regeneration of the catalyst could be then carried out, for example, by increasing the temperature momentarily (see also Figure 3 aged before and after).

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 even decreased when temperature is increased. These results are illustrated more visually in Figure 4.

The experiments were carried out close to the optimum (see Figure 4), and thus clear limited optimum area for the parameters in n-butyl acetate oxidation was not found according to these experiments. However, in practice, for example, temperature has a limiting value due to heating costs and durability of construction materials of the incinerator. Further, this sets a limit to the maximum GHSV when the total oxidation of n-butyl acetate is desired. The concentration is limited by flammability limits and regulations. For example, in Finland the maximum limit for the VOC concentration is 25% of LEL, which means in practice approximately 8 g of solvents in 1 m³ of air [18]. Furthermore, as literature and discussions above show, these results are not directly applicable for the catalytic incinerator, which operates with flow reversal.

4. CONCLUSIONS

According to the study, space velocity, concentration, temperature, and water have an effect on the activity of the catalyst, as expected. GHSV has the largest and negative effect on the conversion of n-butyl acetate over the Pt/Al₂O₃ catalyst. The interaction of GHSV and temperature had more important effect than concentration on n-butyl acetate oxidation. Increasing temperature and concentration and decreasing GHSV enhance the oxidation. Moisture (2.5%) had only a minor decreasing impact on the n-butyl acetate conversion, but it also decreased somewhat the formation of organic by products. Similar results were achieved with fresh and aged catalysts. However, the aged catalyst was slightly more affected by changes in GHSV than the fresh one. These results and the model are valid only in the used experimental region, which in this case, lays in mass transfer limited region of the catalytic oxidation of n-butyl acetate.

ACKNOWLEDGMENTS

This experimental work has been carried out with the financial contribution of the Academy of Finland. Mr. Jouko Virkkala is acknowledged for his contribution to experimental work.

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