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Exploration of Zeolite 5A as a catalyst in the after-treatment system of a CI engine powered by plastic oil blend

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Abstract. Catalytic converters are commonly used for automotive engines to reduce regulatory emissions. Catalysts used in commercial converters are expensive and they work in particular temperature ranges. To overcome those problems, Zeolite 5A powder is chosen and used as a catalytic material in the catalytic converter to reduce the emissions from the Compression Ignition (CI engine). Zeolite 5A was molded into solid by adding distilled water and carboxymethyl cellulose as binder material. The prepared solid mold was used as catalytic material in the exhaust gas after-treatment system. The waste plastics were pyrolyzed into oil and blended equivalently with diesel (50:50 ratios) for this investigation. The performance and emission readings were taken by varying the engine loads (0, 1.32, 2.6, 3.9 and 5.2 kW) in the single-cylinder 5.2 kW CI engine. The NO and HC emission were reduced by 37% and 33% respectively at the full load condition.

1. Introduction

Almost 81% of the world's total industrial energy is reliant on fuel combustion. This provides and remains the dominant supply of energy for the predictable future [1]. In this regard, considerable waste plastic is reused, which is very significant. Also, it is used as an alternative source of oil, which is used to reduce emissions in IC engines. The utility cost is also meager when compared with other fuels inclusive of alternate fuels. The oil properties are also comparable with biodiesel, alcohol, etc for CI engine usage. Excess plastic contains more hydrocarbons, and it also has a high calorific value, which is very much significant from the environmental pollution perspective. But carbon monoxide emission is much greater than diesel fuel usage. The NO and Sox emission also reduces due to their blend with diesel at a particular ratio [2].

Another engineering technology which is used to reduce the emissions is the usage of converter mounted on the vehicle gas manifold. The exploitation of three-way catalytic converters is developed based on the noble metal catalyst (Platinum group: Platinum (Pt), Palladium (Pd), and Rhodium (Rh). These catalysts are used in a significant manner for the conversion of the unburned hydrocarbon emissions into carbon dioxide and water. The carbon monoxide is converted into carbon dioxide, and nitrogen oxide is converted into nitrogen. These metals have particular reactivity, higher instability, quick oxidation, and

ability to get easily broken at 500-900°C temperature range. Various materials are coated by Zeolite. These materials are used in adsorption catalysis. This catalysis is used in the separation process [3].

These zeolite catalysts are used to reduce pressure drop and the overall rate of reaction as bulk fluid and catalytic surface mass transfer. The zeolite films contain special-purpose membrane separations. These types of Chemical Vapor Deposition CVD process involves the formation of silica films which are converted into crystalline nanoporous structure followed by a hydrothermal treatment [4]. The Zeolite contains silica and aluminum in a proportion of 10:50. Also, the crystal size is 1:9 µm. They also work at low temperatures. The molding process of zeolite 5A is done in comparatively low temperatures by the substrate heating method [5]. The molded high silica zeolite 5A has a thin film, which makes it conducive as a catalyst for essential applications in the automobile sector to reduce emissions. Research has proved that the Zeolite powders can be manufactured in hydrothermal conditions using porous silica attained by the selective discharge of the metal structure [6].By using extrusion of paste, the honeycomb structure has been made with the powder synthesized over a multi-hole honeycomb die. structure was studied by using X-Ray diffraction XRD The zeolite and Fourier transformation infrared spectroscopy FTIR adsorption. Zeolite grains are manufactured from this exposed plate morphology method through a suggested induction of crystals in the resulting surface. Finally, the Zeolite-coated honeycombs exhibit mechanical and thermal stability. Another research shows that the influences of micro porous silica manufactured using acid leaching method on metakaolinite. This is the cheapest material for the preparation of Zeolite honeycomb monoliths with precise morphology [7].

In gasoline-powered cars, the automotive industry uses the cordierite ceramic honeycomb structure in the catalytic converter to reduce Carbon Monoxide CO, NOx, and HC emissions. A new honeycomb composite structure consists of micro porous Zeolite and micro porous mullite, which is developed by in-situ crystallization from the sintered kaolin honeycomb. This process of crystallization of Zeolite 5 (ZSM-5) leads to better adhesion and mechanical strength of ZSM-5. This also results in a grouped composition with three-layers resulting in good adhered Zeolite film at the surface. In the first few minutes of operation, a significant amount of the total emission is produced by a gasoline-powered car produce in a single trip. This signifies the existence of the catalytic converter in operating temperatures below 300°Cat the beginning of the trip.

The maximum efficiency of the catalytic converter is in the range of 400-500°C. In the process of reducing the various emissions below 300°C, the catalyst conversion is not effective. To convert the HC emission, the catalytic converter temperature has to reach its operating temperature of 300°C. This is done by using micro porous adsorbents such as Zeolite. The honeycomb structure was converted into four portions from the surface to the core. This treatment was conducted for three weeks, which resulted in a complete change of the glass to Zeolite. The treatment witnessed the arrangement of three layers of Zeolite on the surface, Zeolite and mullite under the surface, and the porous mullite in the middle of the honeycomb structure [8].

The catalytic action of Pt-Zeolite-5has been discussed in evaluation with the Cu-Zeolite-5and Pt/Al_2O_3 , and the results have been found to be more active for Pt-Zeolite-5in low temperatures. The alteration of both C_2H_4 and the NO+ C_2H_4 + O_2 effect over Pt-Zeolite-5around the light-off temperature is deeply hindered by the existence of nitrous oxide. The NO/ C_2H_4 ratio in the feed stream was a critical factor that determines the NOx drop activity induced by Pt-Zeolite-5h, which is more effective than Cu-Zeolite-5, when operating in lower temperatures [9]. The catalyst was manufactured by the ion exchange method in an aqueous solution of Pt (NH₃)₄(NO₃)₂. Two Pt loadings of 0.51% and 5.9% wt were used. The Ion-exchanged catalyst dried rapidly in the air at room temperature. Calcinations was performed at 500°C for 4 hours under the constant airflow. Every catalyst was compressed into disk shape using a die with10-ton pressure. Every catalyst has been ground, compressed and screened into

mesh sizes of 80-120. The relatively small effect on NO_x conversion has been observed using Pt-ZSM-5 catalyst [10].

The reduction of NO_x in exhaust gases is accomplished with a transitional pore size Zeolite, such as Zeolite-5based catalyst, which has been treated using iron into its pores. The treatment process is used for the removal of NO_x using iron-containing ZSM-5 as a catalyst and ammonia as a reducing agent. In exhaust gas, this is chosen for extending the effective temperature range for the Selective Catalytic Reduction (SCR) of NO_x below 400°C, without affecting the NO reduction capacity of the catalyst above 400°C in an adverse manner. In the process, the iron is merged primarily into the pores of ZSM-5, using ion-exchange of the iron in an aqueous solution of the ferrous salt under the inert condition and suitable temperatures. This is done for the reduction of ferrous cations to a size suitable for allowing the tiniest portion of iron to enter the pores of Zeolite. After the process of ion-exchange, the Zeolite was recovered and calcinated [11].

In industrial exhaust gases, the specially prepared iron-containing Zeolite proves to be very much efficient for the selective catalytic reduction of NO_x . The copper ion-exchanged ZSM-5catalyst is processed by the ion-exchange with sodium nitrate followed by copper (II) acetate at room temperature and pH of 6.8. The same procedure has been repetitive in anticipation of the ion concentration. The catalyst ZSM-5exchanged ions with Cu^e ions at 0%, 74 %, and 160%, which has been categorized using X-ray diffraction (XRD), infrared spectroscopy, and ammonia desorption. Most of the catalyst loses water below 100°C. 2 molecules per Cu²⁺ ion emerges at high temperatures. The process of ion exchange occurs in the same temperature range of about 150-350°C, which enables the rearrangement in the ZSM-5catalyst disclosed by XRD [12].

The transferable cations of ZSM-5appear critical for the matrix changes enabling the deformation of the catalytically active center at suitable temperature ranges. The process of de-hydroxylation and water desorption is observed between the temperature range of $350-450^{\circ}$ C for ZSM-5catalyst, and the temperature ranges intersections with the light off temperature for direct NO_X breakdown over the Cu-ZSM-5catalytic converter. Exposure of the Cu-ZSM-5catalyst above 600°C results in deactivation. This happens even in dry conditions, which limits practical use. The converter used for the automotive must withstand 1000°C. Some researches indicate that the ZSM-5catalyst is not able to meet this requirement [13].

In Cu-exchanged Cuban Zeolites, the selective catalytic reduction of nitric oxide by ammonia has been performed. In the presence of extra oxygen over Cu-exchanged natural Zeolites from Cuba, the selective catalytic reduction of NO with ammonia as a reducing agent has been made. Exhibiting good water tolerance, high discrimination for N_2 at the low temperatures, and with the conversion of NO around 95%[14], the Cu (II)-exchanged Zeolites are highly active catalysts.

Over H-ZSM-5, the selective catalytic reduction in NO through ammonia was performed. This process was carried out under the influence of transient ammonia supply. The sudden response experiments between 200°C and 500°C have been used to investigate the results of the ammonia injection on selective catalytic reduction of NO over H-ZSM-5. A minimum NO reduction has been observed at 130°C, which was independent of the ammonia adsorption temperature. In the NH₃-SCR reaction over H-ZSM-5, the results obtained revealed that the oxidation of NO_x was accelerated. Finally, it was concluded that the SCR activity and the NO_x oxidation gets suppressed by the presence of NH₃ in Zeolite [15].

2. Experimentation

2.1. Sample preparation using Carboxymethyl cellulose as a binder

The Zeolite-5A powder was mixed with Bentonite clay (8%), carboxymethyl cellulose binder (5%), and distilled water (34%).Constant stirring was done until a paste-like form was achieved. The torque applied was monitored during the stirring until it reached a uniform value, representing homogeneous mixing. The

Zeolite paste was placed in the prepared mold cavity, and uniform pressure was applied to ensure that no gaps were formed in the mold.



Figure 1. Photographic view of Zeolite Paste.



Figure 2. Photographic view of mold after drying.

The holes pattern was made on the catalytic converter by creating uniform holes (10mm) with the help of plastic pipes. The prepared mold was dried for 96 hours in direct sunlight. After drying, the pipes were removed from the mold. The resulting mold was kept in the furnace initially at 100°C with an increase of 50°C every 30 minutes until the temperature reached 450°C. Then it was finally kept for 1 hour for the inducement of calcinations. Carboxymethyl cellulose binder was used as a binder because it possessed good binding properties enabling the formation of uniform extricable paste. The uniform torque was applied until it reached a minimum and uniform value.



Figure 3. Photographic view of the catalytic converter.

2.2. Fuel and Engine specification

Pyrolysis is the process of extracting plastic oil from the recycle plastic waste by thermal decomposition of organic and synthetic material at elevated temperature and also in the absence of oxygen to extract fuel. The pyrolysis process is generally conducted at the temperature range of 500-800°C. The product from the pyrolysis process is divided into a liquid fraction, solid residues, and gaseous fraction

Specifications	Diesel	PPO	Diesel +PPO
Fuel Density (kg/m ³)	832	793	812.5
Calorific Value (kJ/kg)	45500	42000	43750
Kinematic Viscosity, 40 (°C)	2.11	2.51	2.58
Fire point (°C)	50	47	48
Flash Point (°C)	56	52	54
Cetane Number	55	51	53
Ash Content	0.045	<1.01%	~
7 tsh Coment	0.0+3	wt	

	Table	1.	Properties	of test	oil.
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Figure 4. Photographic view of test engine.

Specifications	Parameters	
Make	Kirloskar TV1	
Number of cylinders	1	
Number of strokes	4	
Fuel	Diesel	
Rated power	5.2 kW	
Type of dynamometer	Eddy current dynamometer	
Cylinder diameter (mm)	87.50	
Stroke length (mm)	110	
Compression ratio	17.5:1	
Orifice diameter (mm)	20	

 Table 2. Engine specifications.

3. RESULTS AND DISCUSSION

3.1. Emissions

The emission tests were performed on a Kirloskar TV1 diesel engine. The tests were performed to check the emissions using Zeolite mold. The emission gases to be considered were nitrous oxide (NO), hydrocarbons (HC), carbon dioxide (CO₂), and smoke. Initially, diesel was used as fuel, and the emission base readings and emission readings with and without catalyst were investigated.

The variation of nitrogen oxides emission (NO), under load for diesel, plastic oil, and plastic oil with converter blends is shown in figure 5. The most common mechanism for the assembly of NO emissions in diesel engines is the thermal mechanism, which is due to the high oxygen level and availability under elevated in-cylinder temperatures. It was often observed that the NO emission of the plastic oil with convertor is significantly less compared with that of diesel and plastic oil without the converter. More specifically, the NO emissions of plastic oil and converter are 45% less than diesel at 100% load, and 65% higher at 75% load. The conversions of NO and propene within the reaction gas mixture of NO+C₃H₆ balanced by nitrogen NO and propane are often observed to be at their maximum at over 300°C. NO conversion is detected to be the very best with 0.8 wt-% Ferrierite zeolite, achieving the conversion of over 60%, while the conversion of NO over the opposite studied catalysts is often detected to be around 50%. At low temperatures, hydrocarbons are adsorbed on the surface, and at around 100°C, desorption is often observed (negative conversions).

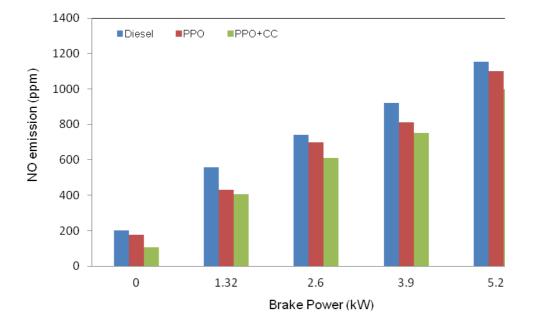
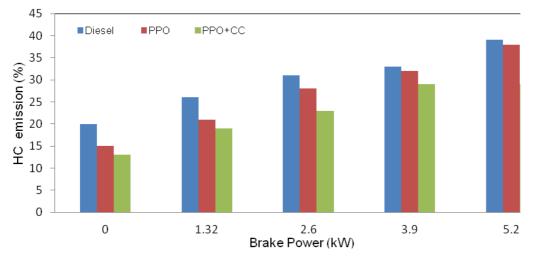
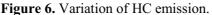


Figure 5. Variation of NO emission.

The figure 6 depicts the variation of unburned hydrocarbon (UHC) emissions with brake power for diesel, oil blends, and the converter. The most common factors affecting the UHC emissions within the exhaust are the under-mixing or over-leaning zones resulting in wall flame-quenching [4],[5]. The HC emission for the plastic oil is less compared to diesel fuel. Plastic oil with catalytic convertor further reduces the HC emissions. The ratio of reduction of HC emission with brake power revealed that the metal and 5A zeolite catalysts as ion-exchangers reduced hydrocarbon emission levels. This depends on unsaturated hydrocarbons, which are often depicted as oxide dissociation reaction occurring catalysts. Also, the chemically unsaturated hydrocarbon is responsible for the removal of absorbed oxygen generated by oxide dissociation.





The Figure7 presents the variation of carbon monoxide gas (CO) emissions against the load. The low equivalence ratio (ϕ) and the high in-cylinder temperatures of the diesel engines resulted in very low CO emissions. High CO exhaust emissions from diesel engines are a symbol of incomplete combustion. The experimental results reveal that the CO emissions decreased because of the load increase for all fuel blends. The CO emissions of diesel are slightly above the plastic oil and catalytic converter. These results indicate deterioration of the combustion process, which is severe in the case of diesel and converter at 75% load. This behavior is often explained by the lower cetane number and the higher aromatic content of the fuel blends, which cause longer ignition delay and shorter combustion periods. Carbon monoxide is reduced significantly while using this sort of zeolite5A as a converter. These sorts of catalysts convert the carbon monoxide gas into CO₂ within the exhaust gas. At a high-temperature, the carbon monoxide gases with practical oxygen resulting in emission decrease.

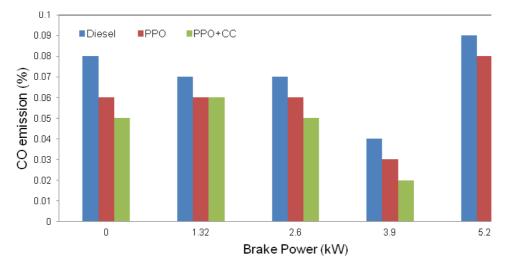
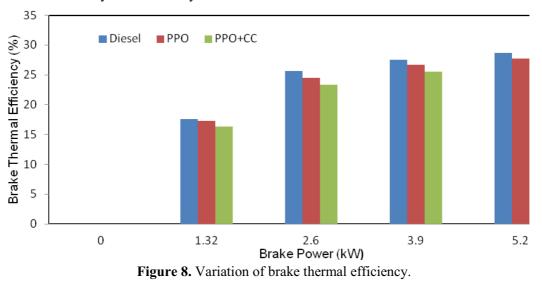


Figure 7. Variation of CO emission.

3.2. Performances

Brake thermal efficiency (BTE) for the diesel, plastic oil with and without catalytic converter were given in the Figure 8. The BTE increases with increases in load. The BTE of plastic oil with catalytic convertor is found to be slightly less compared with without convertor. This may be due to the slight pressure drop created due to the catalytic convertor system.



4. Conclusion

Zeolite was used to prepare the catalyst mold for the substrate structure using carboxymethyl cellulose as a binder using the conventional casting methods. The following conclusions were observed.

- 1. The NO and HC emissions decreased by 37% and 33%, respectively, under the zeolite 5A catalyst usage.
- 2. The CO emission decreased by 29% under the zeolite 5A catalyst without a significant reduction in performance.

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