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EU-Russia Collaborative Project

“Engine and turbine combustion for combined heat and power production”

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BIC, Novosibirsk

WP 5. Emission reduction.

Introduction: Overview, deliverables & milestones, partners contributions

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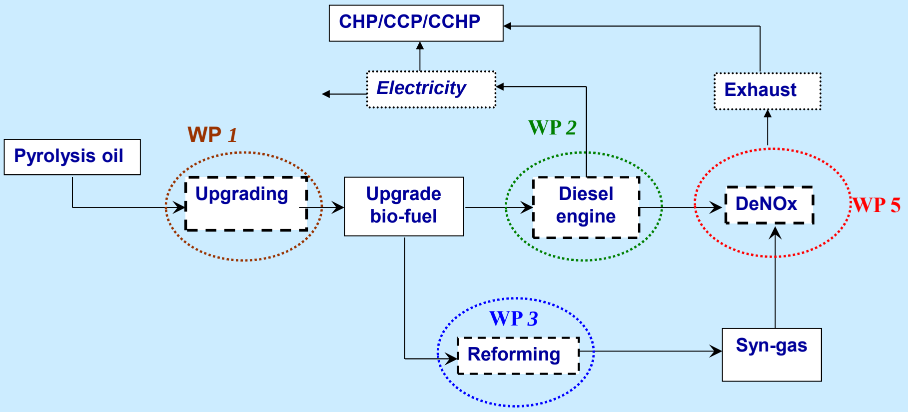
Summary of staff effort

Partic No	Partic short name	WP0 Manag.	WP1 Prod.	WP2 Upgr.	WP3 MGT	WP4 DE	WP5 Exh.	WP6 Ass.	Total person month
1	BTG	**8**	**15**	**20**	2	8	2	2	57
2	ECT	4	2	1	2	**23**	2	2	36
3	UFL	2	2	2	**44**	4	2	4	60
4	BIC	10	10	40	20	120	**360**	10	570
5	NAMI	4	5	15	10	440	60	10	544
6	UAS	2	2	2	1	1	1	**36**	45
7	ZIL	2		3	5	60	20	10	**100**
Total		**32**	**36**	**83**	**84**	**656**	**447**	**74**	**1412**

The main scheme of bio-electricity generation



WP 5. The development of catalysts and a system for NOx removal from diesel engine exhaust gases.

- **WP 5.1: Catalyst research and catalyst screening (BIC)** Fundamental research will be carried out on both catalysts for De-NOx and catalysts for reforming bio-liquids to syngas. Activity, selectivity, conversion degrees, deactivation and regeneration are the items that will be investigated. A series of different catalyst formulations will be screened. The fundamental research should result in the selection of the optimal one.
- **WP 5.2: Testing of the selected catalyst (BIC, NAMI).**

  This optimal bioliquids-reforming and de-NOx catalysts should be further shaped and tested in a special laboratory fixed bed set-up. This facility will be designed and constructed. Catalyst samples should be prepared in sufficient quantities to allow these lab-scale tests at BIC and NAMI, with special emphasis on poisoning/deactivation and stability. With respect to that, long term behaviour of the catalysts will be investigated as well.

WP 5. The development of catalysts and a system for NOx removal from diesel engine exhaust gases.

- **WP 5.3: Catalyst manufacturing and system development (BIC, NAMI)**

  When the performance of the optimal catalysts and their specific features are know sufficiently, larger quantities will be manufactured. Here the shape, support and the catalysts strength are also important, viz. in relation to the type of reactor that could be applied. In this task a suitable reactors will be developed together with all other necessary components of the integral DeNOx system

- **WP 5.4. Exhaust gas cleaning system (BIC, NAMI, ZIL)**

  Based on all the results in the previous tasks, a complete system will be designed, constructed and assembled, and eventually be added to the diesel engine generator for testing and further optimization at NAMI.

WP 5 Deliverables

- **D5.1** Report on catalyst screening and fundamental background (BIC, Month 6, 12)
- **D5.2** Selection of the catalysts for lab-scale testing (BIC, Month 12)
- **D5.3** Report on the results of lab-scale experiments (BIC, Month 18)
- **D5.4** Final selection of catalyst and manufacturing procedure (BIC, Month 24)
- **D5.5** Report on the design of the integral catalytic system (BIC, NAMI, Month 24)
- **D.5.6** Report on the construction and final testing of the integral exhaust gas cleaning system (NAMI, BIC, Month 36)

Approach to the final selection of catalyst and manufacturing procedure:

- Catalysts for syngas production
- Catalysts for DeNox reduction

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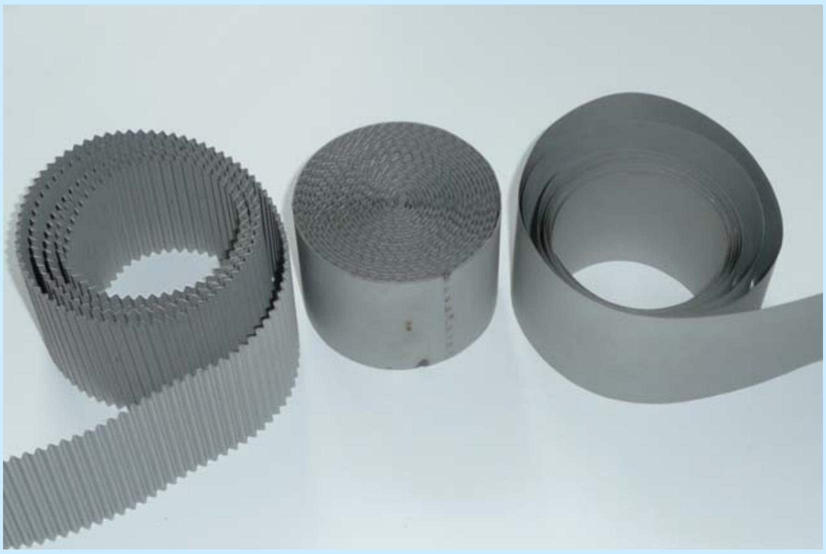
Samples of Monolith Catalysts for Syngas Production



Monolith Catalysts for Syngas Production (final results)

A1: Co3O4 / MnO2/Al2O3/SiO2/Net
A2: Co3O4/MnO2/BaO/Net
A3: Co3O4/MnO2/BaO/Fechral Net
A4: Co3O4/MnO2/BaO/Twill-woven Net
A5: Rh/Al2O3/Net
A6: Ni/BaO/La2O3/ Al2O3 /Net

Reactor and Monolith Catalysts for SynGas Production

Общий вид стенда для проведения испытаний катализаторов и реакторов

Reactor for ATR experiments

- Type – axial reactor.
- Inner diameter – 48 mm.
- Catalysts: $Co_3O_4/MnO_2/BaO$/Fechral Net + $Ni/BaO/La_2O_3/ Al_2O_3$ /Net; Two monoliths.
- Catalyst load – monoliths of 48 mm diameter, 50 mm length.
- Temperature of inlet mixture – 380-390°C.
- Temperature of outlet mixture - 700°C.
- Max temperature in catalyst monolith - 920-950°C.
- Inlet mixture ratio: $O_2/C = 0.8-1.0$, $H_2O/C = 0.5$.

Results of Catalysts Testing in ATR of Diesel Fuel

ATR Reformer								Concentration (dry, N2 balance)			
H_2O g/h	Diesel g/h	Air, l/min	O_2/C	H_2O/ C	T1 ^{0}C Inlet mixture	T2 ^{0}C Cat inlet	T3 ^{0}C Outlet	CO %	CO_2 %	CH_4 %	H_2 %
336	160	15.1	0.54	1.63	355	966	665	8.5	14	0.7	30.0
375	165	15.1	0.52	1.76	344	956	664	8.7	14	0.7	30.0
330	160	15.1	0.54	1.59	382	939	662	10.0	13	0.6	30.0
338	162	11.2	0.53	1.7	355	966	665	8.8	10.7	0.7	30.2
338	162	11.2	0.53	1.7	382	939	662	9.14	9.23	0.6	29.6
338	162	11.2	0.53	1.7	369	932	658	7.84	14.8	1.94	27.6
338	162	11.2	0.53	1.7	408	954	695	8.4	15.0	0.2	27.6

Results of Catalyst Testing in ATR of Biodiesel

ATR Reformer								Concentration (dry, N2 balance)			
H_2O g/h	Biodisel g/h	Air, l/min	O_2/C	H_2O/ C	T1 ^{0}C Inlet mixture	T2 ^{0}C Cat inlet	T3 ^{0}C Outlet	CO %	CO_2 %	CH_4 %	H_2 %
218	150	9.6	0.56	1.25	201	913	664	6.0	8.3	0.35	14.9
218	150	9.1	0.53	1.25	203	907	636	5.6	9.0	0.28	16.0
218	150	9.0	0.52	1.25	204	890	636	6.0	8.3	0.35	14.3
163	150	11.1	0.65	0.94	200	978	708	5.2	8.0	0.28	13.0
163	150	11.1	0.65	0.94	201	971	716	6.0	8.0	0.39	13.6
163	150	11.1	0.65	0.94	206	991	729	5.4	8.0	0.28	13.4
163	150	11.1	0.65	0.94	209	990	729	6.0	8.0	0.39	13.6

Results of Catalyst Testing in ATR of Biofuel Model Composition:

acetone(C3H6O) – 217.1g; Butanol-1(C4H10O) - 217 g; guaiacol (C7H8O2) – 214,6 g; pentanoic acid (C7H14O2) – 215,5 g.

Inlet Conditions		Temperature, ⁰C			Outlet Concentration , vol. %				O2/C	H2O/C
H_2O g/h	Bio fuel g/h	T1	T2	T3	H2	CO	CH4	CO2		
93	152,4	390	950	712	10,4	6,5	1,26	10,6	0,933	0,52
93	166,8	387	918	700	15,8	9,1	1,5	10,4	0,858	0,48
162	166,8	381	960	710	16,9	6,2	1,14	11,6	1,036	0,84
216	166,8	382	933	720	17,6	7	1,27	12,3	1,176	1,11
93	166,8	392	926	709	13,2	8,5	1,44	10	0,858	0,48
93	166,8	387	918	700	14,8	8,8	1,41	9,7	0,859	0,48

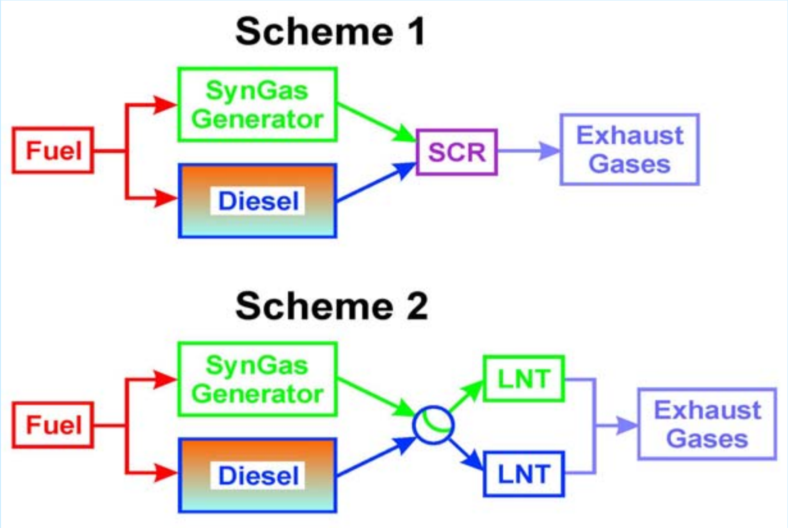
Results of Catalysts Testing in Steam Conversion of Bioethanol

Steam Reformer		Temperature	Outlet concentration (dry)				
Ethanol g/min	H_2O, g/min	T, °C	CO, %	CO_2, %	H_2, %	CH_4, %	H2+ CO
0.13	0.20	600	8.43	14.33	65.27	3.76	73.7
0.13	0.20	700	15.4	10.91	67.57	1.17	82.97
0.20	0.31	750	11.95	11.27	67.78	1.13	79.73
0.20	0.31	750	13.60	11.80	68.93	1.17	82.53
0.20	0.31	750	11.58	10.70	67.90	1.00	79.48

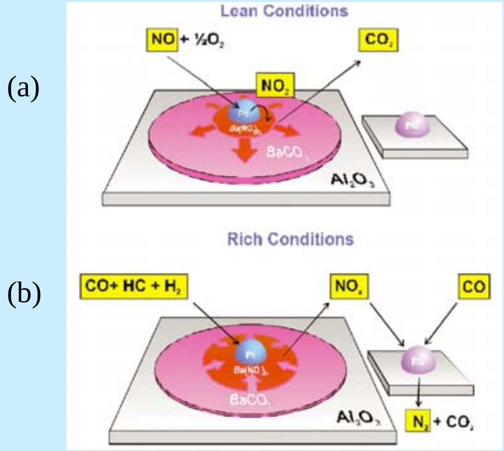
Results of Catalysts Testing in Steam Conversion of Pyrolysis Oil

Pyrolysis oil, g/h	H_2O, g/h	Temperature, °C	Composition of reaction products (dry condition) vol., %			
			CO	CO_2	CH_4	H_2
30	210	675	4.1	32.9	1.3	61.7

Possible Schemes of Synthesis Gas Application in Diesel Engines



Schematic of LNT De NOx (Schema 2)



Lean condition (engine operates on lean fuel mixtures in economy mode during 1-10 min)**:**

NO is oxidized to NO2 on platinum: NO + 0.5 O2 → NO2

NO2 is adsorbed and stored on the catalyst alkaline sites as barium nitrate 2 NO2 + BaCO3 + 0.5 O2 → Ba(NO3)2 + CO2

Rich condition (engine operates in rich-fuel mode) :

Ba(NO3)2 + 2 CO → BaCO3 + NO + NO2 + CO2

NO2 + CO → NO + CO2

NO + CO/HC → 0.5 N2 + CO2/H2O

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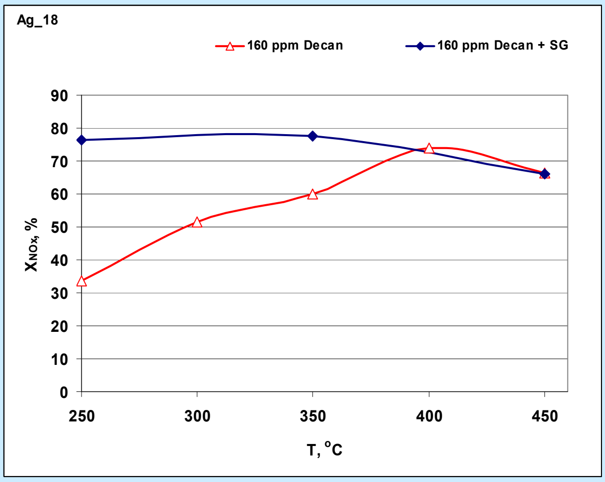
List of DeNOx Catalysts

- **Simple oxides:** MnO_2, Co_2O_3; Fe_2O_3; CuO, NiO; Supports: CeO_2, SiO_2
- **Mixed oxides:** Co_2O_3+MnO_2+ CuO; Co_2O_3+MnO_2+Fe_2O_3; Ag+Co_2O_3+MnO_2+CuO; CuO+Cr_2O_3+NiO(MgO,ZnO); Supports: Al_2O_3, CeO_2, SiO_2
- **Zeolites:** Fe/ZSM-5; Ag/ZSM-5; Ag+CuO/ZSM-5
- **Bimetallic Catalysts:** CuO+Co_2O_3(MnO_2, NiO, BaO); Ag+CuO; Bi_2O_3+MnO_2; Supports: Al_2O_3; CeO_2, Fe_2O_3, ZrO_2
- **Pd and Pt based catalysts:** Pd/CeO_2; Pd/Al_2O_3;Pt/Al_2O_3; Pd+Pt/Al_2O_3; Pd+NiO/Al_2O_3
- **Ag based Catalysts:** Ag/Al_2O_3
- **Rh based Catalysts:** Rh/Al_2O_3; Rh/ZrO_2, La_2O_3+Rh/Al_2O_3; Rh/NiMgOAl$_2$O$_4$/Al_2O_3

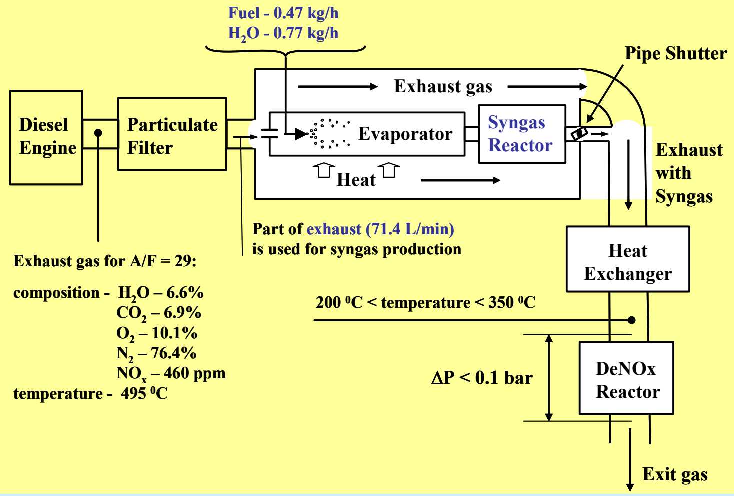
Lab Scale Experiment for DeNOx Reduction



Condition: Catalyst 2% Ag/Al2O3, GHSV = 13300 ч-1, [NOx]o = 460 ppm, [O2]=10%, [CO]o = 930 ppm, [H2]o = 3200 ppm, [H2O]o = 2%, [C10H22]o = 160 ppm, Ar - баланс

A scheme of experimental testing of De NOx catalysts

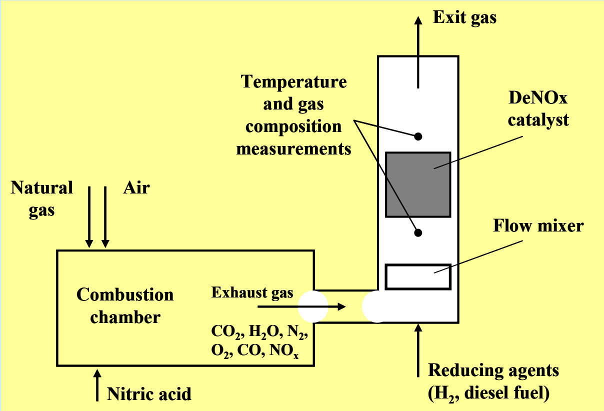
Scheme of Syngas-SCR testing



Exhaust gas for A/F = 29:

composition - H_2O – 6.6%
CO_2 – 6.9%
O_2 – 10.1%
N_2 – 76.4%
NO_x – 460 ppm
temperature - 495 °C

Schematic diagram and photo of NOx SCR reactor block

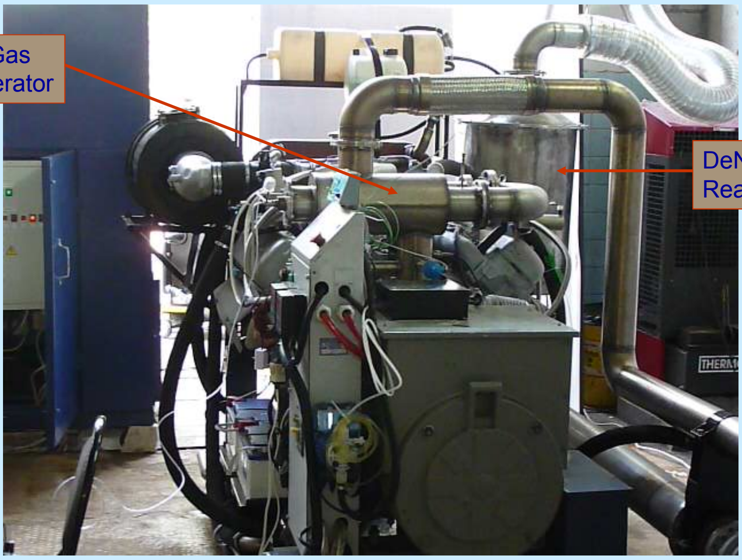


Results of 2%Ag/Al_2O_3 SCR testing

Catalyst bed temperature, °C		Reducing agent		NO_x conversion to nitrogen, %
inlet	outlet	H_2, ppm	diesel fuel, %	
330	372	3000	3.2	88
348	384	3000	3.2	88
369	400	3000	3.2	76
372	407	3000	3.2	74
367	387	0	3.2	71
330	347	0	3.2	73
293	311	0	3.2	70
330	354	0	5.1	80
349	372	0	5.1	80
368	394	0	5.1	82
371	398	0	5.1	81
372	415	3000	5.1	88

Experimental conditions: catalyst load – 1 L, model exhaust GHSV= 9700 h^{-1}, composition of model exhaust gas (vol.%): 6.3 CO_2, 12.5 H_2O, 7.2 O_2, ca. 1500 ppm CO, 500 ppm NOx, rest N_2.

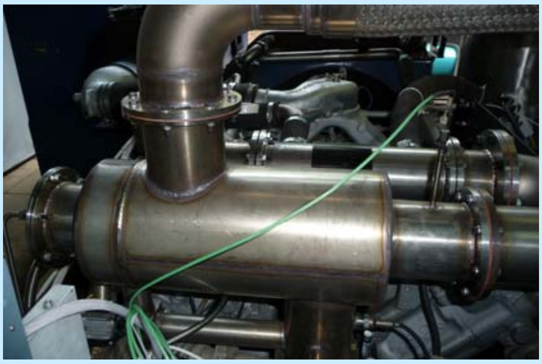
Power Plant with DeNOx System.
(Heat Power 150 kW, Electric Power 100 kW)



SynGas Generator

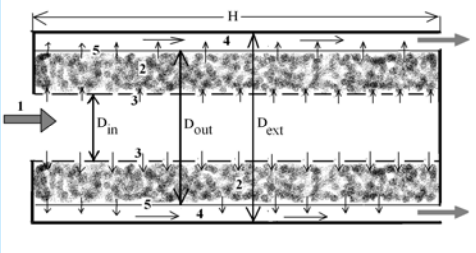
DeNOx Reactor

SynGas Generator – a Part of Power Plant



Reactor type	axial
Reactor inner diameter, mm	100
Catalyst block dimensions (diameter x length), mm	100 x 150
Temperature of gas mixture, °C:	
- reactor inlet	370-380
- reactor outlet	600-620
- maximum in the catalyst bed	920-950

De NOx Reactor



1- Exhaust gas inlet; 2-Catalyst; 3-Pseudoseptum;

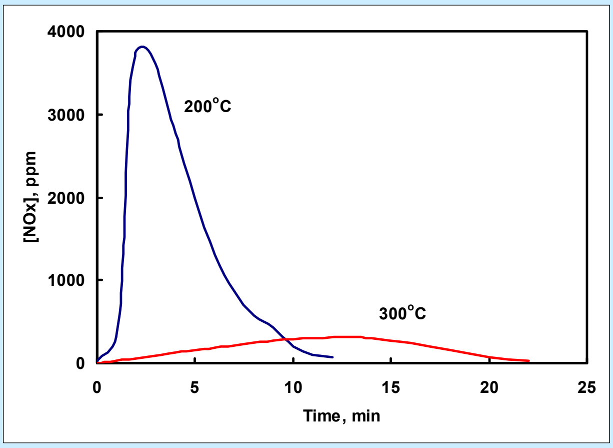
4- Outlet gas reservoir; 5- Clean gas after DeNOx

Parameters of DeNOx Reactor: Din=120 mm, Thickness of catalyst bed =100 mm, Dout=320 mm, Dext=380 mm, Length of reactor H=516 mm, Number of holies Nin=1943, Diameter of perforation din=2 mm, Reactor Type - radial .

Reactor for DeNOx experiments

- Type – radial reactor. Internal diameter 80 mm, external diameter 300 mm, length 400 mm, catalyst loading – 20 liter.
- Catalyst - 2%Ag/Al_2O_3, particles 2- 3 mm.
- Temperature of inlet mixture – 250 - 350°C.
- Max temperature in catalyst bed - 400°C.
- Composition of inlet mixture (depends on diesel engine operation regimes): 350-500 ppm NO, 8-12% O_2, 5% H_2O, 5-6% CO_2 , the rest being nitrogen.
- NOx conversion 70-80%.

Evolution of NOx into the gas phase upon reduction by synthesis gas.



Experimental conditions: rich condition mixture is 2% CO and 7% H2 in nitrogen, V = 300 cm3/min.

Comparison of the methods of NOx reduction in the diesel engine exhaust gases

Reduction method	Additional reducing agent	Temperature range where NOx conversion is > 90%	Fuel penalty	Platinum group metals	Catalyst life
SCR (urea)	Urea	200 – 500 °C	1 – 1.5 % of urea	None	Long
LNT (diesel fuel)	None	250 – 450 °C	> 4 % of diesel fuel	≥ 2 g/l	Short
SCR (synthesis gas + diesel fuel)	None	200 – 350 °C	3.5-4.5 % of diesel fuel	None	Not studied
LNT (synthesis gas)	None	150 – 450 °C	2 – 2.5 % of diesel fuel	None	Not studied