

CATALYTIC COMBUSTION OF WASTE STREAMS COMING FROM THE SOLVENT RECOVERY STAGE OF A PACKAGING INDUSTRY

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INTRODUCTION

Esters and alcohols are widely used as solvents in the packaging industry. They contribute to the increase of volatile organic compound (VOC) emissions and, as such, represent a serious air pollution problem that must be faced. To this end, two main strategies can be pursued: solvent recovery and/or incineration, the former being of course preferred.

Solvent recovery mainly consists of an activated carbon plant, which adsorbs the post-printing exhaust solvents, and a distillation system, which separates the recovered solvent mixture. The waste streams coming from the solvent recovery stage need to be disposed, implying additional costs as well as safety issues. In this framework, an alternative solution is here proposed based on catalytic combustion of these waste streams.

Catalytic combustion enables burning VOCs at low temperatures, thus avoiding NO_x formation. Furthermore, the catalyst allows total combustion without formation of unburnt hydrocarbons (UHCs) and CO. Finally, catalytic combustion can be carried out at fuel concentrations that are outside the flammability range, thus ensuring safe operation.

In this work, catalytic combustion tests were performed for two waste streams, namely the azeotropic stream and the high-boiling-point stream, coming from the distillation plant of the packaging industry Icimendue (www.icimen.com). A Pt-doped perovskite was used as catalyst. Indeed, noble metal-doped perovskites have been successfully proposed for catalytic combustion of hydrocarbons [1-3]. The catalyst was supported over a monolith, thus allowing reduction in pressure drop along with process intensification [4,5].

1 MATERIALS AND METHOD

1.1 Monolith preparation

Combustion tests were performed over 1 wt% Pt/20 wt% LaMnO₃/La- γ -Al₂O₃ catalyst supported on 600 cpsi honeycomb cordierite monolith (NGK) (cylindrical shape: length, 50 mm; diameter, 12 mm). The procedure for monolith preparation is described in Ref. [3]. Briefly, the bare cordierite monolith was coated with a thick La₂O₃-stabilized γ -Al₂O₃ layer by dip-coating and then calcined in air at 800°C. Pt and perovskite were supported on the wash-coat through impregnation with an aqueous solution of lanthanum nitrate hexahydrate (Aldrich, > 99.99%), manganese acetate (Aldrich, > 99%) and hexachloroplatinic acid (Sigma, 8 wt% solution). The sample was dried at 120°C and calcined at 800°C for 3 h.

1.2 Catalytic combustion tests

The monolith was placed between two ceramic foams acting as thermal shields. Monolith and foams were wrapped in a thin ceramic wool layer and inserted into a lab-scale quartz reactor. A K-type thermocouple was placed inside the central channel of the monolith, thus providing the

measurement of the catalyst temperature profiles. Specifically, the temperature was monitored in the center of the monolith.

Experimental tests were run in a lab-scale rig described in more details in Ref. [3]. Briefly, high purity gases (O_2 , N_2) were separately fed and controlled by means of mass flow controllers (Brooks SLA5850). The flow rate of the azeotropic and high-boiling-point mixtures tested in this work was controlled by a pump (Dionex P680 HPLC Pump). Both mixtures were vaporized by heating at $100^\circ C$. A four-way valve by-passing or including the reactor allowed the analysis of the reacting mixture or the reactor off products, respectively. The temperature was controlled by inserting the reactor into an electric tubular furnace (Lenton) equipped with a PID-type controller. Any unburned mixture components were condensed. A constant fraction (20 l(STP)/h) of the resulting gaseous flow rate was dried by a $CaCl_2$ trap and analyzed in a Fisher-Rosemount NGA2000 continuous analyzer to measure CO , CO_2 and O_2 concentrations (CO and CO_2 by infrared detectors; O_2 by a paramagnetic detector).

Table 1 summarizes the composition of the azeotropic and high-boiling-point mixtures as measured by gas chromatography (GC) analysis. Accordingly, the azeotropic mixture is constituted mainly by ethyl acetate and ethanol, whereas n-propyl acetate is the main constituent of the high-boiling-point mixture, which also contains a significant fraction of ethyl acetate.

All catalytic tests were run under fuel-lean conditions (i.e., fuel equivalence ratio, ϕ , lower than unity).

Table 1. Composition of azeotropic and high-boiling-point mixtures tested in this work

compound	azeotropic, wt%	high-boiling-point, wt%
cyclohexane	0.35	-
acetone	0.61	-
ethyl acetate	52.88	8.15
isopropyl acetate	0.04	0.43
isopropanol	1.39	-
ethanol	44.29	0.04
n-propyl acetate	0.38	86.97
n-propanol	0.05	0.20
acetic acid	-	2.92
1-methoxy 2-propanol	-	0.57
1-methoxy propyl acetate	-	0.53

2 RESULTS AND DISCUSSION

2.1 Steady-state behavior

In Figure 1, the results obtained when burning the azeotropic mixture are shown. In particular, the fuel conversion and the catalyst temperature (i.e., the temperature measured in the center of the central channel of the monolith) are plotted versus the flow rate as obtained at the steady state.

The fuel conversion is equal to 100% independently of the flow rate, whereas the catalyst temperature steadily increases with increasing flow rate. This latter trend is mainly due to the higher thermal power developed at higher flow rates. Nevertheless, the difference in temperature between catalyst and furnace is relatively low at the low value of ϕ explored (i.e., under conditions of large dilution for the gaseous mixture).

It is worth saying that, under the adopted reaction conditions, CO concentration in the burned mixture is negligible. According to our previous results [3], this is due to the fast reaction rate of CO oxidation over the $Pt/LaMnO_3$ catalyst employed.

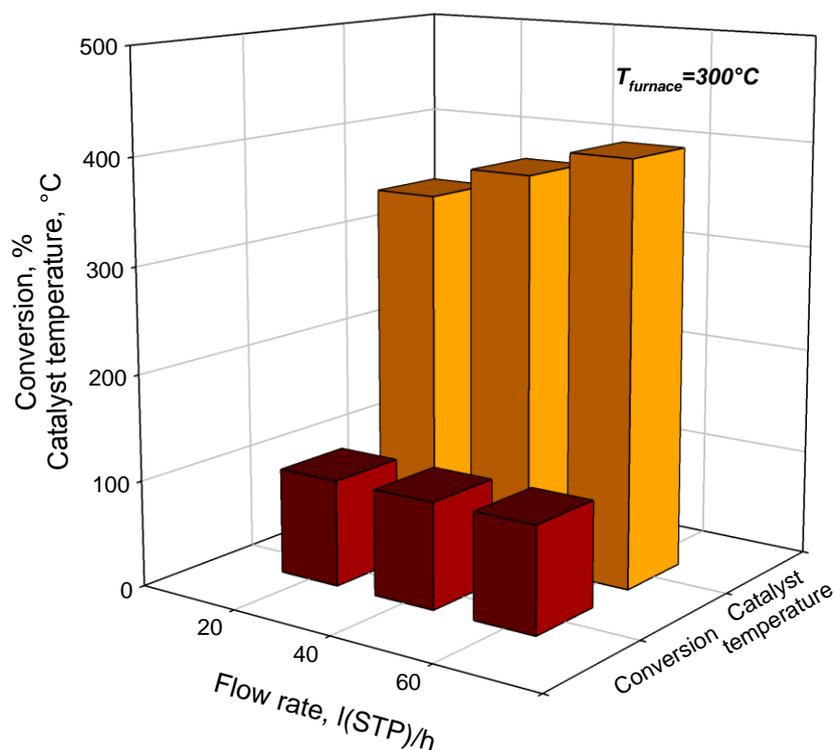


Fig. 1. Fuel conversion and catalyst temperature versus flow rate. $T_{\text{furnace}} = 300^{\circ}\text{C}$; $\phi = 0.23$; fuel = azeotropic mixture.

The results of Figure 1 were obtained at $\phi = 0.23$. When increasing ϕ to 0.4 (while keeping the furnace temperature and the flow rate equal to 300°C and 40 l(STP)/h , respectively), it has been found that the fuel conversion is still complete, whereas the catalyst temperature increases from 375°C ($\phi = 0.23$) up to about 490°C . The higher difference in temperature between catalyst and furnace suggests that the reactor works under self-sustained conditions.

2.2 Ignition behavior

As already seen when feeding other fuels [3,6], it is interesting to investigate the ignition behavior of the catalytic combustor. To this end, experiments were carried out by increasing the furnace temperature and, once ignition has been attained, by decreasing that temperature. Both azeotropic and high-boiling-point mixtures were tested. In Figure 2, the catalyst temperature is plotted versus the furnace temperature as measured during the two phases of heating and cooling for both mixtures.

Let us focus on the heating branch. In the case of azeotropic mixture, at furnace temperatures lower than 150°C , the difference in temperature between catalyst and furnace and, thus, the fuel conversion are negligible. At around 150°C , ignition occurs: the catalyst temperature significantly increases, whereas complete fuel conversion is attained. In the case of high-boiling-point mixture, the same qualitative behavior is observed. The only difference is quantitative. Indeed, as a result of overall lower reactivity, ignition occurs at higher temperature ($\sim 240^{\circ}\text{C}$).

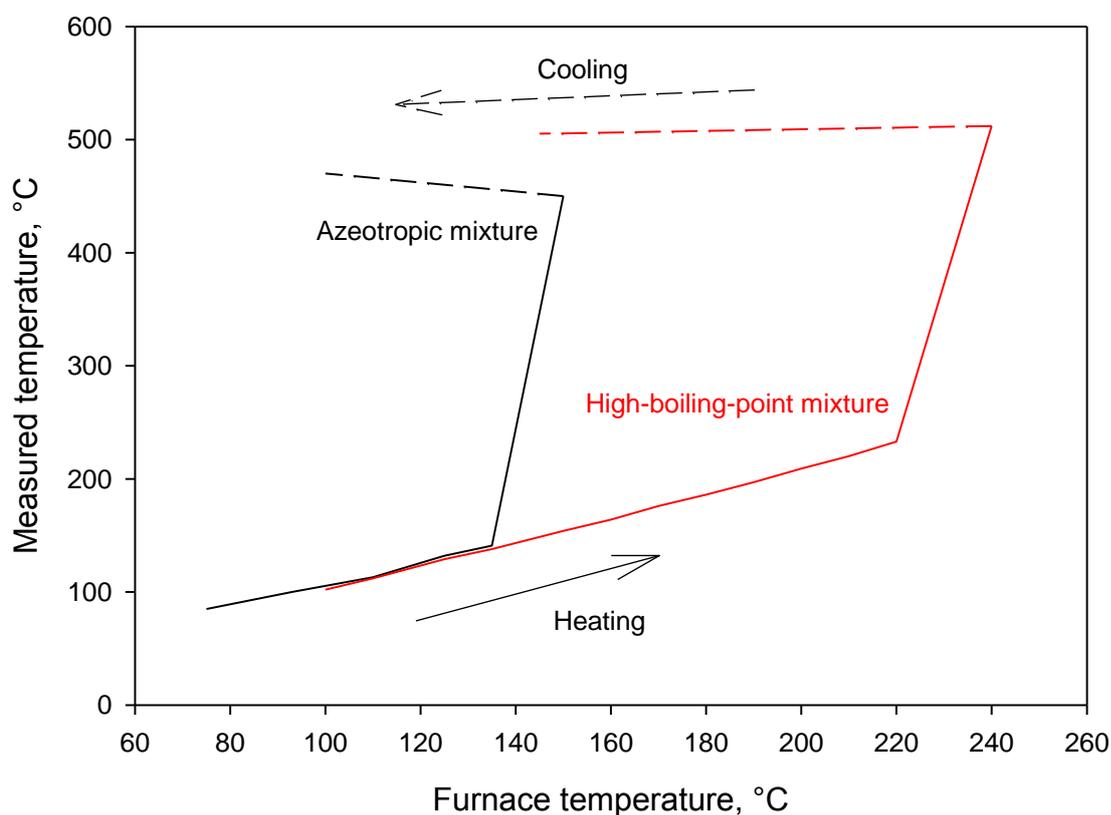


Fig. 2. Catalyst temperature versus furnace temperature for both azeotropic mixture ($\phi = 0.40$) and high-boiling-point mixture ($\phi = 0.47$). Solid lines: heating branch; dashed lines: cooling branch. Flow rate = 60 l(STP)/h.

Figure 3 illustrates the time evolution of the ignition process for both azeotropic and high-boiling-point mixtures, in terms of histories of CO and CO₂ concentration and catalyst temperature.

When ignition occurs, both CO₂ concentration and catalyst temperature abruptly increase. The catalyst temperature profile exhibits a peak that, as described in Ref. [6], is due to the presence of a traveling heat wave associated with a moving reaction front. In the case of azeotropic mixture, the maximum temperature is $\sim 680^\circ\text{C}$. In the case of high-boiling-point mixture, it is higher ($\sim 850^\circ\text{C}$) due to the higher value of ϕ (0.47 versus 0.4). On the other hand, the maximum operating temperature to prevent Pt volatilization is 1000°C . Thus, even in the case of high-boiling-point mixture, temperatures causing thermal deactivation of the Pt/LaMnO₃ catalyst are avoided.

It should be underlined that, before ignition, a low but significant presence of CO has been detected (about 80 ppm in the case of azeotropic mixture; about 150 ppm in the case of high-boiling-point mixture). However, when ignition occurs, CO concentration falls down to zero.

Starting from ignited conditions, the furnace temperature was reduced (cooling branch in Figure 2). Under the reaction conditions investigated, quenching does not occur: the fuel conversion is still complete, whereas the temperature is significantly higher than the furnace temperature [3]. In the case of azeotropic mixture, the catalyst temperature slightly increases, thus suggesting that a downstream shift of the reaction front occurs. Conversely, in the case of high-boiling-point mixture, the catalyst temperature remains substantially constant, thus suggesting that the reaction front is still anchored at the entrance of the catalytic monolith. This means that the high-boiling-point mixture is somewhat more resistant to quenching than the azeotropic mixture.

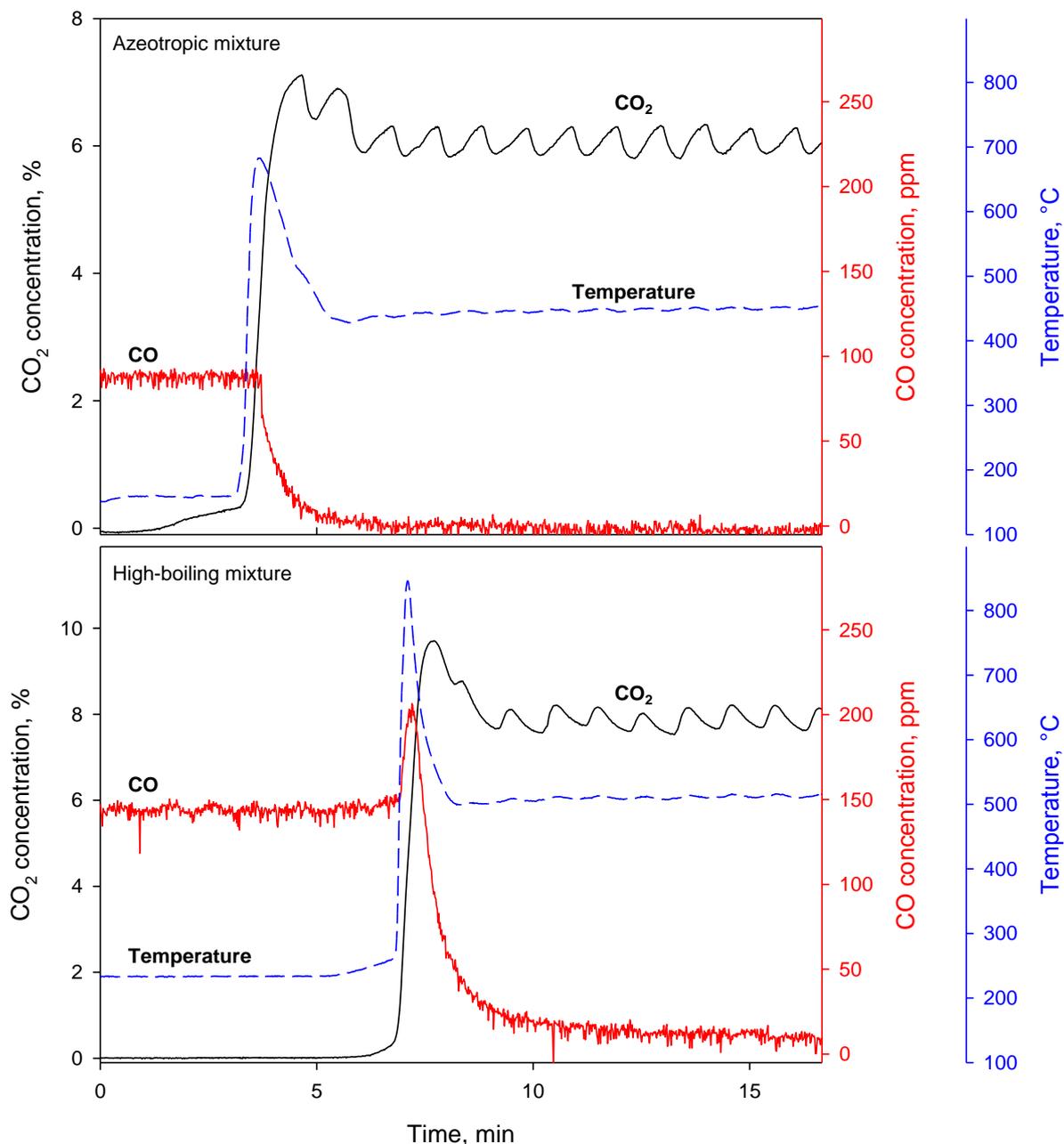


Fig. 3. CO and CO₂ concentration and catalyst temperature versus time for both azeotropic mixture ($\phi = 0.40$) and high-boiling-point mixture ($\phi = 0.47$). Flow rate = 60 l(STP)/h.

3 SUMMARY AND CONCLUSIONS

In this work, we have proposed the catalytic combustion of the waste streams coming from the solvent recovery stage of packaging industries as an alternative approach to their disposal. To this end, a low-cost perovskite-based catalyst, doped with a low amount of noble metal (Pt) and supported over a monolithic reactor, was used to run lab-scale combustion tests for two waste streams, namely the azeotropic stream and the high-boiling-point stream, coming from the distillation plant of the company Icimendue (www.icimen.com). All catalytic tests were performed under fuel-lean conditions.

Results have shown that, due to the good catalyst activity, ignition can be obtained at relatively low temperatures. The ignition temperature is dependent on the composition of the fuel mixtures tested: the azeotropic mixture, which is constituted mainly by ethyl acetate and ethanol, is more reactive

than the high-boiling-point mixture, the main constituent of which is n-propyl acetate, thus exhibiting lower ignition temperature ($\sim 680^{\circ}\text{C}$ versus $\sim 850^{\circ}\text{C}$ - under the reaction conditions explored in this work). On the other hand, once ignition has been attained, regardless of the fuel composition, stable operation can be achieved at very low pre-heating temperatures. The catalyst temperature and the exhaust gas temperature both increase with increasing flow rate and equivalence ratio. However, the catalyst temperature is always lower than 1000°C , thus preventing Pt volatilization (and preserving the catalyst durability). Furthermore, the tunability of the exhaust gas temperature can be exploited to fulfill the features of devices that can be coupled with the catalytic burner to convert thermal power into electric power, thus improving the overall sustainability of the process.

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