

Forced Unsteady State Operation of a Catalytic Converter during Cold Start-up for Oxidizing CO Over Pt/ γ -Al₂O₃ Catalyst

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Abstract CO oxidation in the catalytic converter hasn't showed best performance particularly during cold start-up, since the catalyst is not active during this period. The purpose of this experiment was to develop the forced unsteady state operation procedure of CO oxidation using 0.05%-w Pt/ γ -Al₂O₃ and space velocity of 0.406 mmol/s/gram. The catalytic converter was gradually ramped-up, while introducing the feed gas containing CO in the air. The feed gas was modulated following a square wave model with switching time variation at 3, 6, 15, and 30 s and various operation modes. To gain the intrinsic reaction rate, the external mass transfer criterion was determined. Ramping-up the temperature from 50 until 150°C increased the CO conversion with different profiles between steady state and dynamic flow rate. The dynamic system with modulated CO feed flow gave lower light-off temperature and higher average CO conversion than the steady state system which gave light off temperature 115°C and average CO conversion of 48.86%. The switching time of 3 s gave highest average CO conversion during ramping-up, which was 79.35%. Meanwhile the dynamic operation system with modulated feed flow gave higher light-off temperature and lower average CO conversion than steady state system.

1 Introduction

Environmental sustainability has been used as an indicator and a major concern of countries in the world nowadays as the huge increase of exhaust gas emission from various chemical industries and automotive vehicles (Shelef and McCabe, 2000). The exhaust gas emissions from the automotive vehicle contain some types of substances that are harmful to human health and the environment, such as unconverted hydrocarbon (HC), carbon monoxide (CO), sulfur oxides (SO_x), and nitrogen oxides (NO_x) (Patel and Patel, 2012). Carbon monoxide is gas with high toxicity and highly harmful to human health such as circulatory system disorders (cardiovascular), nervous system (neurobehavioral effects), unconsciousness, and death as reported by Raub *et al.* (2000). In densely populated countries, the increase in CO levels by an average of 1 mg/m³ in proportion to the increase in the number of deaths amounted to 2.89% and the total number of deaths from cardiovascular disorders amounted to 4.17% according to Chen *et al.* (2011). CO also contributes indirectly to environmental damage such as global warming and ozone depletion Badr and Probert (1995). It was also reported that 55-60% of CO gas emissions is caused by human activity particularly emitted from automotive vehicles (Kašpar *et al.*, 2003).

The rate of CO emissions caused by human activity increased rapidly since the development of the industry. The increase of the emission rate is typically inline to the increase of the population growth and economy according to Badr and Probert (1995). A number of studies regarding the catalytic CO oxidation in a fixed bed reactor over noble metal catalyst have been conducted (Engel and Ertl, 1979, Nibbelke *et al.*, 1997). Koltsakis *et al.* (1997) investigated a two-dimensional model of catalytic converter, featuring a number of innovations regarding the catalyst transient behavior over time and the reaction kinetics. The oxygen storage submodel showed most important parameter to influence the catalytic converter performance accounting for the redox and temperature dependence of the adsorbed oxygen availability under transient operation. The improved adsorbed oxygen concentration on catalyst site was also found by Budhi *et al.* (2004) and Budhi (2005) in the case dynamic reactor with composition modulation of the feed gas. As a result, the increased conversion can be achieved when proper switching time can be determined. Arvajova *et al.* (2018) investigated the influence of dual CO light-off on Pt/Al₂O₃ catalyst in the presence of propylene where the conversion of CO might decrease in the certain temperature range. Other observation was on the presence of NO and lower oxygen concentration where its effect

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was exaggerated (Scholz, 2006). The development of the global kinetic model for the oxidation of CO and hydrocarbon mixtures became an important trend. The model was validated with the experiments and captured the light-off behavior with varying Pt/Pd. It was found that at Pt/Pd ratio of 1:1 was optimal. Other model of Pt/Pd ratio studied for low temperature combustion of engine. It was found that a single hydrocarbon species could not be used to determine the best catalyst for exhaust gas abatement. The improvement of catalytic reaction can be increased by changing the flow rate or concentration. In the case of CO oxidation, only oxygen (0.5%-v in He) flowed to the reactor during the first cycle, while only CO (0.5%-v in He) flowed to the reactor during the second cycle. This mode was periodically repeated at every 10 s and the reactor performance was observed over time (Nievergeld, 1998). This result showed better reactor performance when compared to the steady state operation (Balenovic, 2002). Barshad and Gulari (1985) reported the formation of intermediate compound, in which the active site occupied by oxygen could still adsorbed CO and increased the reaction. In this study, the oxidation of CO over 0.05%-w Pt/ γ -Al₂O₃ in a fixed bed reactor with dynamic feed gas and ramping up reaction temperature during start-up operation was investigated. The results were compared between operations under steady state as base case and unsteady state as a novel start-up procedure.

2 Material and Method

2.1 Material

Materials used in this experiment were Pt/ γ -Al₂O₃ catalyst, silica gel, soap, CO, air, H₂, and N₂. The 0.05%-w Pt/ γ -Al₂O₃ with particle diameter range of 0.595–0.707 mm and bed porosity of 0.4 used in this experiment was a commercial catalyst. The catalyst weight loaded into the reactor was varied and in the upstream bed there was also loaded inert material to create a well-developed flow regime before entering the catalyst section. The initial catalyst activity should be maintained by performing catalyst activation before running the oxidation of CO. Silica gel was used to adsorb moisture contained in the feed gasses.

2.2 Experimental setup

Figure 1(a) and Figure 1(b) present the arrangement of the experimental setup for catalytic oxidation of CO used in this study. It consists of the feed gas section, modulator section, reactor section, and gas analysis section. The modulator section was used to change the feed flowrate periodically as function of time with aim to create the forced unsteady state operation. The modulator section was equipped with an analog adjuster to set the time scale based on required switching time. The reactor section consists of sintered quartz glass reactor, heater, glass wool, and thermocouple. The reactor was placed inside tubular furnace, while the thermocouple was placed in the bottom part of the reactor to measure the temperature.

The preliminary experiment was required to determine the heater voltage for ramping-up reaction temperature. The temperature ramping-up was conducted to gradually in the reaction temperature from 50°C to 150°C for 10 minutes by varying the heater voltage.

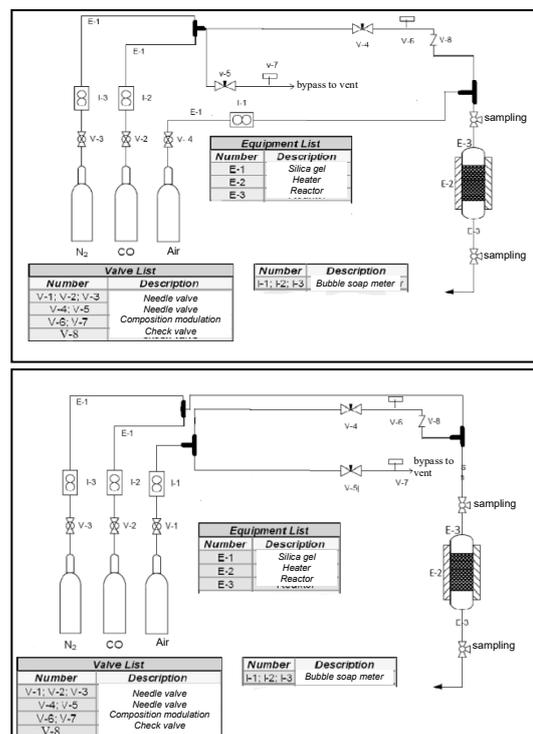


Figure 1. Experimental setup of mode 1 (top), mode 2 (below).

In this experiment, the influence of external mass transfer was determined to by varying the amount of catalyst and the feed gas flowrate. Based on the results, it should be indicated by plotting the relation between CO conversion and ratio of flowrate to catalyst weight. In addition, the main experiment was carried out by ramping-up the reaction temperature under steady and unsteady state operation. The steady state condition was used as a base case for comparison to unsteady state condition. Moreover, the steady state experiment was also used to determine the time required to reach the steady state condition. For unsteady state condition, there were 2 operation modes consisting of constant air flowrate (modulated mixed gas at 0 or 15 ml/s) and constant mixed gas flowrate (modulated air at 0 or 15 ml/s). Each mode used different switching times, i.e. 3, 6, 15, and 30 s. The concentrations of CO in the feed and product streams were measured using combustion gas detection system (Bacharach PCA-3) in real time.

2.3 Catalyst activation

The catalyst activation should be maintained the same at the beginning for every run in order to clean the catalyst surface from any adsorbed impurities, particularly from the previous experiment. According to Campman (1996), the catalyst cleaning can be accomplished by heating the catalyst up to 473 K, while flowing N₂ for 1 h. The process is continued by flowing the mixture of H₂ and N₂ for 2 h.

This step aims to reduce the catalyst and remove all adsorbed impurities from the catalyst surface. After catalyst reduction, the reactor temperature is lowered to reaction temperature while keeping the N₂ flow passing through the reactor to avoid other gases adsorbed over the catalyst surface.

2.4 Kinetic regime determination

This state aims to determine the amount of catalyst and minimum flow rate so that the reaction of CO is only affected by the kinetic, without external mass transfer limitation. The experiment was conducted at constant feed gas flow rate over catalyst weight ratio (F/W) to keep similar residence time. The conversion of CO was measured and plotted over feed gas flow rate. For internal mass transfer limitation, the catalyst diameter was calculated according to Campman (1996), and this experiment was carried by optimizing the catalyst diameter, but the relative pressure drop along the catalyst bed was still less than 3%.

3 Results and Discussion

3.1 Line-out procedure

At the beginning of the reaction after the feed gas was introduced into the catalyst bed, the reactants were adsorbed over the catalyst surface. It was found that the catalyst exhibited a higher activity at initial start-up. The mechanisms of adsorption, surface reaction, and desorption commenced and changes in conversion was observed as function of time as shown in Figure 1. The steady state condition was achieved after approximately 180 min. Therefore, to minimize the reversible start-up effects on experimental results, prior to kinetic measurements, a line-out procedure had to be carried out (Campman, 1996).

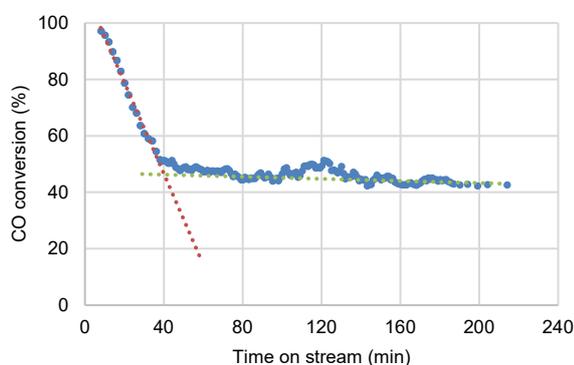


Figure 2. Line-out procedure of the catalytic converter.

3.2 Steady state condition

The feed gas containing lean CO was reacted with air at 142°C under steady state condition. The time required to reach a constant conversion is called steady state time. The steady state times for feed flow in the range of 0.2 – 0.8 mmol/s are shown in the Figure 3. As shown in Figure

3, the steady state condition was reached faster at higher feed flow rate under the same space velocity. It was induced by adsorption equilibrium that had to be obtained to carry on the system towards steady state condition. During low flow rate, the feed gas was less turbulence and it caused the mixing in the radial direction along the catalyst bed was less perfect. The collision probability of adsorbent particles with adsorbate particles did ease with reducing feed flow rate. When the adsorption was about to reach the equilibrium, the oxidation of CO on the catalyst surface and CO₂ desorption shifted the equilibrium. As the results, steady state condition was more slowly reached. Based on Figure 3, the feed flow rate affected the steady state time exponentially. It could be forecasted that the steady state time was not influenced by the feed flow rate at high flow rate. It showed that mass transfer resistance for adsorption process was neglected.

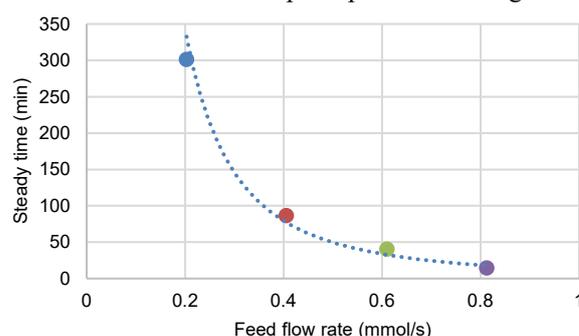


Figure 3. Time required to reach the steady state condition for F/W 0.4 mmol/s/gram catalyst.

Next to steady state time differences, the flow rate variations produced different steady state CO conversion. When the CO conversion was only affected by intrinsic reaction rate, the steady state CO conversion should be determined by residence time in the reactor. The differences between observed conversion proved the existing of regime where the external mass transfer affected the reaction rate and regime where the reaction rate was independent against the mass transfer. Figure 4 shows the CO steady state conversion for different feed flow rate variations. The minimum feed flow rate to diminish the external mass transfer effect for the reactor performance was 0.6 mmol/s.

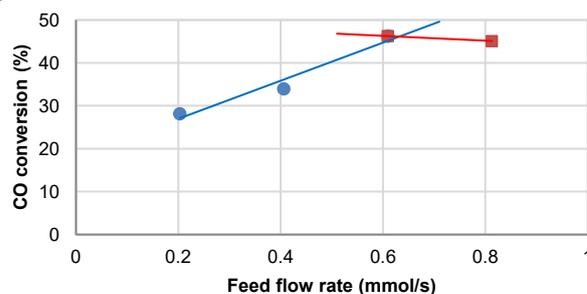


Figure 4. Steady state CO conversion over flow rate.

3.3 CO oxidation with temperature ramping-up

CO oxidation was performed in the temperature ramping-up from 50-150°C within 10 min, which was assumed as the time required by the catalytic converter to reach hot run condition. The CO conversion profile against the time is showed in the Figure 5. This data was obtained at constant feed flow rate (0.6 mmol/s) where the external mass transfer was not found.

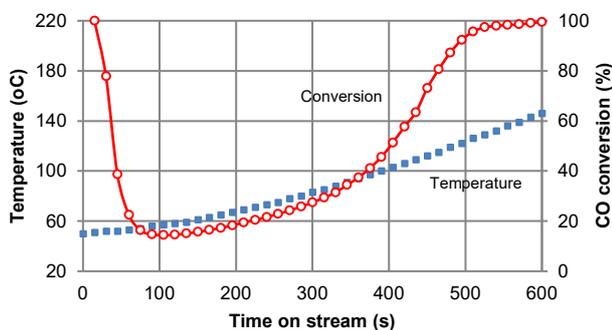


Figure 5. Ramping up temperature and CO conversion as function of time: F/W 0.4 mmol/s/gram.

3.4 Modulated mixed feed gas

The CO conversion profiles against time in the dynamic operation with switching time variations throughout ramping-up from 50°C to 150°C are showed in the Figure 6 (a) – (d). The difference between the CO conversion profiles as the results of dynamic operation was caused by time response of reactors towards switching time. At lower switching time, the reaction system was not able to respond the change that occurred during dynamic operation. As consequences, the recorded behavior of reactor would resemble the operation with constant feed flow. At switching time of 3 s, the reactor indicated the sliding regime, which approached the behavior of constant feed flow (without feed modulation). Starting at the switching time of 6 s, the reactor showed the dynamic regimes, while further switching time induced the reactor to reach the quasi-steady state. This phenomenon indicated that the response time of the reactor occurred between 15 and 30 s. Increasing and decreasing the CO conversion as function of time related to the feed flow. When the mixed gas did not flow, the catalyst surface would lack of CO and the O₂ would saturate the empty site of catalyst. This period was corresponding to the sharp rise of CO conversion. When CO flowed again, a part of CO could be hardly adsorbed over the catalyst surface at the beginning due to the saturation of O₂. On the other hands, high feed flow rate also made CO have no time to react. As a consequence, a sharp drop CO conversion occurred.

3.5 Modulated air flow rate

Conversion profiles against time in dynamic operation with switching time variations throughout ramping-up from 50°C to 150°C are shown in the Figure 7 (a) – (d). The modulated pressured air gave the similar results with

the modulated mixed gas experiment. The switching time of 3 and 6 s didn't show the oscillation pattern, while for 15 and 30 s showed the oscillation pattern obviously. There were two parameters used to evaluate the performance of catalytic converter, which were light-off temperature and average conversion. In this research, light-off temperature (T_{75}) was defined as the temperature resulting 75% conversion.

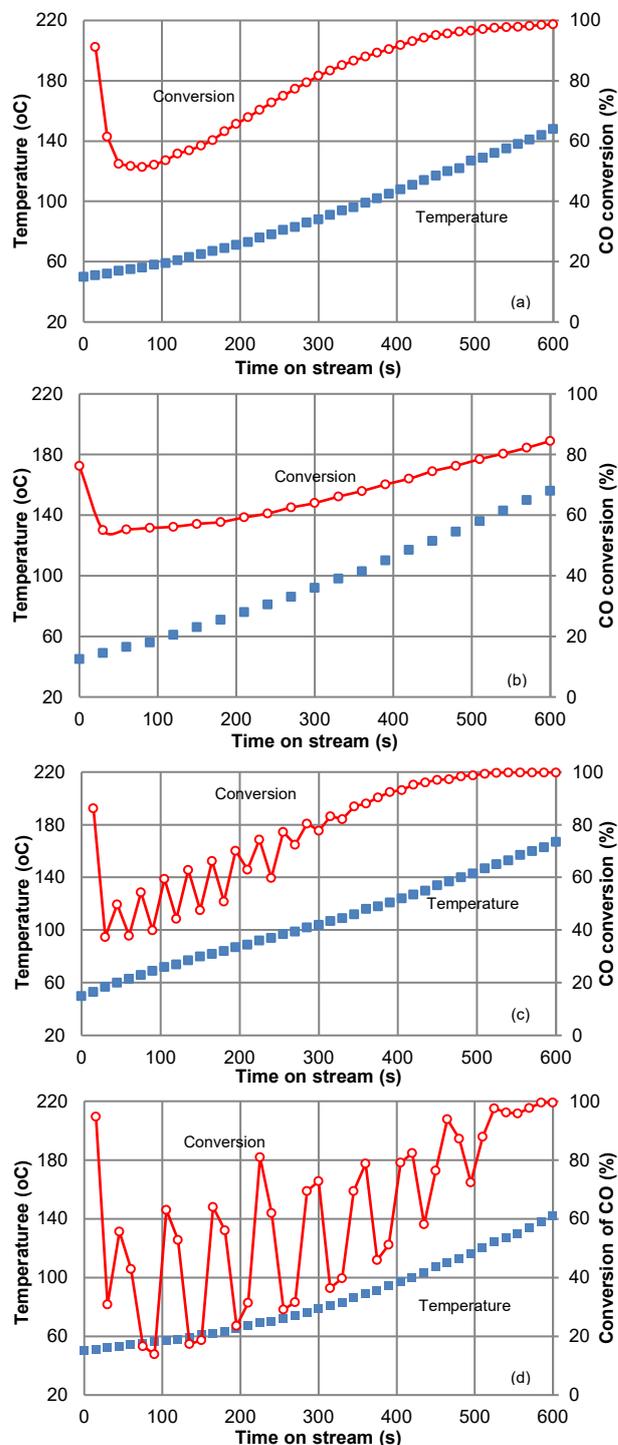


Figure 6. Temperature and CO conversion as function of time with air flow rate 0.325 mmol/s and mixed gas feed flow rate 0.650 mmol/s modulated with switching time: (a) 3 s, (b) 6 s, (c) 15 s, and (d) 30 s.

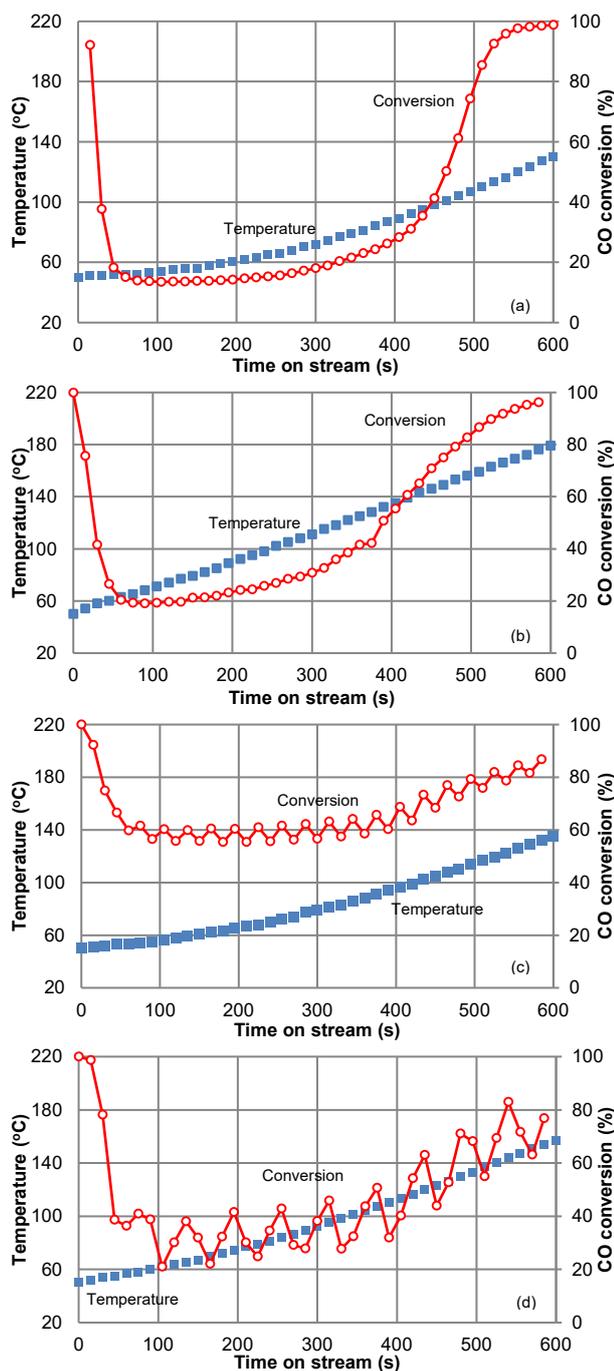


Figure 7. Temperature and CO conversion as function of time on stream (F/W 0.4 mmol/s/gram) with mixed feed gas flow rate of 0.325 mmol/s and modulated air flow rate 0.650 mmol/s with switching time: (a) 3 s, (b) 6 s, (c) 15 s, and (d) 30 s

The CO emission to the environment throughout the ramping-up process was predicted to have low value of its T_{75} . In this research, the constant feeding flow method had light-off temperature of 115°C. The modulation of mixed gas feed did tend to lower its light-off temperature, except for 6 s switching time. The modulation of air feed increased the value of light-off temperature, except for 3 s switching time. This phenomenon occurred due to the difference oxygen availability in the active site of catalyst during the reaction. There would be the period where the air feed flow rate was not fed to the system when we were

running the pressured air modulation variation. The conversion was low because of the active site filled by low oxygen concentration. Since the differences of the conversion profile against the temperature between steady and dynamic operation, low light-off temperature did not guarantee to produce high average conversion.

The modulation of mixed gas feed would always give higher CO average conversion than modulation of pressured air feed for all switching time variations. It also induced higher CO conversion than steady feed flow operation. This forecast did correspond with the light-off temperature which was lower. In 6 seconds switching time, even its light-off temperature was higher, the average conversion resulted was still high. This was caused by the concentration of oxygen in the active site of catalyst was still high during modulation of mixed gas feed operation. For Pt catalyst, CO had adsorption constant which was higher than oxygen. If CO accumulation was allowed in the catalyst surface, the presence of CO will be a reaction inhibitor. By allowing oxygen to be adsorbed in the beginning, the modulation of mixed gas feed would isolate the reaction mechanism at the stage with high reaction rate.

Figure 8 shows the achieved reactor temperature as function of CO conversion at various switching time. The steady state condition is also presented as comparison. The switching times of 6 and 30 s resulted in higher temperature to achieve certain CO conversion compared to steady state. The switching time of 3 s could reach lower temperature than steady state, while for 15 s switching time, lower conversion was related to lower temperature. The dynamic operation during cold start-up, in principle, might induce the complicated phenomena at macro and microscales of reactor, depending of the switching time applied. The amount of adsorbed component on catalyst surface induced by the dynamic system would have correlation to reaction rate at every temperature, which ramped up during cold start up.

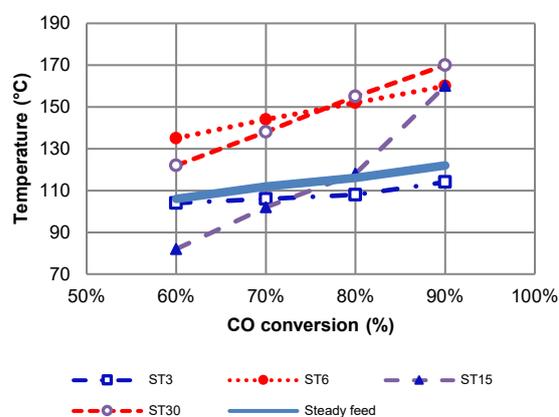


Figure 8. Achieved temperature and CO conversion at various switching times for mixed feed gas mode

4 Conclusion

The oxidation of CO over Pt/ γ -Al₂O₃ catalyst in a fixed bed reactor has been performed. Forced unsteady state operation was applied to improve the catalytic

performance. The modulation of mixed feed gas would tend to give lower light-off temperature than the steady feed flow with light-off temperature of 115°C. The modulation of pressured air had higher light-off temperature. The modulation of mixed gas feed gave higher average CO conversion than steady feed flow. The modulation of pressured air gave lower average CO conversion, except for 15 s switching time. The modulation of mixed gas feed with 3 seconds switching time gave the highest average CO conversion 79.35%, while the steady operation only gave 48.86% average CO conversion. The modulation of mixed feed gas would be much interesting to be applied due to better reactor performance to reduce the CO in the exhaust gas emission.

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