

# Partial Zero Emission in Automobile Exhaust Application: Driving Toward a Clean & Green Future

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Abstract: An aftertreatment system is developed to achieve partial zero emission using a cold start zeolite-based hydrocarbon (HC) trap in combination with the conventional three-way catalytic converter. The feasibility of the system is demonstrated in a 10 horse power (hp) gasoline engine. An approximately 93% reduction in cold start hydrocarbon emissions is achieved by the system. The "Flow Swing Over Valve" technology is implemented to route the exhaust gas to the hydrocarbon trap during cold start operation till the engine reaches stoichiometry. To divert exhaust flow, butterfly valves are placed in front of each reactor. The ability of ZSM-5 zeolite to absorb a wide range of HC molecules in the cold exhaust gas was discussed with HC desorption and activation of catalyst. Various experimental tests are conducted, and the results show a conformal reduction in HC and other exhaust gases. The combination system is operating with targeted back pressure. The potential benefits of using this technology to meet ULEV/SULEV standards are highlighted in this paper along with the challenges related to execution.

*Keywords*: Hydrocarbon, Cold Start, ZSM-5 Zeolite, Catalyst, Valve Technology, Stoichiometry.

### I. INTRODUCTION

A key portion of unburned hydrocarbon (HC) emissions in the unique drive cycle of automotive engines is produced in the initial operating condition before the engine reaches stoichiometry, commonly called the "cold start" period. During cold start, the emission conversion is difficult for a conventional three-way converter because exhaust heat is not adequate. A catalyst is fully effective only if temperature reaches approximately 250°C-340°C, which is called "light off." The converter takes time – a delay period – in heating up

to start significant chemical reactions. During this delay period, approximately 70%-85% of hydrocarbons is left open to the environment causing "photo chemical air pollution." Hydrocarbons react in the presence of nitrogen oxides and sunlight to form ground-level ozone, a major component of smog. The major causes for these emissions are non-stoichiometric combustion, dissociation of nitrogen, and impurities in the fuel and air. [1, 2]

Currently, to decrease HC emissions and increase the higher conversion rates of three-way converters, electrically heated filaments are used to heat the catalyst and simultaneously reduce emissions. This technology, however, is not effective. To reach the goal of an ultra low emission vehicle (ULEV), a new technology needs to be implemented. We have designed a phenomenal converter system to trap cold start HC emissions, with two chemical adsorbent/absorbent reactors; one is filled with ZSM-5 zeolite and the other with Pt: Pd: Rh catalyst for a Briggs & Stratton 10 hp gasoline engine. Our research study of adsorption and absorption principles shows that the properties of ZSM-5 zeolite has a higher tendency to absorb/adsorb hydrocarbon emissions. Accordingly, we have used ZSM-5 zeolite as our absorbent using the Flow Swing Over Valve technology. The primary approach of this concept also factors complexity, durability, and cost. Engine specifications, operating mechanisms, valve technologies, and other tests validating design and comparing emission levels are explained in detail, below. [3, 4]



II. ENGINE OVERVIEW TABLE I ENGINE SPECIFICATIONS

Engine Make	Briggs & Stratton		
Engine Model No	20S232-0036-F1		
Displacement	305 cc		
Bore	3.12 Inch		
Stroke	2.44 Inch		
Max Power	10 hp		
Exhaust Specifications	Comes with Stock Muffler		
Fuel Type	Gasoline		



Figure 1. Briggs and Stratton 10 hp Engine

Engine dynamometer test data is plotted in Table II. As per results, the converter is designed to meet the requirements.

TABLE II ENGINE DYNAMOMETER TEST DATA

Power	10 hp		
Torque	19.8 Nm		
Exhaust Back Pressure	12.6 mmHg (Idle rpm) 32.9 mmHg (Max rpm)		
Exhaust Temperature	586°C (Idle rpm) 704°C (Max rpm)		

### III. DESIGN CONCEPT & VALVE OPERATION

# A. Design Parameters (Calculated)

Converter volume = 650 cc Intake air flow (CFM) = 15.342 CFM Volume Flow Rate= 34.77 m<sup>3</sup> Density of the Exhaust emissions = 1.43 Kgm-3 Mass Flow Rate = 47.63 Kghr-1



Figure 2. Shows the Representation of Paths and Valves

- In Figure 2, exhaust gas flow paths and valve positions are illustrated. Path A shows the flow through zeolite and the three-way converter (TWC). Path B shows the flow through only the TWC.
- The concept and all operation details of the converter are explained in detail, below.
- Initially, exhaust gases coming out of the engine are directed toward the zeolite absorbent reactor chamber in Path A by closing the three-way converter in Path B.



• Two valves A&B are placed to bypass exhaust gases using a split joint. The valves placed inside are driven by the motor. Motors of each valve are electronically assisted through an ECU coding using Arduino board.



Figure 3. Shows the Valve Motion Circuit Diagram

- A temperature sensor is placed in front of the TWC to read the temperature of flow and catalyst and it is mapped in ECU.
- Another spring-type, Valve C, is placed in the second split joint, which is mechanically operated; it is located in the outlet of the zeolite reactor chamber to restrict back flow coming from the TWC Chamber.
- Once the engine is operated, depending upon gas temperature, Path B is blocked and the flow is directed toward the Path A zeolite chamber to absorb the hydrocarbon emissions.
- Because of operating pressure, spring Valve C automatically opens and directs the flow to TWC.
- Until TWC reaches its "light off," Path B is blocked by closing Valve A, and gases will flow through both of the reactors with optimized back pressure.
- After the temperature sensor measures the catalyst's temperature at 300°C, the flow through Path A is continued for five seconds to wash out the hydrocarbon emissions from the zeolite chamber w.r.t ECU programming.
- Absorbed hydrocarbons will start desorbing completely after the temperature reaches 300°C. The hydrocarbon molecules absorbed inside the converter will not perform any blocking action in the front face of TWC. The burning starts after the engine reaches stoichiometry.



Figure 4. Shows the Valve A Open, Valve B Closed and Vice Versa

- After 10-15 seconds of operation, flow through Path A is blocked by closing Valve B. By opening Valve A, flow is directed to the TWC-only Path B.
- Subsequently, Path A is blocked and the mechanicallyoperated spring Valve C closes automatically and restricts the back flow from TWC.



Figure 5. CAD Model with ECU Unit and Valves

• As a result, after TWC reaches its "light off," the flow is diverted directly to it for normal conversion operation.

IV. ABSORBENT SELECTION CRITERIA

The key characteristic parameters used for the selection of absorbent are highlighted below:

- Disintegration Temperature of the Absorbent;
- Desorption Temperature;
- Limiting Reaction (Saturation Pressure)
- Back Pressure
- Number of Active Spots Remaining post-Process
- · Commercial Availability and Feasibility



Based on these parameters, we evaluated activated carbon: BEA zeolite and ZSM-5 zeolite. Additionally, we zeroed down to ZSM-5 zeolite because of its higher affinity toward absorbing/adsorbing carbon materials. Its higher disintegration, desorption temperature, and availability shows the practical usage.



Figure 6. ZSM-5 Zeolite Pellets

V. PROPERTIES OF ZSM-5 ZEOLITE



Figure 7. Zeolite Crystalline Structure

- Empirical formula Na<sub>n</sub>Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>·16H<sub>2</sub>O 19<n<96.
- The crystallographic unit cell of ZSM-5 has 96 T sites (Si or Al), 192 O sites, and a number of compensating cat-ions depending on the Si/Al ratio that ranges from 12 to infinity.
- ZSM-5 of any pore size can adsorb and absorb hydrocarbons and to some extent other carbon-based emissions. It has a pore size ranging from 4.6 angstroms to 5.4 angstroms.
- No deterioration up to temperature of 1100<sup>o</sup>C.
- The ZSM-5 zeolite limiting factor is calculated as 1.75.

- Desorption starts at a temperature significantly above the light off temperature of the commercially available catalytic converters.
- Inexpensive and available in varied sizes, powder, extrusions.
- For any adsorbent/absorbent, limiting factor for the adsorption-desorption cycle must be in the range of 1.5-2.0. ZSM-5 zeolite is in adequate limit of 1.75.

### VI. DESIGN VALIDATION

To validate any converter design, it is necessary to confirm the flow uniformity and structural resonance. We validated our design by analysing it through CFD & FEA.

- A. CFD Analysis (Flow Uniformity)
- 1) Boundary Conditions

For CFD, geometry is meshed with polyhedral mesh and a refined prism layer mesh near the wall. Internal flow field uses the compressible Navier-Stokes equation. The High Reynolds number k- $\varepsilon$  turbulence model is used with standard wall functions for near-wall treatment. The equations of mass and momentum are solved using a simple algorithm for velocity and pressure in the fluid domain. Constant density is used for the solid region. CFD model has approximately 0.4 million cells with maximum skewness angle of 85 degree. [5]

TABLE III CFD BOUNDARY CONDITIONS

Domain	Туре	Value
Inlet	Mass Flow Rate	47.9 Kg/hr
Outlet	Pressure outlet	1 bar
Three-Way Converter	Porous Media	Porosity = $0.8136$ Cell density = $400/6.5$
Zeolite Chamber	Porous Media	Porosity = 0.786





Figure 8. CFD Uniformity Plane Section at Inlet of Zeolite Chamber & TWC

Below, Figures 9 and 10 show the uniformity plot of ZSM-5 zeolite chamber and TWC, respectively. The reactor chambers' uniformity is > 0.85, however, the target is > 0.90 for initial confirmation of the analysis. To reach the uniformity target, inlet and outlet cone optimization is done in later stages.



Figure 9. Shows the Uniformity Plot of Zeolite Reactor Front Face > 0.85



Figure 10. Shows the Uniformity Plot of TWC Front Face > 0.86

### 2) Pressure Drop

Below figures show the pressure drop obtained in both cases:

Case A – Zeolite Valve Open, TWC Valve Closed (Flow through both catalysts.)

Case B – Zeolite Valve Closed, TWC Valve Open (Flow through only the TWC.)



Figure 11. Shows Zeolite Valve Open and TWC Valve Closed



Figure 12. Pressure Drop Contour Plot Observed Pressure Drop is 63.16mbar.





Figure 13. Shows Zeolite Valve Closed and TWC Valve Open



Figure 14. Pressure Drop Contour Plot Observed Pressure Drop is 42.49 mbar.

Above, Figures 12 and 14 show the pressure drop between two cases. For Case A, the observed pressure drop is 63.16mbar; for Case B, the observed pressure drop is 42.49mbar.

The calculated pressure drop is within target criteria. Hence, it will not affect engine performance. To achieve optimized back pressure, the after treatment system is tested in cold flow air condition (explained in testing section). 3) Flow Distribution

Below, figures show the flow distribution in both the pathways which is Valve A is open and Valve B is closed, vice versa.









Figure 16. Flow through Path B (Refer Figure 2)

#### 4) Observations

- As per above results, the uniformity and pressure drop are within the target criteria.
- Further studies show that the difference of pressure drop between Cases A&B is 20.67 mbar.
- The uniformity of the zeolite reactor in catalyst front face is 0.856, and the uniformity of TWC converter front face is 0.86.
- To check the local temperature conjugate, a heat transfer analysis is necessary. The chosen materials have service temperature above 800°C (SUS409L).



- B. Finite Element Analysis
- FE Model is developed with four noded quad shell elements for most of the components as a mid-surface mesh.
- Weld between all components is modeled with quad shell elements 3 mm in thickness.
- Inlet flange is meshed using hexahedral elements.
- The converter and mat are considered as CONM2 1D mass and applied at the independent centre point of shell using RBE2.
- For all components, globally, the element size is taken as 4mm.
- BOM materials and properties are assigned. Valves are meshed and analyzed under stationary condition (without valve motion).



Figure 17. FEM Model of Converter Assembly

### 1) Boundary Conditions

- Inlet flange bolt holes are constrained in all d.o.f., and other clamp joints placed inside pipe to mount the system are constrained in all d.o.f.
- Engine excitation frequency is calculated at rated speed, which is 31.66 Hz; factoring in safety, the target set is 1.4 times the latter, 44.33 Hz.



Figure 18. FEM Model with Boundary Conditions



Figure 19. Mode 1- 273.05 Hz Vertical Mode of Zeolite Catalyst Assembly





### 3) Observations

- It is observed that the first mode occurred in zeolite catalyst assembly, which is of 273.05 Hz.
- Critical areas are concerned with the clamp having mode shapes bending and twisting in first-, second-, and third order vibration frequencies.
- As per this result, the resonance between the engine and exhaust system will not occur.
- Further studies, like static, dynamic balancing, and thermal durability are needed for additional confirmation.



VII. PROTOTYPE FABRICATION:

A. Sample Preparation and Details

TABLE IV ZEOLITE CHAMBER DETAILS

Shell dimension	Dia 96 X L 82mm	
Shell volume	557 cm <sup>3</sup>	
Cross sectional area	68 cm <sup>2</sup>	
Wire mesh weight	92.4 gm	
Wire diameter	0.2 mm	
Wire mesh +Zeolite density	0.30 g/cc	
Zeolite used	ZSM-5	
Zeolite pellets size	1/8 <sup>th</sup> inch	
Zeolite pellets	80 gm	
Zeolite pellet diameter	1.68 mm	

- Initially, a zeolite shell chamber with above specifications is fabricated. To restrict the motion of wire mesh, metal straps are welded in both ends.
- To maintain the optimized back pressure wire mesh is selected with 0.2 mm of diameter, and zeolite pellets are loaded layer-by-layer with wire mesh to restrict the movement of pellets during engine operation.

TABLE V. ZEOLITE SHELL AND LOADING OF PELLETS



• The 80 gm of zeolite is stuffed in four layers, each layer with 20 gm to maintain uniform absorption.

- Then both the cones are welded in the ends of the shell to complete the converter assembly.
- Table 5 Shows the loading of pellets and the completed zeolite chamber assembly with metal straps.

Substrate dimension	Dia 86 X L93 mm
Cell density/Wall thickness	400/6.5
Substrate cross section area	$58 \text{ cm}^2$
Catalyst (Pt:Pd:Rh)	0:26:4 (30gm/cuft)
Support mat	Expandable mat
Design gap	3.5 mm
Shell dimension	Dia 96 X 99 mm
Shell material	SUS 409

TABLE VI. THREE WAY CONVERTER DETAILS

• Three way converter catalyst is wrapped with the mat and stuffed using universal testing machine (UTM).



Figure 21.Stuffed Three Way Converter Assembly

• Cones are welded at the both the ends of shell to complete the TWC assembly.



B. ECU unit Assembly



Figure 22. Shows the Microcontroller Assembly

- A programmed microcontroller is assembled in the metal box and it is welded in the pipe section with metal straps.
- To ensure lower temperature, the metal box is insulated, and a battery connected with the microcontroller unit is positioned inside of this assembly.
- Wire connections to the temperature sensor and the motors are insulated properly to ensure safety.
- The temperature sensor sensitivity is measured as per standards and is capable of withstanding temperature up to 1100°C. It is positioned by drilling the hole in upstream of the TWC assembly.
- Leak test is done to check all the joints and welds, measuring under 0.2 LPH.



Figure 23.Shows the Rotary Valve Placed In the Pipe

- Valve shown in Figure 23 is positioned in pipe with minimum allowable tolerance of ±0.2mm to ensure the motion.
- Valve is then mounted with the motor joint and a metal bush ring is seated to avoid leak.



Figure 24. Shows the Final Prototype of After System

### VIII. TESTING AND VALIDATION :

A. Raw Emission Test Results

TABLE VII SHOWS RAW EMISSION TEST RESULTS

Parameters	Average Values		
-Hydrocarbons (ppm)	1937		
Co <sub>2</sub> Carbon-di-oxide (%)	8.30		
NO <sub>x</sub> - Nitrous oxides (ppm)	100		
Co - Carbon Monoxide (%)	5.76		

• Test is conducted under rated rpm of the engine.



Figure 25.Shows the Raw Emission Testing of Briggs & Stratton Engine



- B. Back Pressure Validation
- Sample is mounted in the flow adapter, and adapter is interfaced with the air tank.
- Blower output is connected to the air tank.
- Pressure sensor one is placed 50mm before the converter assembly.
- Pressure sensor two is open to the atmosphere.
- Outlet pressure of the test sample is kept as 1atm.
- Pressure drop is measured under cold flow condition.



Figure 26. Shows the Back Pressure Test Setup

1) Test Conditions

 TABLE VIII

 TEST CONDITIONS TO MEASURE THE BACK PRESSURE

Parameters	Time (sec)	Mass Flow Rate (kg/hr)
Stage 1	0 to 120	45
Stage 2	120-240	47.9
Stage 3	240-360	50
Stage 4	360-480	55
Stage 5	480-600	60

Test is conducted under two cases.

Case 1 - Path A (refer Figure 2) with dual chambers (Bypass Flow)

Case 2 - Path B (refer Figure 3): Straight Flow



Figure 27. Shows the Bar Chart of Pressure Drop Measured Across Two Cases 1 and 2

### 2) Observation

- Pressure drop measured in cold condition for 47.9 Kg/hr in case 1 and case 2 is 9.8 and 7.3 mbar, respectively.
- The difference between CFD and test results is due to CFD being measured in hot condition while the test is conducted in cold flow condition.
- Our aim is to measure amount of pressure drop in zeolite chamber, which is of 2.5mbar in cold condition. (acceptable limit).
- C. Emission Test Results and Comparison
- 1) Test Conditions
- Test is conducted under four conditions: idle and maximum rpm ranges with and without zeolite chamber (explained in detail, below)





Figure 28. Shows the Ultra Low Emission Converter Testing

The emission test is done under precise test conditions which the engine is allowed to cool down up to 4 hours for each hydrocarbon measurement.



Figure 29. Shows the Results Measured in AVL Gas Analyzer

TABLE IX EMISSION TEST RESULT COMPARISON

Test Conditions	CO %	HC (ppm)	CO2 (%)	No (ppm)
Raw emission - Max.rpm	5.76	1937	8.30	100
With only TWC - Idle rpm	3.89	1225	4.40	120
With only TWC -Max.rpm	3.30	462	4.60	10
With TWC and Zeolite chamber - Idle rpm	2.87	79	3.9	19
With TWC and Zeolite chamber - Max. rpm	3.57	74	5.10	18

To read the results accurately in "cold start" each emission test is conducted with a time gap.



Figure 30. Shows the Amount of Emission Reduction w.r.t rpm

- 2) Observations
  - Compared with engine raw HC emission, ultra low emission converter emission is greatly less: approximately 93%, from 1937 ppm to 74 ppm.
  - It is observed that with only the three-way converter, HC emission is approximately 1225 ppm during idling conditions whereas it is approximately 79 ppm with TWC and zeolite chamber.
  - Also, TWC HC emission is approximately 462 ppm during Max.rpm conditions whereas it is approximately 74 ppm with TWC and zeolite chamber.
  - Other emissions like  $No_x$ ,  $Co_2$  etc. also decreased considerably.



### IX. CONCLUSION

An aftertreatment system achieved partial zero emission by a cold start zeolite based hydrocarbon (HC) trap in combination with the conventional three-way catalytic converter. The feasibility of the system is also verified in a 10 hp gasoline engine. Approximately 93% reduction in cold start hydrocarbon emissions is achieved by adsorption system. The "Flow Swing Over Valve" technique is successfully executed to route the exhaust gas to the hydrocarbon trap. The capability of ZSM-5 zeolite to absorb a wide range of HC molecules in the cold exhaust gas is proven with HC desorption and activation of catalyst. The system also is able to meet the targeted back pressure. The absorber/adsorber system can be effectively used on vehicles to comply with low emission norms.

### X. ACKNOWLEDGEMENT

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### Definitions/Abbreviations

Pt:Pd:Rh - Platinum:Palladium:Rhodium

ECU - Electronic Control Unit

HC - Hydro Carbon

NO -Nitrous Oxide

CO - Carbon Monoxide

CO2 - Carbon - Di -Oxide

ZSM5 - Zeolite Socony Mobil-5

LPM - Litre Per Minute

ppm - parts per million

Nm - Newton meter

hp - horse power

RPM - Revolutions Per Minute

TWC - Three Way Converter

D.O.F- Degrees Of Freedom

ULEV/SULEV- Ultra / Super Ultra Low Emission Vehicle



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As a corporate executive in the United States and India for over three decades, Dr. Rajadurai managed strategy on power train development and emission control for low, ultra low, super ultra low and partial zero-emission systems.



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