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SCIENCE DIRECT®
Catalysis Today 100 (2005) 243–248
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Use of experimental design in development of a catalyst system

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Available online 25 March 2005

Abstract

NO_x storage and reduction experiments have been performed with stationary operation of a heavy-duty diesel engine rig. An optimization of the NO_x reduction performance has been done using experimental design. The adjustable parameters in this study were cycle time, injection time, injection rate and bypass time (period of reduced flow through catalysts). NO_x was reduced by 50–60% (3.3–4.1 g/kWh) with a fuel penalty below 5%. It was shown that experimental design was efficient for optimizing the NO_x reduction and this systematic approach enabled important conclusions to be drawn about the system performance.

Keywords: Experimental design; Design of experiments; DoE; NO_x storage and reduction; NSR; Injection parameters; Fuel penalty; Bypass; System optimization

1. Introduction

1.1. Background

The legislative limits for permitted NO_x emissions in exhaust gas from heavy-duty diesel engines will be decreased by 60% (3.0 g/kWh) until 2008 in the European Union [1]. In the USA and Japan a similar trend can be seen. Thus, the development of a NO_x after treatment system for heavy-duty trucks seems unavoidable. The aim of this work is to develop a fully operational after treatment system that reduces NO_x from the exhaust of a heavy-duty diesel engine. This after treatment system is based on the NO_x storage and reduction approach: the diesel engine runs in a continuous lean mode, i.e., there is a high concentration of oxygen in the exhaust gas. Under these conditions NO_x can be stored as $Ba(NO_3)_2$ on a $BaCO_3$ surface on the catalyst [2]. After a period of 1 or 2 min, diesel fuel is injected into the exhaust stream creating rich conditions. Then, the stored NO_x is desorbed and reduced to nitrogen.

1.2. The project

The engine rig consists of an 11 dm^3 Scania diesel engine, oxidation catalysts and NO_x storage and reduction catalysts. A bypass system has been installed to reduce the catalyst flow under the regeneration periods. This helps to avoid a high fuel consumption to obtain rich conditions [3]. Also without the bypass flow, there is a risk that the heat created from hydrocarbon oxidation could destroy the catalyst. It is the aim of this project to develop an after treatment system able to control the NO_x reduction performance under transient conditions.

1.3. Project sub task: optimizing parameters

The degree of NO_x reduction is dependent on a number of uncontrolled parameters, e.g., temperature which is governed by engine speed and torque as well as several other controllable parameters (described in Section 3.2). This study is focused on steady-state engine experiments (constant speed and torque, i.e. load points) and was performed to optimize the controllable parameters for maximum NO_x reduction with low fuel penalty at each given load point. The results will be used when implementing a control strategy for a European transient cycle (ETC).

1.4. Design of experiments (DoE)

Experimental design or design of experiments (DoE) has been used for many years within the field of catalysis.

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2004.09.066

The applications cover, for example, catalytic reactors [4], catalyst formulation and preparation [5–7], catalytic kinetic modeling [8,9] as well as NO_x reduction experiments [3]. DoE is an important tool and in this article, we have focused on the use of small designs in the application for NO_x reduction in a full-scale engine rig, where the design parameters are of a practical nature (i.e. the parameters that are easily modified). The objective of DoE is to gain information with as few experiments as possible. Without the use of DoE in this project, the time and labor needed for the investigation would increase significantly using other methodologies such as variation of one parameter at a time. The experiments define an experimental space (i.e. range of parameter values) where a simple linear model may be fitted to estimate the effects of the parameters under investigation. In this study we used so called screening designs. Their purpose is to model main factors and to capture general trends. Screening designs are characterized by a limited number of experiments to save time, so called center points to estimate the reproducibility and the ability to model the responses (in this case NO_x reduction and fuel penalty) with linear terms. In this article we have also included one interaction term and some experimental constraints. This article is intended to be a methodological description of how to deal with complex experimental systems. The methodology is shown to be very efficient in this project but is applicable for every NO_x storage and reduction system as well as any experimental optimization task.

2. Experimental

2.1. Experimental setup

The experimental setup used in the NO_x storage and reduction experiments is shown in Fig. 1. The setup contains a bypass line to bypass most of the exhaust gas under the regeneration periods. Thus a portion of the exhaust bypasses the catalyst and is not subject to treatment. However, the NO_x emissions which bypass the catalyst are not regarded as a major contributor to the total NO_x emissions. The catalysts consist of NO_x traps with a total volume of 18.9 dm^3 and oxidation catalysts of 9.4 dm^3 to pre-oxidize NO and the injected hydrocarbons. The NO_x traps contained Pt/BaO among other components on an Al_2O_3 support, the oxidation catalyst was Pt on Al_2O_3. The system has been described previously in detail [10,11]. Gas sampling is made up- and downstream of the bypass line so that the whole exhaust gas flow is subject to gas analysis.

2.2. Parameter definition

There are many parameters that influence the NO_x reduction performance. The catalyst temperature is one main parameter for NO_x conversion because of its strong influence on reaction kinetics and equilibrium. The temperature is, however, governed by the engine speed and torque, which are uncontrollable under normal operation of the engine in a vehicle. Thus, the temperature is not regarded as a controllable parameter. The parameters for injecting the reducing agent are, however, controllable and are used for optimizing the NO_x reduction performance. Fig. 2 illustrates the injection parameters. A cycle consists of two phases, one longer lean period (NO_x storage) and one shorter rich period with reduced flow (NO_x release and reduction, bypass time). The rich phase or ''bypass time'' starts with an injection of reducing agent (here: Swedish MK1 diesel) into the exhaust stream possibly followed by a time period with no injection and just the reduced flow. The bypass time can thus be equal to or longer than the injection time. The design parameters chosen were:

1. Cycle time (ct) (s).
2. Injection time (it) (s).
3. Injection rate (ir) (mg/s).
4. Bypass time (bt) (s).

Other parameters are just functions of the ones above, making them impossible to vary independently (i.e., storage time = cycle time − bypass time, injected amount = injection time × injection rate). For every design experiment, 5 cycles were run. The responses, namely NO_x reduction and fuel penalty were calculated as an average of the three last cycles. The fuel penalty is the ratio between the injected amount and the engine fuel consumption given in percent.

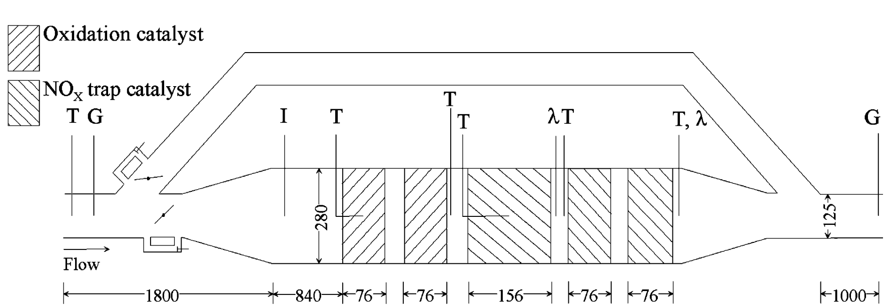

Fig. 1. Catalyst setup. G = gas sampling point, T = thermocouple, λ = broad band λ-sensor, I = injector.

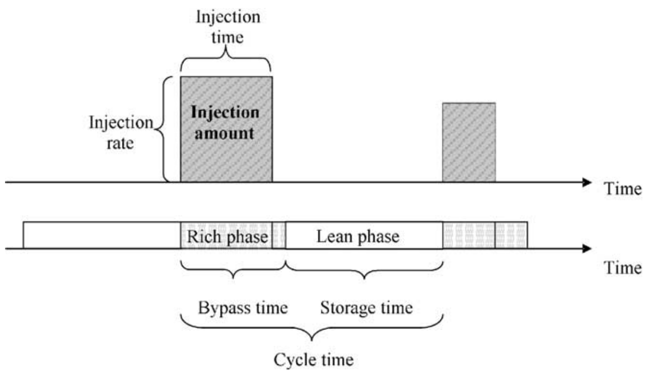

Fig. 2. Schematic view of the injection parameters and valve settings.

2.3. Load points

Since the results were to be used for transient cycle operation, several representative load points from the ETC were optimized, each with one individual design. These were:

- 1000 rpm/1000 Nm;
- 1250 rpm/1000 Nm;
- 1500 rpm/500 Nm;
- 1500 rpm/1000 Nm.

These load points are well spread in order to cover different exhaust gas temperatures as well as different NO_x levels. Additional load points with lower torque (0–300 Nm) were investigated but the exhaust gas temperature was too low (below 260 °C) for effective NO_x reduction.

2.4. D-optimal design

Screening designs were developed for each load point. Because of the constraint that the injection time cannot be longer than the bypass time (see also Fig. 1), a normal reduced (fractional) factorial design could not be used (where all combinations of high and low levels of the factors may be present). The type of design that handles these constraints is called a D-optimal design and can be very similar to a fractional factorial design. The different levels of each design parameter were chosen from the results of previous experiments. The designs were generated in the software Modde 6.0 by Umetrics and are shown in the left part of Table 1. In Table 1 it can be seen that the constraint that the bypass time cannot be less than the injection time is satisfied. In a standard fractional factorial design, the bypass times indicated in bold face would have been set to 10 s (bypass time at low level together with injection time at high level). All parameters except the injection rate were accurately controlled. Due to the pneumatic instrumental setup the injection rate varied from its setpoint, however its measured value was used for the modeling. Because the effect of the injected amount was of interest, the interaction term between injection time and injection rate was included, which has a physical interpretation (amount = time × rate). In screening designs, the number of experiments is kept low, resulting in a reduced design compared to a full-factorial design. The drawback of this reduction is that some factors may be confounded with others. In this case the effect of the bypass time will be confounded with the three-way interaction ct × it × ir, which is acceptable since three-way interactions are very rare. Also some two-way interactions will be confounded with each other but the only two-way interaction of interest is the injected amount (it × ir), so any other two-way interactions were neglected. In this design, the bypass time will not be confounded with the injected amount or any other main effect. For further details about different designs and their properties, see [12]. The designs for the other load points were developed in a similar manner and not displayed in detail here.

3. Results

3.1. Design evaluation

The data were modeled using partial least squares (PLS) with NO_x reduction and fuel penalty as responses. Also the injected amount (ir × it) was added to the model. As seen in Fig. 3, the cycle time has a negative coefficient indicating that

Table 1
D-optimal design and results for load point 1000 rpm, 1000 Nm

Experiment name	Run order	Cycle time (s)	Injection time (s)	Injection rate (mg/s)	Bypass time (s)	NO_x reduction (%)	Fuel penalty (%)
N5	1	120	5	3783	40	41.4	2.4
N2	2	240	5	3827	10	29.5	1.2
N6	3	240	20	3795	40	32.6	4.9
N10	4	160	10	1910	20	36.4	1.8
N11	5	160	10	1920	20	34.7	1.8
N3	6	240	5	959	40	16.5	0.3
N9	7	160	10	1920	20	39.6	1.8
N1	8	120	5	960	10	22.7	0.6
N7	9	240	20	941	20	31.4	1.2
N12	10	160	10	1920	20	39.3	1.8
N4	11	120	20	938	40	41.2	2.4
N8	12	120	20	3777	20	43.7	9.7

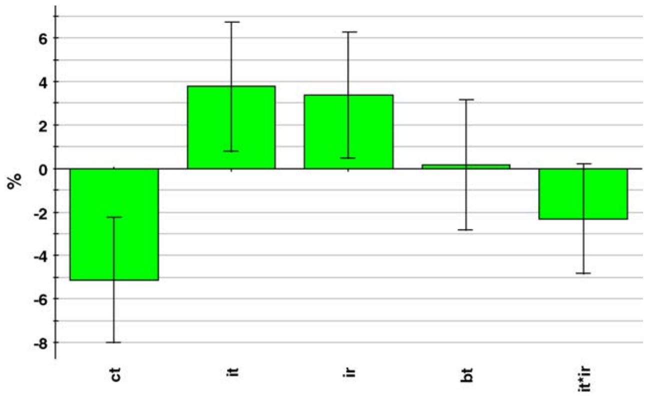

Fig. 3. Coefficient plot for the PLS model for 1000 rpm, 1000 Nm load point. The columns describe the change in NO_x reduction when changing the parameters from the center level to the high level with a 90% confidence level indicated by the bars. (ct = cycle time, it = injection time, ir = injection rate, bt = bypass time, it × ir = injected amount).

the cycle time should be as low as possible. Both injection time and injection rate have positive coefficients indicating that high levels are favorable, however, the injected amount (it × ir) is negative indicating that either injection time or injection rate should be set to a high level. As indicated by the confidence interval bars in Fig. 3, the model term it × ir is not statistically significant. However, the objective in this work was not to construct a ''true'' model but rather a ''useful'' one. The confidence bars are good indicators of how much uncertainty is present in the model. In this case the model term it × ir was judged to be useful. The coefficient for bypass time is small indicating it has only a small effect on the NO_x reduction. It also has a large uncertainty which means that the bypass time could be set to any level within the investigated range. Inspection of Table 1 confirms that the experiments with the highest NO_x reduction and with a low fuel penalty are N4 and N5 which are characterized by a short cycle time (120 s), either injection time or injection rate at high levels (both at high levels would give an unacceptably high fuel penalty) and bypass time being at a high level (40 s). These conclusions can also be drawn from a response surface plot as shown in Fig. 4. In Fig. 4 it can be seen that N4 (lower right corner) and N5 (upper left corner) gives good NO_x reduction with low fuel penalty whereas N8 (upper right corner) gives a too high fuel penalty.

3.2. Continued optimization

Inspection of time trend plots (NO_x concentration downstream the catalyst) from the design experiments showed that in order to achieve high NO_x reduction, successful catalyst regeneration was essential. The subsequent baseline in NO_x concentration during the following storage period indicated how effective the catalyst regeneration was, see Fig. 5. Since an effective catalyst regeneration was indicated for most of the experiments, it was suspected that the experimental space was not optimal. Additional experiments were then performed to confirm that the cycle time could be reduced even further. The injection time was kept short (5 s) but the injection rate was reduced to 2000 mg/s and the bypass time was reduced to the same level as the injection time (5 s). The baseline in NO_x concentration during the storage period was unchanged and it was concluded that it was due to a built-in limitation of the system.

3.3. NO_x reduction results

The designs for the other load points were evaluated in a similar fashion but the details are not given here. The results for all design experiments are however, shown in Table 2. The parameter settings are the best for optimal NO_x reduction with a low fuel penalty. The achieved NO_x reduction was between 51 and 63% and the fuel penalty was below 5%. From the evaluation of the designs together with inspection of trend plots for other measured signals and complementary modeling results (described in [11]), it became evident that:

- At higher temperatures (460–540 °C) the NO_x storage capacity was limited while the storage rate was not limiting. Thus, the storage time needed to be short. Also at

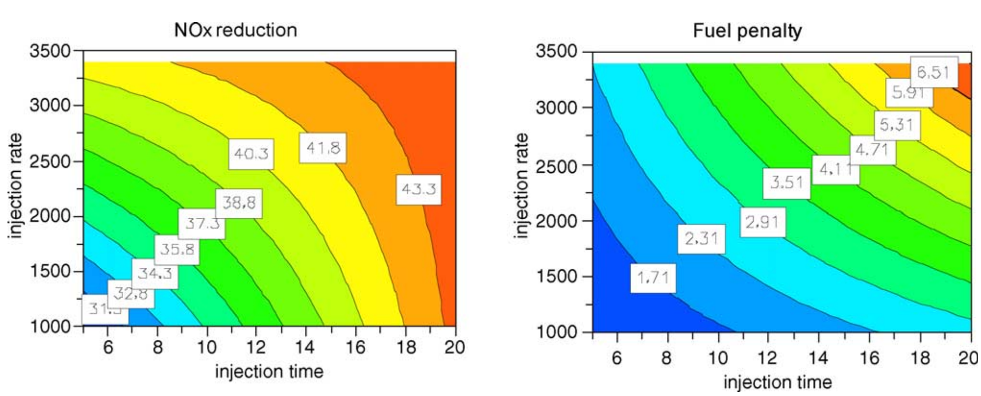

Fig. 4. Response surface plots showing NO_x reduction and fuel penalty for various settings of injection time and injection rate. The cycle time is fixed at a low level (120 s) and the bypass time is fixed at the center level (20 s).

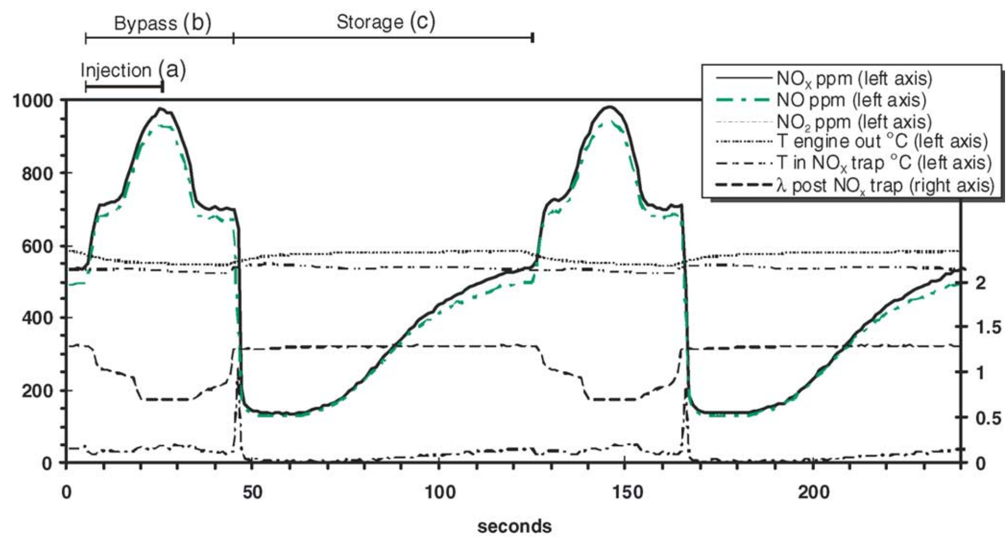

Fig. 5. Time trend plot showing different signals from the system during 2 cycles. The gas sampling point was after the catalyst. (This experiment was N4, it = 20 s ir = 938 mg/s, bt = 40 s, ct = 120 s). The plot illustrates: (a) the injection period (4–24 s, 124–144 s) where the injected reducing agent creates a breakthrough peak and the lambda value goes well below one; (b) the bypass period where at the end the outlet NO_x levels suddenly decrease when the bypass line is closed; (c) the storage period beginning with a baseline in NO_x levels at about 140 ppm indicating the maximum NO_x storage rate followed by a decrease in NO_x storage rate resulting in an increase in NO_x levels.

high temperatures, the injected hydrocarbons were more effectively used, and less hydrocarbons were needed to regenerate the NO_x storage catalyst (to release and reduce NO_x). The bypass time and the injection time were thus chosen at low levels.

- At lower temperatures (374–460 °C) the NO_x storage capacity was high, but the regeneration and NO_x storage rates were limiting. Thus the storage time should be long. Also at low temperatures the rate of catalyst regeneration was slow. The bypass time and injection time were thus optimal at high levels.

The findings agreed well with the expected influence of temperature on reduction kinetics and NO_x adsorption equilibrium.

4. Discussion

4.1. Optimized parameters for ETC test

After finding the optimal settings (according to the designs) for all load points, continued optimization is planned, similar to the experiments performed for 1000 rpm, 1000 Nm described above. When discussing optimality, it is important to keep in mind that the parameter settings are optimal only for the investigated parameter range. This means that other parameter settings may give even better results but were not investigated in this first study. However, by inspection of trend plots of the post-catalyst NO_x concentration curve, it became obvious that shorter cycle times would be even more beneficial for some load points

Table 2
Results from the design experiments. At the bottom some alternative figures are given for comparison

Load point	1000 rpm, 1000 Nm	1250 rpm, 1000 Nm	1500 rpm, 1000 Nm	1500 rpm, 500 Nm
Temperature in NO_x trap (°C)	539	519	462	374
Cycle time (s)	65	80	160	160
Injection time (s)	5	5	10	20
Bypass time (s)	5	10	20	40
Storage time (s)	60	70	140	120
Injection rate (g/s)	2	3.8	3.7	2
Injected amount (g)	10	19	37	40
NO_x reduction (%)	63	58	56	51
Fuel penalty (%)	2.6	2.9	2.5	5.0
Lambda rich/lean	0.9/1.3	0.7/1.5	0.7/1.7	0.85/2.3
NO_x engine out (g/s)	0.2	0.2	0.3	0.2
NO_x engine out (g/kWh)	5.3	6.3	5.9	8.2
Post-catalyst NO_x (g/kWh)	2.0	2.6	2.6	4.1
NO_x reduction (g/kWh)	3.3	3.7	3.3	4.1

Table 3
Parameter settings for a first dosing strategy used for ETC evaluation

Load point	1000 rpm, 1000 Nm	1250 rpm, 1000 Nm	1500 rpm, 1000 Nm	1500 rpm, 500 Nm
Cycle time (s)	65	65	70	160
Injection time (s)	5	5	10	20
Bypass time (s)	5	5	10	40
Storage time (s)	60	60	60	120
Injection rate (g/s)	2	2	3	2
Amount to inject (g)	10	10	30	40

(even though they were not investigated in the first designs). Furthermore, the bypass time should be set equal to the injection time for high temperatures.

These new parameter settings will be used in a first temperature based dosing strategy. The parameters are shown in Table 3.

4.2. Overall NO_x reduction performance

As seen in Fig. 5, the NO_x baseline during storage is not zero but approx. 140 ppm, which indicates a system limitation. However, the NO_x reduction performance is not possible to improve further just by adjusting the parameters discussed in this paper. Other measures are possible although not as easy to implement. These measures include an even more reduced flow during regeneration (by means of more sophisticated valve control or by different equipment design), increase in NO_x storage catalyst volume or decrease of engine output NO_x levels. These aspects are subject to future investigations.

5. Conclusions

An engine rig has been constructed with the aim of developing an exhaust after treatment system based on the NO_x storage and reduction technology. NO_x reduction experiments have been performed under stationary engine operation. Parameters such as the cycle time, the injection time, the bypass time, the total injected amount and the injection rate have been varied using DoE. The system optimization has given approximately 60% NO_x reduction using longer bypass and cycle times at low temperature and short cycle times and short injections at high temperatures. A dosing strategy will be based on these parameters and tested on-line as a control model under transient conditions in a European Transient Cycle test.

DoE was proven to be efficient for the development of parameter settings for maximizing the NO_x reduction with low fuel penalty.

- The reduced designs gave valuable information in relatively few experiments.
- The design results in combination with physical/chemical knowledge of reactions and catalysis, gave conclusions about system limitations.
- The design enabled discrimination between different effects and could pinpoint the main effects and indicate which experiments to proceed with.

Acknowledgements

The authors would like to thank the Division for Combustion Engines at Lund University and Scania CV AB for providing the engine rig, Scania CV AB and Volvo Truck Corp. for further contributions to the project, Bengt Cyrén for implementation of the engine rig control, Tom Hademark, Jan-Erik Nilsson and Jan-Erik Everitt for practical assistance. The Swedish National Energy Administration is gratefully acknowledged for the financial support of the project.

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