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Article

Optimizing CO Reductions in a Diesel Oxidation Catalyst under Diesel Dual Fuel Exhaust Conditions

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Abstract. A Diesel Dual Fuel (DDF) engine is an adapted diesel engine that uses natural gas and diesel fuel as the energy source at the same time. Natural gas is mixed with air at the intake manifold while diesel fuel is injected into the combustion chamber directly to initiate the combustion process. Based on the past DDF literatures, they are indicated that Carbon Monoxide (CO) emissions were more substantial at low load conditions than those when running in diesel engine modes. The Diesel Oxidation Catalyst (DOC) that is installed to this diesel engine is, therefore, not capable to reduce CO emissions abide by to the emission regulation. Literatures also indicate that the exhaust temperature, mass flow rate, Oxygen (O_2) concentration, CO concentration, as well as Propane (C_3H_8) concentration may affect CO conversion efficiency of the catalytic converter. In the present work, Design of Experiments (DOE) is employed to explore the behavior of various factors that affect CO reductions in the catalytic converter. Once the knowledge is founded, the optimization of CO reductions in the catalytic converter at 90% is studied extensively.

Using Fractional Factorial Design for screening factors on CO conversions, it is found that the exhaust temperature, mass flow rate, O_2 concentration, and CO concentration affect CO conversions of the catalytic converter significantly. Optimization of these factors, by using Box-Behnken Design, for reducing CO concentration of 6200 ppm which is the maximum CO amount emitted from the tested engine shows that 90% of CO conversion can be reached at the exhaust temperature of 200^{0}C, the mass flow rate of 25 kg/h, and the oxygen concentration of 16%.

Keywords: Diesel dual fuel, diesel oxidation catalyst, CO emissions, design of experiment.

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1. Introduction

A DDF engine is a modified diesel engine that mixes natural gas with air before entering the combustion chamber. The diesel injector injects diesel fuel to ignite the mixer [1]. This technique help decreasing the quantity of diesel fuel usage with slight modification on the engine. In addition, it also decreases NOx and soot emissions because of lower combustion temperature and less amount of diesel fuel [2]. However, CO and THC concentrations in the exhaust of this adapted engine are higher than those of the conventional engine [3], [4].

From literature review, there are many parameters that affect CO conversion efficiency for Pt-Pd diesel oxidation catalyst (DOC) [5]. High O_2 concentration will increase the efficiency, while high CO concentration will decrease the efficiency [6]. At higher exhaust temperature, pre-CAT temperature, CO will decrease with better efficiency [7]. And lastly, the exhaust flow rate in which lower flow rate leads better efficiency.

With many parameters for CO-reduction, therefore, this research is done by using Design of Experiment (DOE) concept to find the proper condition for improving CO reduction efficiency. This technique is employed to help analyzing the relationships and interaction among each factors [8]. Many researches in aftertreatment applications have implemented DOE for system optimization [9], [10], [11]. However, none of these is employed for studying relationships among exhaust environments on catalyst performance. For this research study, the Fractional factorial design is first used to screen factors that have no or little effects to CO conversion efficiency. This design also help reducing the numbers of the experiment due to the limited time and resources. After the parameters that are influenced CO conversion efficiency are reduced, the Box-Behnken design is chosen for studying 3-level factors effect. This design is one of the response surface methods that is very useful to find the quadratic relationship among factors.

2. Simulation and Experimental Setup

In the current study, the research methodology is focused on simulation approach. This is due to the fact that the ultimate goal is to optimize proper conditions for CO reductions which if done by experiments, it will be time consuming process and yield high operating costs. Modeling DOC can be found in many past literatures in both 1-D and 3-D [12], [13], [14]. Once calibrated with the experimental data, the model can be used to benchmark and optimize the design which is favorable for time and cost reduction before implementing to the real engine and exhaust setup.

2.1. DOC Model

The model of the DOC was built on a computer program, called AVL-BOOST. This software package is employed to simulate flows in the engine model and its components. The flow model for each component involves simultaneous solutions of the continuity, momentum, energy, and specie equations. These equations are solved in one-dimensional (1-D), which means that all quantities are averages across the flow direction. The model can be viewed as a series of many discretized volume where each flow model is represented by a single volume and every pipe is divided into one or more volumes. DOC model can be viewed as a series of tube bundles representing catalyst brick. Figure 1 shows a DOC model in AVL-BOOST where ATB1 is the inlet boundary condition, ATB2 is the outlet boundary condition, and CAT1 is the DOC model.

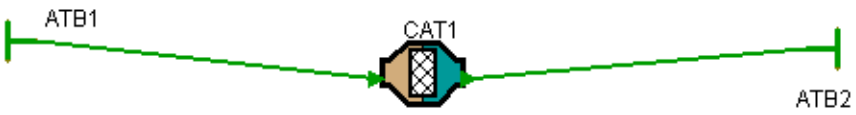

Fig. 1. DOC model in AVL-BOOST.

2.2. Chemical Kinetic Parameters

The DOC is composed of catalyst that accelerated the reaction between exhaust gas and DOC. The reaction equation can be expressed by employing the surface mechanisms called Langmuir Hinshelwood [14], [15], [16]. The kinetic model of CO and C_3H_8 can be described as follows.

$$\dot{r} = \frac{\left[K_1.e^{\left(\frac{-E_1}{T_S}\right)}.y_{CO}.y_{O_2}\right].\left[1+K_2.e^{\left(\frac{-E_2}{T_S}\right)}.y_{CO}+K_3.e^{\left(\frac{-E_3}{T_S}\right)}.y_{C_3H_6}\right]^{-2}}{\left[1+K_4.e^{\left(\frac{-E_4}{T_S}\right)}.y_{CO}^2.y_{C_3H_6}^2\right].\left[1+K_5.e^{\left(\frac{-E_5}{T_S}\right)}.y_{NO}^{0.7}\right].T_S} \quad (1)$$

$$\dot{r} = \frac{\left[K_1.e^{\left(\frac{-E_1}{T_S}\right)}.y_{C_3H_8}.y_{O_2}\right].\left[1+K_2.e^{\left(\frac{-E_2}{T_S}\right)}.y_{CO}+K_3.e^{\left(\frac{-E_3}{T_S}\right)}.y_{C_3H_6}\right]^{-2}}{\left[1+K_4.e^{\left(\frac{-E_4}{T_S}\right)}.y_{CO}^2.y_{C_3H_6}^2\right].\left[1+K_5.e^{\left(\frac{-E_5}{T_S}\right)}.y_{NO}^{0.7}\right].T_S} \quad (2)$$

where r = Reaction Rate (kmol / m^3 s), K = Term in reaction rate equation (variable), E = Activation temperature of each reaction (K), T = Temperature of solid (K), and y = Mole fraction of species (-)

2.3. Simulated Exhaust Gas

AVL-BOOST model is calibrated and compared to the experimental data. The experiment is done on the synthetic exhaust gas generating system as shown in Fig. 2. The system is designed to control temperature, gas concentrations, and exhaust flow rates separately. Therefore, the system can generate various exhaust characteristics that DOC experiences while FTIR is used to measure emission species. More details of this setup can be found in [17], [18].

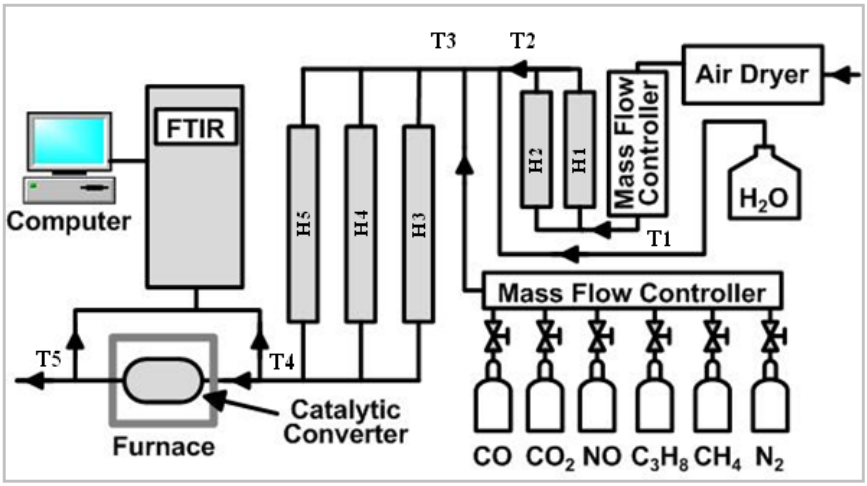

Fig. 2. Synthetic exhaust gas generating system.

Since exhaust gas compositions depends tremendously upon each engine operating conditions, the catalyst efficiency changes significantly during a cycle driving test. In this work, the acceleration phase in the city cycle is selected as an exhaust representative that the catalyst experiences. This is due to the fact that CO emissions from DDF combustion during the acceleration phase is relatively high in the city cycle as shown in Fig. 3. [19].

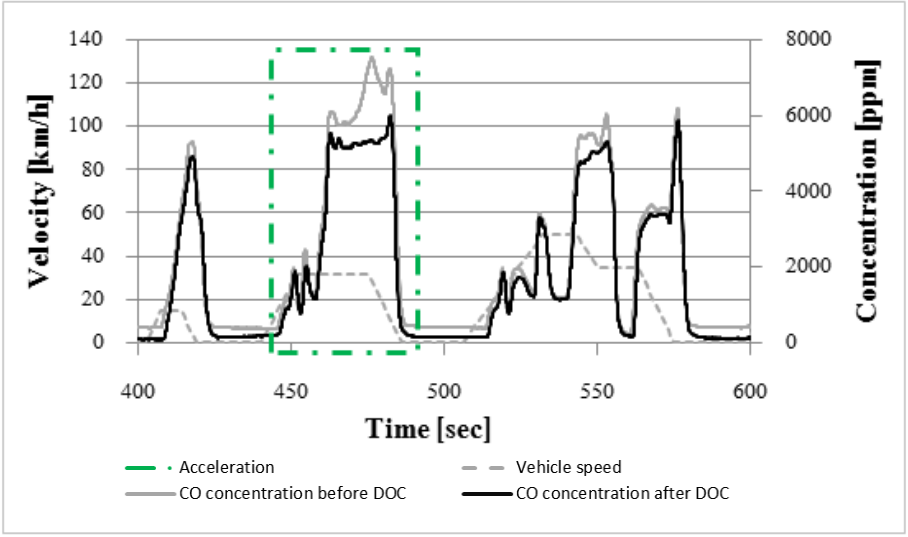

Fig. 3. CO Emissions during new european driving cycle (NEDC) test.

DOE factors for the simulation were referenced from the DDF experimental result as shown in Table 1. The low/high levels are indicated based on the min/max values of measurable parameters from Fig. 3. In this simulation, C_3H_8 is used as a representative of Non Methane Hydrocarbon (NMHC). There is a tremendous high concentration of Methane (CH_4) emissions in the exhaust, but in this work, however, CH_4 is excluded from the analysis. DOE of CH_4 emissions will be studied in the next phase of this research study.

Table 1. Parameters for DOE.

Factor	Unit	Low level (-1)	High level (+1)
Flow Rate (A)	$\frac{kg}{h}$	24	93
Temperature (B)	$^{\circ}C$	122	173
O_2 (C)	%	8	17
CO (D)	ppm	530	5780
C_3H_8 (E)	ppm	1567	7533

2.4. DOC Physical Properties

The properties of the DOC can be seen in Table 2. Note that this DOC is manufactured specifically to meet EURO IV emission standard for a natural gas vehicle [20] and it is not an Original Equipment Manufacturer (OEM) part. Definitions of each DOC parameters in Table 2 can be found in [21].

Table 2. Tested DOC properties.

Parameter	**Tested DOC**
Cell Per Square Inch (CPSI)	300
Cell Shape	Square
Volume (L)	3.4
PGM Loading (g/ft^3)	210
Mass ratio of Pt : Pd	1:5
Washcoat	Al_2O_3

3. Results from Simulation

3.1. Comparing Results from Simulation and Light-off Temperature Experiment

In the first step, the kinetic model of DOC as seen in Eq. (1) is calibrated comparing to the CO and C_3H_8 Light-off Temperature experiments individually. 1000 ppm of CO and C_3H_8 is fed into DOC which lies in the furnace at the rate of 10 liter/min (space velocity 176.47 hr $^{-1}$) sufficient for emission analyzer flow requirement. Since the goal is to find proper kinetic parameters for CO in this model, thus, only K_1 and E_1 for CO and C_3H_8 are tuned based on the experimental data due to temperature ranges for active site on catalyst. It is found out that K_1 (kmol.K/m^2.s) and E_1 (°C) are 12.7 x 10^7 and 8 x 10^3, respectively, for CO and 55x10^7 and 12.2 x 10^3, respectively, for C_3H_8, which correspond to values found in the literature [6]. The rest of kinetic parameters are employed using default values recommended in AVL-BOOST user manual.

An example of CO light-off temperature experiment is shown in Fig. 4. Experimental data below 100°C is closed to the noise of the emission analyzer and is not considered during tuning process. Slope of the simulation curve matches well with the experimental data.

The temperature for 100% CO conversion can range from 135 to 280 °C depending on the catalyst of the DOC [22, 23].

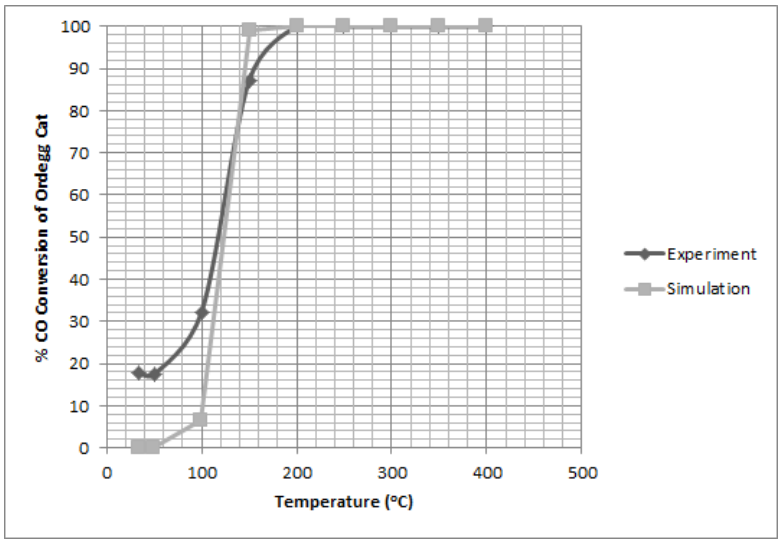

Fig. 4. CO light-off temperature experiment comparing to simulation.

3.2. Results from Design of Experiment

3.2.1. Fractional factorial design

Once the model is calibrated, DOE is performed by using Design Expert, a software package for DOE analysis. Fractional factorial design is firstly used for designing the current DOE in order to filtering factors that mostly impact CO conversion efficiency. In addition, this DOE methodology is selected to help reducing the number of experiments. Figure 5 shows a normal probability plot output from Design Expert. If any points are significantly deviated from the straight line, it means that those factors have large effects on the response.

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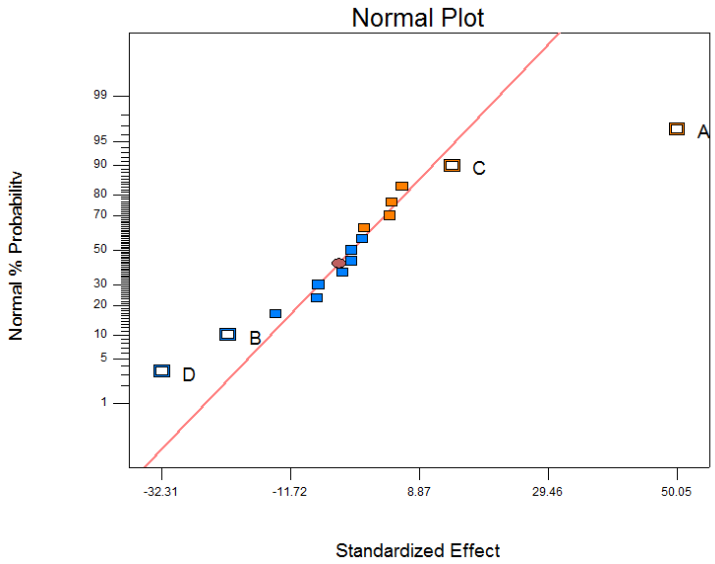

Fig. 5. Normal probability plot between factors and response.

Figure 5 indicates that Factors A, B, C, and D significantly impact CO conversion efficiency. In order to show more details of these, Figs. 6 to 9 are constructed. Figures 6 to 9 have shown individual effect plots of each factors on CO conversion efficiency. In general, within the range of tested DOE parameters, increasing temperature from 122 to 173°C will largely increase CO conversion efficiency from 20% to 70%. Increasing O_2 concentration from 8% to 17% will slightly increase CO conversion efficiency from 25% up to 45%. On the contrary, increasing CO concentration from 530 ppm to 5780 ppm and flow rate from 24 kg/hr to 93 kg/hr will decrease CO conversion efficiency from 50% to 25%. Trends from these experiments are found to be consistent to the literature found in [5], [7], and [12].

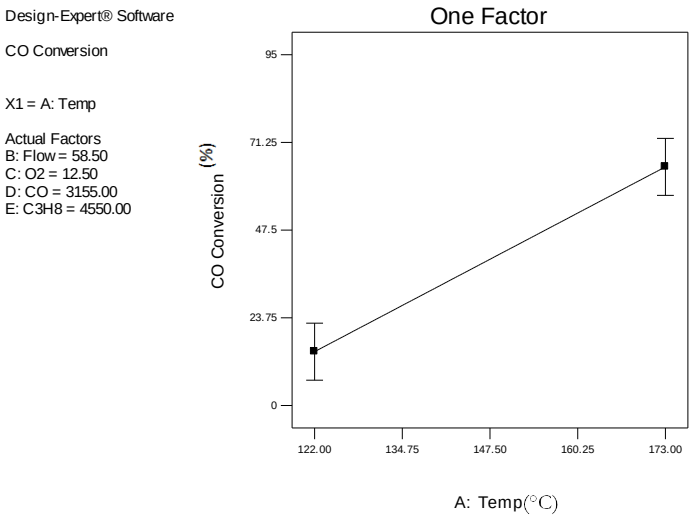

Fig. 6. Effects of Temp. (Factor A) on CO conversion efficiency.

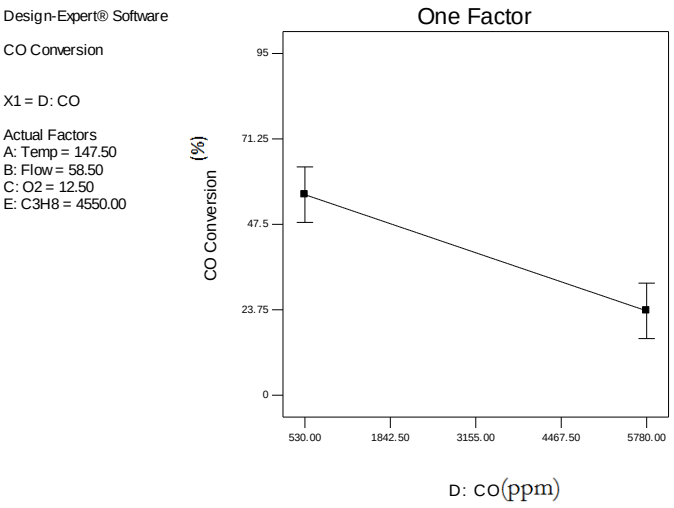

Fig. 7. Effects of CO concentration (Factor D) on CO conversion efficiency.

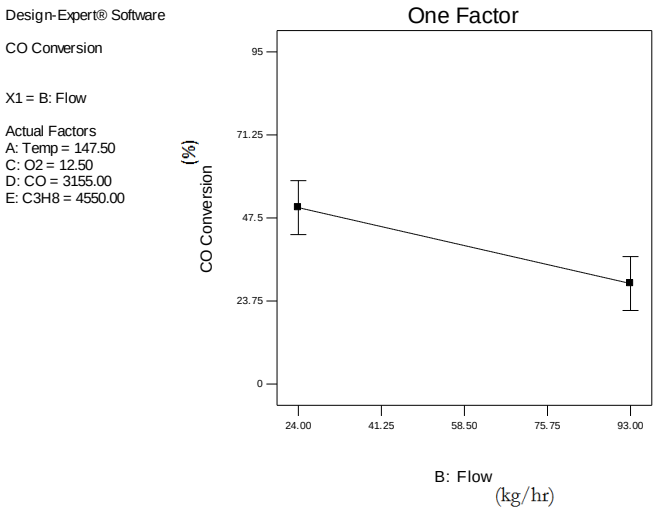

Fig. 8. Effects of exhaust flow rate (Factor B) on CO conversion efficiency.

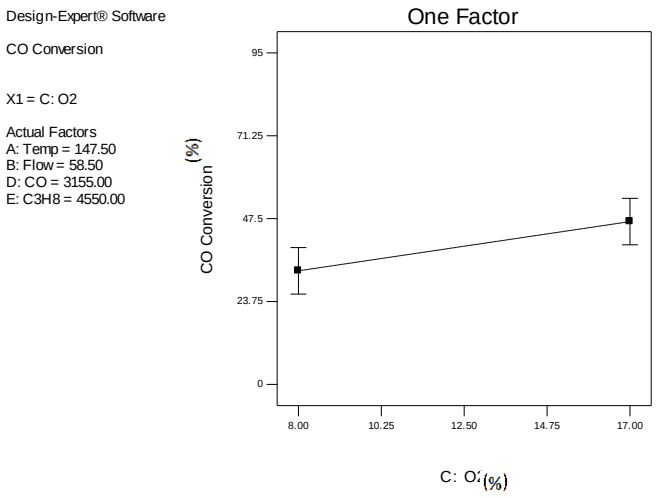

Fig. 9. Effects of O_2 Concentration (Factor C) on CO Conversion Efficiency

Results from above figures have shown that these 4 factors - exhaust temperature, exhaust flow rate, CO and O_2 concentration affect CO conversion efficiency. In the next step, these 4 factors were then analyzed to yield a proper condition for reducing CO. As for C_3H_8 (Factor E), it provides no effect on CO conversion efficiency. This is due to the fact that the range of temperature on DOE is too low for DOC to oxidize C_3H_8. Therefore, the amount of C_3H_8 concentration remains the same.

3.2.2. Box-Behnken design

The four factors Box-Behnken design is implemented to find proper conditions of reducing CO [17]. Table 3 shows ranges of each parameters for optimizing CO conversion efficiency.

Table 3. Parameters for optimizing CO conversion efficiency.

Factor	Unit	Low level (-1)	High level (+1)
Flow Rate (A)	kg/hr	125	200
Temperature (B)	$^{\circ}C$	25	96
O_2 (C)	%	8	16
CO (D)	ppm	100	6200

These factors are then simulated to get results by using Design Expert. However, before analyzing these results, the correctness must be checked. By plotting the normal probability plot, it shows that the plot is linear, as seen in Fig. 10 which is similar to the Fractional factorial design shown in Fig. 5. This indicates that the data can be used for further analysis.

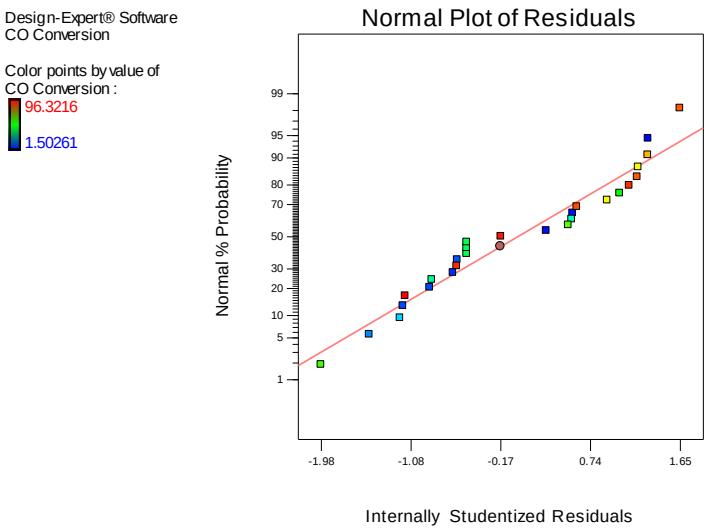

Fig. 10. Normal probability plot on Box-Behnken design.

The result was then analyzed to create the regression model that helps predicting CO conversion efficiency. Table 4 shows the regression analysis based on Box-Behnken design. From Table 4, the model can be created as "CO Conversion (%) = 47.80 + 41.55A – 9.89B + 6.83C – 19.74D". This come with "R-sq of 0.8643". This value indicates that there is 86.43 % to correctly predict CO conversion efficiency based on this analysis.

Table 4. Regression analysis based on Box-Behnken DESIGN.

Source	Sum of Square	Mean of Square	P value
Model	27126.3	6781.60	< 0.0001
A-Temp	20717.2	20717.26	< 0.0001
B-Flow	1173.6	1173.66	0.0128
C-O2	559.00	559.00	0.0749
D-CO	4676.478	4676.47	< 0.0001

Figure 11 demonstrates an example of outputs from Design Expert for CO conversion optimization. At low-load engine conditions, it is found out that to reach CO conversion efficiency more than 90% at CO concentration of 6200 ppm, the exhaust temperature, the exhaust flow rate, and O_2 concentration must reach 200°C, 16%, and 25 kg/h, respectively.

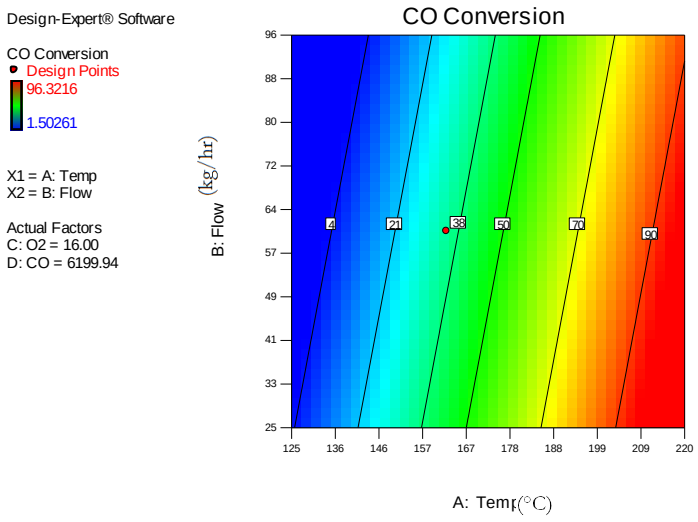

Fig. 11. Proper conditions of 90% CO conversion efficiency for CO concentration of 6200 ppm.

4. Conclusions

This research uses DOE concept to study CO reductions in a DOC model in order to determine factors that affect CO conversion efficiency during low load conditions of DDF exhaust-like conditions. The model is then implemented to determine proper conditions for CO conversion efficiency at 90%. Results shows that exhaust flow rate (A), exhaust temperature (B), O_2 concentration (C), and CO concentration (D) are major factors that influence CO conversion efficiency. Low exhaust flow rate, high exhaust temperature, high O_2 concentration, and low CO concentration can help increase CO conversion efficiency. At a significance of 0.05, the relationship between factors and response can fit into the regression model as "CO Conversion (%) = 47.80 + 41.55A – 9.89B + 6.83C – 19.74D". This model can correctly predict up to R-square of 86%. For reaching 90% CO conversion efficiency and with CO concentration of 6200 ppm at low load conditions, the exhaust temperature should be at 200°C, with the flow rate of 25 kg/h, and O_2 concentration of 16%.

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Nomenclature

C_3H_8	Propane	FTIR	Fourier Transform Infrared Spectroscopy
CH_4	Methane	K	Pre-exponential factor0
CO	Carbon Monoxide	NEDC	New European Driving Cycle
CO_2	Carbon Dioxide	NMHC	Non Methane Hydrocarbon
CPSI	Cell per Square Inch	OEM	Original Equipment Manufacturer
DDF	Diesel Dual Fuel	PGM	Platinum Group Metal
DOC	Diesel Oxidation Catalyst	r	Reaction rate
DOE	Design of Experiment	THC	Thermal hydrocarbon
E	Activation temperature (K)	y	Mole fraction of species

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