# A Laboratory Study of Low-Temperature CO Removal from Mobile Exhaust Gas Using In-Plasma Catalysis



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#### Abstract

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The combination of nonthermal plasma (NTP) with catalytic methods has been shown to improve catalyst light-off temperature via reactions among plasma discharge products and by-products. Thus, NTP may improve selectivity, process, and removal efficiency. In this study, NTP was combined with a catalytic film of mixed metal oxides (ceria-zirconia-gamma alumina layer) in the discharge zone to investigate low-temperature CO removal. Three different reactors having identical geometries were used: a plasma reactor, a catalytic reactor, and a hybrid plasma-catalytic reactor. The CO removal efficiency of 36.5% was achieved using hybrid plasma-catalytic reactor at 80 °C with 860 J/lit. The temperature and flow rate were found to have significant impacts (*P-value*  $\leq 0.05$ ), which is unexpected due to the key role of hydroxyl and active radicals induced by plasma discharge. Calculated synergy factor of about 2 signals call for further study on the hybrid properties of catalytic efficiency and plasma physics for optimal CO removal.

Keywords Carbon monoxide  $\cdot$  Conversion  $\cdot$  Plasma  $\cdot$  IPC  $\cdot$  SIE  $\cdot$  Synergy factor

# **1** Introduction

Plasma as an ionization bed avoids barriers for the activation energy of primarily exothermic reactions and thus acts as common catalysts. Catalytic methods to the pollutant concentrations lower than 1000 ppm are found to be not beneficial from economic aspect. Also, the main barriers in using catalytic methods, including catalyst deactivation and poor performance under water vapor and sulfur conditions, limited those techniques. Plasma catalysis is applied not only in environmental control process but also in conversion of organic flue, hydrogen production, and other applied technologies of plasma chemistry [1]. The air pollution treatment using plasmacatalytic hybrid process is known as an acceptable approach due to a high efficiency and economical effectiveness. The

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high distribution of active species, reduction of energy consumption, increase in catalytic activity and selectivity, as well as low sensitivity to poison are the main advantages of plasma-catalyst reactors. In activated reactions by plasma, intermediate species or "by- 40 products" (such as ions, energetic electrons, radicals) induced by plasma discharges decrease the activation energy of chemical reactions found to be useful in low-temperature activation of catalyst, and this prevents the poisonous condition in active sites and improves selectivity and high-energy efficiency [1-8]. One method of plasma-catalyst combination is the positioning of catalyst in the discharge region of plasma reactor known as in-plasma catalysis (IPC) technique [6, 9-11] by which the plasma and catalysis occur simultaneously and have interactions with each other. The combinationa of plasma and catalyst presents a synergistic. This effect is generated by various mechanisms of performance promotion [9].

The technology of IPC possesses energy saving which seems to be important to the treatment of exhaust gases from stationary and mobile sources.

The main benefit of NTP is its high chemical efficiency. Higher gas temperature changes reaction kinetics known as the ozone dissociation agent. Also, it is useful in hydrocarbon destruction. So, finding the desired temperature range of inlet gas stream is a fundamental factor in the acceleration of chemical reactions particularly in redox reactions. One way of chemical

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activity in NTP is ozone generation. It is a two-stage process; the generation of free oxygen radicals increases with inelastic collision of electrons (R1) and the interaction of free radicals with each other results in  $O_3$  generation (R2) [5].

$$O_2 + e \rightarrow O^+ + O + 2e \tag{R1}$$

$$O_{2} + e \rightarrow O + O + e$$

$$O_{2} + e \rightarrow O - +O$$

$$O + O_{2} + M \rightarrow O_{3} + M$$
(R2)

where M is equal to  $O_2$  or  $N_2$ .

DBD is the most known technique of ozone generation. The role of ozone injection in heterogeneous oxidation and removal efficiency of CO is shown by Kim et.al (2014) and Kirkpatrick et.al (2011) [12, 13]. Hydroxyl radicals and ions were the other two important components of active plasma contributing to CO oxidation reactions [14]. Radicals and other reaction by-products such as O, OH,  $H_2O$ ,  $H_2$ , and  $H_2O_2$  take part in some fast reactions (R3 to R8):

 $H + O_2 \leftrightarrow OH + O \tag{R3}$ 

$$O + H_2 \leftrightarrow OH + H$$
 (R4)

 $OH + H_2 \leftrightarrow H + H_2 O$  (R5)

$$O + H_2 O \leftrightarrow OH + OH$$
 (R6)

$$HO_2OH \leftrightarrow H_2O + O_2 +$$
(R7)

$$H_2O_2 + O_2 \leftrightarrow HO_2 + HO_2 \tag{R8}$$

Due to the high molar fraction of  $N_2$ , the air ionization in NTP discharges results in the generation of high quantity of  $N_2^+$  ions (considering of other positive ions). Then, low ionization potential and high dipole movement of water molecules may lead to fast ion exchange (R9):

$$N_2^+ + H_2O \rightarrow N_2 + H_2O^+, k(300^\circ k)$$
  
= 2.2 × 10<sup>-9</sup> cm<sup>3</sup>/sec (R9)

Overall, ionization process can be concentrated on the formation of water ions. However, the water molar fraction of air is low. Then, induced water ions react with neutral water molecules in a relatively fast ion-molecule reaction (R10):

$$\begin{split} H_2 O^+ + H_2 O &\rightarrow H_3 O^+ + O H^o, k(350k) \\ &= 0.510^{(-9)} \text{cm}^3/\text{seck}, \\ \Delta H &= -12 \text{ kcal/mol}, \end{split} \tag{R10}$$

Thus, the generation of  $H_3O^+$  ions and OH radicals can be predicted, which in turn result in the acidic behavior of NTP. The selective generation of OH radicals in NTP discharges is the reason for being used in air cleaning from various pollutants [1]. The prominent reaction in CO oxidation by hydrocarbon burning is [14].

$$CO + OH^{\circ} \leftrightarrow CO_{2} + H^{\circ}, \quad FRC_{(m^{3}mol^{-1}k^{-1}s^{-1})}$$
$$= 4.4T^{1.5}\exp(+373/T)$$
(R11)

However, at low temperatures, Forward Rate Constant

 $(FRC)_{\left(m^{3}mol^{-1}k^{-1}s^{-1}\right)}$  of CO+OH reaction is not dependent on temperature. Temperature dependence of reaction results from temperature effects on OH concentration of equilibrium. So, gas temperature is found to be critical in the generation speed of OH radicals [14]. Thus, in the present study, gas temperature was chosen as a complementary parameter to optimize energy consumption and also to keep hydroxyl equilibrium for inelastic collisions. The presence of reducing gas to accelerate chemical reactions was another complementary parameter. It (propane) has an important role in the chemical reaction rates of reactants in gas mixtures. In the presence of hydrocarbons in gas stream, OH radical was found to be prominent radical that consumes unburned hydrocarbons. HO2 radical from intermediate oxidation reactions of hydrocarbons oxidize NO to NO2. Also, OH° radical preferably reacts with unburned hydrocarbons, and thus oxidation of NO and NO2 to nitric acids and nitrous was minimized [15]. This subject results in the increase of process selectivity to CO oxidation and the reduced generation of harmful byproducts. Plasma significantly decreases the partial pressure of unburned hydrocarbons. This may be due to the fact that propane is burned significantly with plasma activation. The energy density of plasma is a key factor affecting UHCs, CO, NO<sub>x</sub>, and generated intermediate species of combustion [16]. In the presence of hydrocarbons (e.g., ethane, propene, propane), radicals of OH and proxy are the dominant oxidizers, and required energy for oxidation of NO molecule can be decreased. However, proxy radicals during oxidation cycle are converted to CO<sub>2</sub> and H<sub>2</sub>O molecules and also provide the participation conditions of radical chain reaction with alkyl hydroperoxide radicals R-OOH. In case of unsaturated hydrocarbons, adding extra radical results in the oxidation of radical chain reaction of hydrocarbon polymerization [17].

The presence of  $N_2$  as balanced gas prevents the dissociation of produced  $CO_2$  due to boomerang resonance [1].

The main technical removal of carbon monoxide pollutant emitted from stationary and mobile sources at indoors and outdoors and based on plasma-combined catalyst which are supported by precious metals, in particular, PGM<sup>1</sup>, have been investigated by some researchers. In addition to the high cost of these catalysts, they have also performance limitation in low temperatures. In the present study, CO removal using plasma combined mixed metal oxide catalyst was investigated at low temperature.

<sup>&</sup>lt;sup>1</sup> Platinum group metals

Cerium was found as a good catalyst for CO Oxidation, which stores oxygen and then releases it to react with CO during rich conditions of temporary excitation. The addition of Ce to catalysts is related to its excellent properties including oxygen storage, improvement of light-off properties, better distribution of precious metal, resistance to sintering, NO reduction, and preferential oxidation of CO (PROX-CO) [15, 18]. The synergistic effect of alumina and solid solution of CeO<sub>2</sub>- ZrO<sub>2</sub> was highly attended by some researchers for the study of structure, texture, redox, thermal stability, and oxygen storage capacity (OSC) of alumina and Ce<sub>1-x</sub>- Zr<sub>x</sub>O<sub>2</sub> combination [19–21].

As we know, most of the unburned hydrocarbons and CO emissions are during cold phase or startup of mobile source, and the catalyst (PGMs catalysts) is inactive at these temperatures. In the present study, it is tried to improve removal efficiency by combining NTP with low cost mixed metal oxide as well as controlling test conditions with chemical considerations and the improvement of optimum consumption of radicals such as OH and  $O_3$  without ozone injection. In fact, the generated ozone by the NTP process will be consumed during chemical reactions.

### 2 Materials and Methods

In the present research, three types of reactors were applied. A coaxial nonthermal plasma reactor to CO removal using plasma alone, a catalytic reactor to CO treatment using catalyst alone, and a single stage plasma-catalytic reactor (plasma driven catalysis) to CO treatment consisting of; a catalytic mixed metal oxide film of ceria-zirconia-gamma alumina (CZA) which was coated with sol-gel dipping method used as catalyst in nonthermal plasma discharge zone, two inner and outer tubes from quartz (as catalyst film substrate) and Pyrex (as outer dielectric) with outer diameter of 4 and 10 mm respectively were applied as dielectric. Tungsten wire was used as cathode and copper foil as anode, and high-voltage AC power supply was applied to support strong electric field.

1-2. Preparation and Coating of Catalytic Film on Substrate Using Sol-Gel Dipping Method: About 0.062 mol of AlCl<sub>3</sub>.(6H<sub>2</sub>O) precursor was used to synthesize gamma alumina by sol-gel technique [22, 23], and commercial CeO<sub>2</sub> (0.006 mol) and ZrO<sub>2</sub> (0.02 mol) were applied to prepare the slurry of ceria and zirconium by means of a suspension method [24]. After preparing gamma alumina sol, the slurry of ceria and zirconium were added to gamma alumina sol under stirrer. Polyvinyl alcohol (PVA) which is stated as a surface stabilizing agent was added to keep the control of nanoparticle size and prevent the aggregation of particles [25–27]. This process is shown in Fig. 1. The quartz substrate applied as inner dielectric material (outer diameter of 4 mm) was heated before coating [28]. Dip coating process was done for coating of prepared CAZ sol [22]. The substrate was immersed with a speed of 3.5 cm/min, kept for 5 min, and then drawn out with the speed of 23.3 cm/min. After that, substrate was dried and then calcined at 700 °C with temperature rate of 7.5 °C/min. The morphological and quantitative analyses of coated catalytic film were analyzed using FE-SEM and EDS.

2-2. The Design of Experiment (DOE) The key points in the practical application of any chemical process in a specific plasma system are to find the proper region and optimum plasma parameters among the various inherent possibilities of nonequilibrium system [1, 29]. Dynamic sampling method was used to keep stable and precious gas mixture concentration (according to ASTM D5835). For an online reading of gas concentrations of CO, C<sub>3</sub>H<sub>8</sub>, and O<sub>2</sub>, Testo 350 was applied before and after reactor. Four temperature ranges of 23110 °C, three gas flow ranges of 0.63 l/min, and four C<sub>3</sub>H<sub>8</sub>/CO ranges of 0-0.1 were considered for gas mixture properties. Humidity and oxygen percent were kept fixed at %7 and %10, respectively. To best control of humidity under different temperature conditions, air circulation over silica gel bed (to decrease humidity for conditions that humidity was higher than 7%) and bubbling the gas stream through a water bath with a specific temperature (i.e., dual midget bubbler/ impinger system to increase humidity when humidity was lower than 7%) were used. Also, the different temperature conditions were considered, and the temperature of water in midget bubbler/impinger was changed based on the test temperatures (in the first midget bubbler, the temperature was set at higher than required temperature to oversaturated the gas. In the second impinger, the desired temperature was set and additional steam condensed). The main effects of factor interaction have been discussed from designated parameters of optimum removal efficiency [30].

#### 3 3-2. Specific Input Energy (SIE)

One of the most important issues of nonthermal plasma applications for the emission control objectives in industrial and exhaust gases of mobile sources is minimum energy consumption compared to competence technologies [5]. Therefore, SIE is an important parameter in the estimation of energy consumption and was calculated using the following formula [18, 31–33]:

$$SIE (J/L) = \frac{P (discharge power (W))}{Q (gas flow rate (L/s))}$$
(1)

Fig. 1 Preparation steps of stable

CZA sol using sol-gel technique



# 4 4-2. Removal Efficiency of CO

The conversion rate of CO (%) was determined by online reading of CO concentration at inlet and outlet of reactors. Then, it was calculated using the following formula [34–38]:

$$CO_{removal} = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}} \rightarrow 100\%$$
(2)

**5-2. Synergy Factor (S. F)** Nonthermal plasma could accelerate chemical reactions at low temperatures with the generation of active species of speedy electrons. If those species are able to increase more cycles of chemical transformations, then plasma high productivity will be able to combine with low-energy consumption of catalysts [39], and thereby microdischarges can be formed in catalyst porosity [5]. However, plasma generation in inner pores of catalyst is difficult due to the balance between Paschen minimum and pore size [40]. Based on the common definition of synergistic effect [41], if at the same conditions of tests the removal efficiency of hybrid reactor was greater than the sum of removal efficiency in individual reactors, there is a synergistic effect ([Plasma]+[Catalyst]<[Plasma-Catalysis]). That

definition is applied to determine the existence of a synergy effect. But, synergy effect may change under different test conditions, and it may be strong or weak depending on the conditions. In other words, synergy effect can be a function of different test conditions of temperature, space time, etc. The abovementioned relation does not explain the range of synergy effect as a quantitative manner. Thus, there was a need to define a synergy factor (as a quantitative value) which was varied for each test condition.

To explain the positive effects of NTP combination with a catalyst properly on removal efficiency, synergy factor coefficient was considered. This factor in the present study was calculated using the following formula [42]:

$$%C_{exp} = A + B - (AB/100)$$
  
SF = C<sub>obs</sub>/C<sub>exp</sub> (3)

where

SF=synergy factor  $C_{exp}(\%)$ = expected removal efficiency  $C_{obs}(\%)$  = the removal efficiency of hybrid reactor A= the removal efficiency of plasma reactor

B=the removal efficiency of catalytic reactor.



Fig. 2 EDS results of substrate coated by CZA catalytic film

Accordingly, if the calculated synergy factor (SF) is 1, the effect of plasma with catalyst interaction is additive, but if it is higher than 1, the interaction will be synergistic.

### 5 Results and Discussion

Carbon monoxide removal was tested using three types of reactors including a plasma alone, a catalytic alone, and an IPC reactor. The morphological and quantitative analyses of coated catalytic film are shown in Figs. 2 and 3.

The effects of some factors on removal efficiency were found significant based on the reactor type. Accordingly, the interaction of factors and related significance value are given in Table 1. Also, mean removal efficiency of CO in three types of tested reactors is shown in Figs. 4-6.

The results of CO removal using three types of techniques in three ranges of gas stream temperature revealed the synergy effect of combining plasma with the catalyst (Fig. 7).

|         | Line | Intensity | Frror | W%           | At%    |
|---------|------|-----------|-------|--------------|--------|
| Element | Line | (keV)     | (%)   | <b>vv</b> 70 | 111/0  |
| С       | Ka   | 0.0265    | 0.11  | 14.11        | 27.07  |
| 0       | Ka   | 0.2094    | 0.009 | 28.81        | 41.50  |
| Na      | Ka   | 0.0642    | 0.009 | 1.87         | 1.88   |
| Al      | Ka   | 0.0902    | 0.127 | 1.63         | 1.40   |
| Si      | Ka   | 1.816     | 0.127 | 30.66        | 25.15  |
| Cl      | Ka   | 0.0163    | 0.127 | 0.45         | 0.29   |
| Zr      | La   | 0.014     | 0.127 | 0.58         | 0.15   |
| Ce      | La   | 0.0025    | 0.005 | 0.33         | 0.05   |
| Au      | La   | 0.0133    | 0.004 | 21.56        | 2.52   |
| Total   |      |           |       | 100.00       | 100.00 |
|         |      |           |       |              |        |

Specific input energy in CO conversion using hybrid reactor shows the optimum performance of reactor for treatment of high flow rate (3 l/min) at lower energy consumption compared to other tested flow rates (0.6 and 1.4 l/min) (Fig. 8).

The effect of gas stream temperature on removal efficiency. In plasma alone reactor at room temperature, the absence of propane shows better removal efficiency, but with the presence of propane, increasing temperature improved removal efficiency significantly, and maximum mean conversion rate was achieved at 110 °C, 0.6 l/min, and C<sub>3</sub>H<sub>8</sub>/CO ratio of 0.05 (Fig. 4). This was due to propane decomposition at high partial temperature, generation of ions, and reactive radicals and so speed up chemical reactions of CO conversion. In hybrid reactor, the effect of temperature increase on removal efficiency of CO is conversable between two temperatures of 80 and 110 °C. During its increase up to 80 °C, removal efficiency was better at high flow rate (3 l/min). But, temperature above 80 °C gave better removal efficiency at the low flow rates (Fig. 6). Due to the increase in temperature from 50 to 80 °C, the generation of active species especially O and OH



Fig. 3 FE-SEM results of CZA film coated on quartz tube (A: cross section of quartz substrate coated by CZA catalytic film, B: SEM MAG = 5kx, view field: 41.5  $\mu$ m, C: SEM MAG = 50kx, view field:

4.15  $\mu$ m, D: diameter of CZA nanoparticles with SEM MAG = 350kx, view field: 0.593  $\mu$ m, E: porosity diameter of CZA nanoparticles with SEM MAG = 350kx, view field: 0.593  $\mu$ m)

Table 1 Significance value of main factors on removal efficiency of CO

Treatment reactor Plasma reactor Catalytic reactor IPC reactor Main effects of factors

| Temperature                                     | ++ | - | +- |
|-------------------------------------------------|----|---|----|
| Flow                                            | ++ | - | -  |
| C <sub>3</sub> H <sub>8</sub> /CO ratio         | -  | + | -  |
| Temperature * flow                              | -  | - | ++ |
| C <sub>3</sub> H <sub>8</sub> /CO * flow        | -  | - | -  |
| Temperature * C <sub>3</sub> H <sub>8</sub> /CO | -  | - | -  |
|                                                 |    |   |    |

++ Highly significant

+ On the edge of significant

- Interesting but not significant

radicals reaches to maximum level and shows the best oxidation efficiency of CO, yet the additional temperature enhancements result in lower concentration of OH radicals and thus lower CO oxidation. In other words, the formation of those radicals reaches maximum concentration at 110 °C using plasma alone reactor, but the combination of plasma and catalysis reduces this value to 80 °C at hybrid reactor [12]. The highest mean conversion rate was achieved at 80 °C, 3 l/min, and  $C_3H_8/CO$  ratio of 0.05 (Fig. 6). It should be noted that in both reactors (plasma alone and hybrid), removal efficiency was high at the presence of  $C_3H_8$  (Figs. 4 and 6). The improvement of removal efficiency with temperature increase was reported by Leray et.al (2014) [3].

The positive effect of temperature on removal efficiency is described by improvement in the secondary decomposition of

hydrocarbons as well as the increase in impaction surface of active molecules following proper temperature and the decrease of gas stream viscosity in reactor space [5, 14, 43]. In fact, different temperatures result in different densities of gas stream which in turn lead to different reduced electric field strengths [44].

In catalytic alone reactor, the positive effect of temperature increase on removal efficiency was significantly dependent on the  $C_3H_8$ /CO ratio. As we can see from Fig. 5, the absence of  $C_3H_8$  resulted in better removal efficiency in low flow rates of study range. In the presence of propane ( $C_3H_8$ /CO = 0.05), temperature increase up to 110 °C results in the highest mean removal efficiency at 3 l/min.

The effect of flow rate on removal efficiency: Mean removal efficiency in the plasma alone reactor significantly increased with a decrease in flow rate (Fig. 4). It was improved in hybrid reactor with an increase in gas stream flow rate (Fig. 6), and this improvement was potent in the presence of propane. The improvement in removal efficiency of CO due to the positive effect of flow rate was explained by mean power enhancement of discharges, and thereby space time decreases. The mean power of discharge determines the mean electron density which in turn gives the excitation rates and molecule separation in gas [45].

At the catalytic reactor, the effect of  $C_3H_8/CO$  ratio was found important. As we can see from Fig. 5, in the absence of propane, the mean removal efficiency was better in 1.4 l/min. But, in the presence of propane, its ratio to CO played an important role in the determination of proper flow rate for removal efficiency. When this ratio was about 0.05, high



Fig. 4 Interactions of temperature, flow rate, and  $C_3H_8$ /CO ratio on CO conversion in plasma reactor (the SIE at the three levels of flow rate: 300 J/l (0.6 lit/min), 780 J/l (1.4 lit/min), and 2130 J/l (3 lit/min)



Fig. 5 Interactions of temperature, flow rate, and C3H8/CO ratio on CO conversion in catalytic reactor

removal efficiency was achieved at 3 l/min and 110  $^{\circ}$ C, but in ratio of equally 0.1, better removal efficiency was obtained at 0.6 l/min and 23  $^{\circ}$ C.

The interaction of gas stream temperature and flow rate was found significant ( $P_{value} < 0.05$ ) in hybrid reactor which was important from SIE aspect. Based on the studies, this effect could be explained by the key role of some active species particularly OH radicals at the presence of hydrocarbons. Energy density of plasma is a key and important parameter

which affects unburned hydrocarbons, CO, NO<sub>x</sub>, and generation of intermediate species. Plasma reduces the partial pressure of unburned hydrocarbons significantly. Thus, propane was burned with plasma activation [16]. In the presence of hydrocarbons (e.g., propane), radicals of proxy, OH and HO<sup>•</sup><sub>2</sub> are the prominent oxidizers improving reaction selectivity to CO<sub>2</sub> and  $H_2O$  production [14, 15]. However, the amount of CO<sub>2</sub> at the outlet of reactor was not measured in the present study.



Fig. 6 Interactions of temperature, flow rate, and  $C_3H_8$ /CO ratio on CO conversion in hybrid reactor (the SIE at the three levels of flow rate: 650 J/l (0.6 lit/min), 1650 J/l (1.4 lit/min), and 3450 J/l (3 lit/min)





Specific input energy (SIE): Specific input energy is in direct relation with the increase of gas stream space time, although its effect on removal efficiency of pollutant can be positive or negative. In the present study, energy consumption increased with space time enhancement, whereas this increase did not have a significant effect on removal efficiency, and best removal efficiency of CO occurred in lower space time and thereby lower energy consumption compared to higher space times (Figs. 8 and 9).

Figure 9 shows the removal efficiency of CO as a function of SIE in three levels of gas stream flow rate. It explains that decreasing gas flow rate results in higher energy consumption. However, the removal efficiency is better in high flow rate (3 lit/min), and in this flow rate, the effect of increasing SIE on removal efficiency is clearly shown. This may emphasize the key role of the interaction of temperature and space time besides power consumption on the removal efficiency. That interaction was found significant and very obvious in high flow rate (3 lit/min). At higher flow rate (3 l/min) compared to lower flow rates (0.6 and 1.4 l/min), increasing energy consumption resulted in improving removal efficiency. But, in lower flow rates (enhancement of space time), the increase of SIE did not improve removal efficiency significantly, and the enhancement of temperature was not strong.

As we can see from Figs. 8 and 9, from specific input energy aspect, optimum removal efficiency was achieved at 860 j/l (SIE) for treatment of 3 l/min (flow rate) at 80  $^{\circ}$ C (Fig. 8).

The synergy effect of plasma and catalyst in improving oxidation reactions was shown by Liray et.al (2014) and Kirckpatrick et.al (2011) [3, 13]. In both studies, platinum group metals (platinum and palladium) have been used as precursor metal of catalyst, and the key role of NTP on improvement of light-off temperature has been highlighted.



Fig. 8 Optimum removal efficiency of CO at low temperatures in hybrid reactor (IPC)



Fig. 9 Removal efficiency of CO as a function of flow rate in hybrid reactor

Based on the OSC property of  $CeO_2$  in catalysis of CO and HC reactions with water under rich conditions, the synergy effect of plasma and catalyst is logical. Accordingly, the formed H<sub>2</sub> then reduces NO<sub>x</sub> to N<sub>2</sub>. So the harmful by-products were decreased [22]. Since the maximum removal efficiency of each three applied reactors was lower than 70%, thus we have used the Abbott's formula to calculate expected removal efficiency (%Cexp). Calculation of synergy effect as synergy factor will be useful in further studies to finding optimum conditions of performance in plasma catalyst hybrid reactors to achieve higher removal efficiency.

The results of this study confirm the key effects of gas stream properties on energy consumption besides the improvement of removal efficiency (Fig. 8). The effect of gas flow rate on energy consumption was direct while that of gas temperature and propane was found to be indirect.

The synergy factor for all the experimental test conditions was calculated and reported in our previous work [46], but based on optimum conditions of removal efficiency (T=80 °C, flow=3 l/min) as well as specific input energy aspect, the best SF coefficient was achieved about 2.03 which emphasizes more studies about plasma-catalytic hybrid process for CO control.

### **6** Conclusion

Carbon monoxide removal using plasma-catalytic hybrid technique was tested from different viewpoints of improving removal efficiency, catalytic performance temperature, energy consumption, hydrocarbon decomposition, and synergy factor of hybrid process. The mean removal efficiency of CO (36.33%) was achieved using single stage hybrid reactor at optimum experimental conditions of 80 °C (temperature),

3 l/min (flow rate),  $C_3H_8/CO=0.05$ , and specific input energy of 865 j/l. The study of main effects of multivariate factors shows that the interaction of flow rate and temperature using plasma driven catalysis can be attractive from optimum temperature for the generation of hydroxyl radicals (80 °C), and optimum removal efficiency of CO at high flow rates because with lower flow rate at the same temperature the efficiency decreased, which is due to the recombination reactions of hydroxyl radicals. It was concluded that carbon monoxide removal improved due to hydrocarbon decomposition and thereby the generation of hydrocarbon radicals. Also, our findings confirm the positive synergy effects of plasma and catalytic techniques in CO removal, and synergy factor of 2 was achieved. This value of synergy factor confirms the necessity of additional applied and research studies in the field of combined plasma-catalytic process for optimal CO removal.

#### **Compliance with Ethical Standards**

**Conflict of Interest** The authors declare that they have no conflict of interest.

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