Catalytic Converters
A Comprehensive Investigation

Catalytic Converters are required for nearly every internal combustion engine in use today. This paper is a look into the creation, current innovation and future uses of these devices crucial for the continued health of the global climate.
There are millions of cars being driven worldwide with a daily consumption of nearly 90 million barrels of oil with 6200 megatonnes of CO₂ annually produced in the United States alone. Considering how much of an impact all of that green house gas had on the global climate however the most dangerous chemicals are considered those of nitrogen oxides including NO and NO₂ and hydrocarbons made up of un-burnt fuel. To filter nitrogen oxides as well as other dangerous chemicals coming from the exhaust, automotive manufacturers put catalytic converters on their cars.

**History**

The Catalytic converter was invented by a French engineer named Eugene Houdry in 1953. Eugene Houdry began work on the catalytic converter after reading a report published about the increase of smog in Los Angelis California due to the increased number of cars in the LA area. Houdry went to a company called Oxy-Catalyst which was also looking to develop a way of curbing the emissions of automotives. Although the first catalytic converter was developed in 1953 the application was impossible at the time due to the lead in the gasoline used in the United States at the time. The lead in the gas coated the catalyst materials in the converter rendering them useless and due to leads high boiling temperature, it cannot be liquefied or sublimated like other common contaminants. The device’s practical use was not until 1976 when federal law required all cars to be equipped with a catalytic converter leading to leaded gasoline to be phased out although not outlawed until 1996. Unfortunately Houdry died in 1962 and never saw the implementation of his design but his legacy lives on with the modification of
his original design called the three-way catalytic converter developed by a team of engineers, led by Carl D. Keith. Today the required reduction of pollutants is over 95% which continues to challenge the designers of catalytic converters.

*Catalytic converter connected to engine*

Species

The modern three-way catalytic converter is used mainly in automotives was developed in 1981 for the standard gasoline automotive is so named because it has three catalytic reactions that take place inside it. The three reactant pollutant categories which give the three-way converter its name are nitrogen oxide, carbon monoxide and unburnt hydrocarbons. The first process is that of a reduction catalyst where there is a reduction of nitrogen oxides into nitrogen and oxygen in a ceramic honeycomb coated with platinum and rhodium. This process requires the use of hydrocarbons as a reactant in the reduction of NO emissions as well.
2CO + 2NO → 2CO₂ + N₂

HC + NO → CO₂ + H₂O + N₂

2H₂ + 2NO → 2H₂O + N₂

The second process uses the oxidation catalyst of a platinum and palladium honeycomb. This process oxidizes carbon monoxide into carbon dioxide and requires one O₂ molecule for every CO molecule.

2CO + O₂ → 2CO₂

HC + O₂ → CO₂ + H₂O

Because all of these processes require oxygen, they work best when there is air left over after the engines combustion process. This is done with the aid of a computerized closed loop fuel injection system which runs the engine at a higher than the stoichiometric point. stoichiometric combustion being when the ideal mixture of gas and air are used for complete combustion so above stoichiometric means there is still air left over after combustion to aid the reactions in the catalytic converters.

In diesel engines the main catalytic converter in use is a Two-way catalytic converter which has only the two oxidation processes. These involve the oxidation of carbon monoxide into carbon dioxide and hydrocarbons into carbon dioxide and H₂O. the reason why there is no nitrogen oxide reactions is because the diesel reaction has too few hydrocarbons in its exhaust to
effectively convert them as well as an exhaust temperature of 80–180 °C which is below the light off temperature of hydrocarbons and de-sulphurisation of the catalysts, which generally requires temperatures above 650 °C. This requires the addition of other reducers for the maximization of the process.

\textit{Cross sectional view of catalytic converter}

Materials

The most common materials used in a catalytic converter vary for several different reasons but three main types remain a constant.

The first and most important material category is that of the catalysts used. A catalyst is a material that reduces the energy required for a chemical reaction to occur without the catalyst
itself being altered or expended. The way which this is done is with a material that can easily exchange electrons with other materials so that when two materials that can combine are in close proximity they are more likely to have their electrons land in the places necessary for this combination. The secret to this exchange is having a material with an ideal d-orbital electron level. The catalysts are all almost exclusively precious metals of exorbitantly high cost. Platinum is the most effective and commonly used but also the most expensive which leads to the implementation of alternative of rhodium although it is still very expensive. The oxidation catalyst that can replace platinum is palladium and although Cerium, iron, manganese and nickel are also possible catalysts they have problems such as reactions with carbon dioxide reactions and dioxin formation.

*Reactants and products in a catalytic converter*

The honeycomb portion of the catalytic converter is either a ceramic or metallic substrate. The advantage of a metallic honeycomb substrate is that the wall thickness can be varied to optimal
performance although the process is still limited due to its expense. Ceramic structures are more cost effective utilizing predominantly a Cordierite monolith which has a wall thickness of 0.007 in compared to that of .002 in for the metallic form. The catalysts are sprayed in the smallest droplets possible on the honeycomb to reduce cost and maximize contact area.

*Metallic honeycomb structure catalytic converter*

*Metallic honeycomb structure catalytic converter*
The washcoat is a coating designed to increase the efficiency of the catalyst which is often as a mixture of silica and alumina. The coating makes the surface rougher to increase surface area so the microspheres of catalyst have more contact area with the pollutants.

Pollutants

There are several key pollutants that are addressed by the catalytic converter, each with its own effects on the environment for several reasons.

NO and NO$_2$ or nitrogen oxides the chemicals react with sunlight in the upper atmosphere to create oxygen which adds to the ozone layer and increase global warming. What happens with NO is that it rises up to the upper atmosphere where it reacts with partly oxidized organic species to create NO$_2$. NO$_2$ then reacts with sunlight to make nitrogen and oxygen gases allowing the oxygen to go into the ozone layer and increase global warming as shown in the below equations.

$$\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3\text{O}$$

$$\text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}$$

NOx compounds are also responsible for creating smog and acid rain. This makes the reduction of nitrogen oxides of crucial importance to the health of the planets ecosystem.

Carbon monoxide is a highly toxic odorless colorless chemical which combines with hemoglobin to produce carboxyhemoglobin, which is ineffective for delivering oxygen to bodily tissues. This causes a lack of oxygen which can lead to damage to the brain, heart or central nervous system or even death. In the atmosphere carbon monoxide reacts with HO which is harmless enough on its own except that HO is crucial for the destruction of methane and troposphere ozone.
One form of pollutant which is very hard to eliminate is sulfur compounds including sulfur dioxide and sulfur trioxide which are created in the combustion process of fuel containing sulfur. The sulfur oxides further oxidize using nitrogen oxides as a catalyst to produce sulfuric acid and in the case of automotive exhaust manifest in the form of acid rain.

\[ \text{SO}_2 + 2 \text{H}_2\text{S} \rightarrow 3 \text{S} + 2 \text{H}_2\text{O} \]

The main way of combating this process is the reduction of sulfur in the fuel source however the catalytic converter also plays an important role by reducing the nitrogen oxides. However the corrosion caused by the compound continues to pose a problem in the automotive exhaust system.

Carbon Dioxide is a greenhouse gas and the most common one produced in every day human activity. Today the carbon dioxide concentration in the atmosphere stands at 380 parts per million (ppm) compared to a pre-industrial high of 280ppm. That is an increase of 30% with the level rising about 2ppm per year this is very bad for global warming considering it has been more than 800,000 years since levels were this high and that was due to spikes in volcanic activity. However that was abated by the forest covering the earth over the course of hundrads of thousands of years and with so much less natural forest in our age it may be many times that before we can return the levels to their ecological equilibrium. Despite the threat from this emmision the catalytic converters commonly in use have no way of abaiting its exhaust in the atmosphere leaving carbon monoxide emmisions the largest and least regulate emission in the modern combustion engien. Luckily there is hope for reducion corbon dioxide
emissions in the near future which is addressed later in this paper.

### Exhaust concentrations for different chemicals

*Percentages of pollutants removed in standard three-way converter*

Problems

One of the original problems with the catalytic converter is the requirement of above stoichiometric air quantities which decrease the power of the engine. This problem was far
more pronounced in the 70’s when the catalytic converter was run with engines using a carburetor. Since the implementation of the fuel injection system, particularly the closed loop control system, the power loss has been reduced significantly since the excess oxygen can be monitored and the fuel mixture adjusted accordingly. However, the main problem in this case is the post production removal of the catalytic converter by some car owners who want extra power but in a modern car there will not be any noticeable power increase without retuning the fuel injector system.

One continuing problem which seems to be worsening is the theft of catalytic converters due to the concentration of precious metals in them. Theft is often an especially large problem for sports utility vehicles and trucks with high ground clearance and easily accessible exhaust systems. The only real solution for the increase instance of theft would require a change in automotive undercarriage design to limit the access to the catalytic converter or at least have a car alarm capable of sensing an invasion in the undercarriage. The problem with making the catalytic converter more internal in the car is that this can increase the chance of heat buildup and a possible meltdown.

A catalytic converter meltdown is unlikely but catastrophic when it does occur due to the constriction of the exhaust flow. A meltdown is caused by a large build up of hydrocarbons which continue to burn inside the converter and raise its internal temperature. If unchecked the temperature can raise to the point where the substrate honeycomb actually melts and constricts the flow of exhaust, sapping the engine power. Generally the only warning of this is
given by a check engine light which is often ignored which is another reason why the warnings should be more specific for the driver to interpret the problem.

Another problem that is becoming more prominent as the emissions standards continue to rise is the large amount of pollutants emitted due to cold starting the engine. When the engine is started in a cold state the catalytic converter in particular takes a large amount of time to heat up to optimal operating temperatures. A large amount of pollutants are released unregulated during this warm up period and are taken into account for the vehicles overall emissions. To solve this there are several methods with the three-way catalyst that involve heating faster either with a form of block heater or having another reaction section closer to the engine so it can heat faster. The most promising solution however is one where the chemicals that need higher temperatures to process effectively are stored in some way until the converter is properly heated.

One of the most technical problems with the catalytic converter common in diesel automobiles is the lack of significant reduction of nitrogen oxide due to the lack of unburnt hydrocarbons. This is a problem due to the increased strictness of many emissions laws and requires the addition of at least one element to the system for legal emission compliance. One method is to add a reducer to the mixture which requires a distribution method and occasional replenishing. This can be accomplished with either Selective Non Catalytic Reduction (SNCR) or Selective
Catalytic Reduction (SCR) which use either ammonia or the less toxic urea.

The SNCR reaction is as follows

\[ \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \]

While the SCR reaction is as follows

\[ 4\text{NO} + 2(\text{NH}_2)_2\text{CO} + \text{O}_2 \rightarrow 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2 \]

These reactions are used in conjunction with either ceramic or metallic catalysts. Base metal catalysts, such as the vanadium and tungsten are cheap but have short life spans due to relatively low thermal durability and the catalytic potential with sulfur compounds which corrode and further reduce the system life span. Zeolite is also a promising component which can act as either a catalyst or filter to aid in separation of nitrogen and oxygen.

Zeolite is an artificially manufactured ceramic which is already used in medical equipment for the use of separating oxygen in air from the nitrogen to produce high oxygen concentrations. Zeolites are porous crystal structures with channels. They are made up of silicon and oxygen.
but often have aluminum atoms as well.

Zeolite Crystal formation

Zeolite formations have seen promising results in the reduction of nitrogen oxides especially a new form using zeolite nanofibers produced by the University of Akron.

Zeolite nanofibers

These heat treated nanofibers are capable of substantial catalytic conversion of nitrogen oxides at low temperatures in conjunction with urea. The nitrogen oxide reduction has shown to be as high as 90% in laboratory tests but practical application has yet to be seen.
Lean-Burn Engines

A up and coming engine design utilizes high compression ratios and high air fuel ratios above that of the stoichiometric value of 14.7lb of air for each pound of gasoline. This gives considerable fuel savings in the engine but it also creates a problem for catalytic converters. Three-way catalytic converters require a certain amount of unburnt hydrocarbons to operate however with such an efficient burn, the availability of combustible hydrocarbons in the catalytic converter is greatly reduced. This gives the same problem as with diesel engines as far as the reduction of nitrogen oxides go and has spurred a vast amount of research in the field. As of 2003, over 50 different catalyst candidates have been found to solve the problem however there are only a few that will really work.

The best solution to the problem was developed by a Dutch researcher Karen Scholz who designed a lean burning system where the engine alternates from long periods of lean burning to short spurts of rich burning for the soul purpose of getting the catalytic converter to work properly. A catalyst of barium is used to store the nitrogen oxide emissions by absorption until it becomes saturated. At a interval timed to coincide with the saturation, the engien will begin running rich so as to give the nitrogen oxides hydrocarbons to react with and cleanse the catalytic converter so that the engine can go back to the more efficient lean burning cycle. This is good
Showing the effect fuel mixture has on pollutant emissions

Fig. 20. Principle of operation of an NSR catalyst: NOx are stored under oxidising conditions (1) and then reduced on a TWC when the A/F is temporarily switched to rich conditions (2).
Showing how NOx can be stored during lean burn period

Air fuel ratio effect on pollutant concentration depending on lean or rich burn
Future Innovations

One of the newest innovations in the field of catalytic converters is a design referred to as a four-way catalytic converter which will have a system for getting rid of the last and most prominent pollutant to be addressed in the combustion process, CO₂. The system will have a separate chamber added on to whatever catalytic converter is implemented before hand with a forced air fan blowing the exhaust onto a CO₂ absorbent zeolite material which will compound the carbon dioxide until it has reached a concentration of 14.67 grams when it will be sealed off and have an addition of 16 grams of magnesium to the carbon dioxide chamber. The magnesium will burn at around 2000°C which will consume the carbon dioxide until all that is left is magnesium oxide and black carbon which can be collected and disposed of at gas stations at the same time that the magnesium is replenished. This would effectively reduce the carbon dioxide emissions substantially and usher a new era of clean automotive operation. There are also new catalysts in development that require no precious metals while increasing efficiency so that the problems with catalytic converter theft will become a problem of the past.
Conclusion

Over the past 25 years there have been many innovations in the field of catalytic converters but it remains one of the least appreciated and most chemically complex automotive components. Much more study and innovation is required in the development of this field because as a planet we will likely still be using combustion engines well into the next few decades and with the advent of decreased oil quality due to over drilling and the increase of population desiring to live outside of urban centers and commute to work there is an expected increase of global fuel consumption of 100% by the year 2030. So the advancement of this technology is paramount to the continuation of sustainable life on are planet.
Works Cited


