ÇUKUROVA UNIVERSITY

INSTITUTE OF NATURAL AND APPLIED SCIENCES

MSc THESIS

Use of Fusel Oil As A Reductant Agent in A SCR System At Low Temperatures

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Department of Automotıve Engıneerıng

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ABSTRACT

Within the study, the efficiency of NO_x transformation rates at low temperatures was examined by using fusel oil for reducing and a catalyst made of Mo-Cu-Ag/TiO_2 in the HC-SCR system. The properties of the catalyst were determined by BET, SEM, FTIR and XRD analysis. The experiments were conducted in the range of 200-300 °C, at 3 different space velocities (30000 h^{-1},40000 $h^{-1}$and 50000 h^{-1}) and under 5 various motor loads (1, 2, 3, 4 and 5 KW). A 2-cylinder V-type diesel engine were used during the experiments. As the outcome of the performance tests, the maximum NO_x transformation efficiencies were obtained at 290 °C, the highest test temperature, at all space velocity values and engine loads. The highest NO_x conversion rate among all tests was obtained as 85.94% at 290 °C at 1 kW at 30000 h^{-1}. Increasing the exhaust gas temperature from 200 to 290°C had a positive effect on the NO_x transformation efficiency.

Keywords: SCR, Exhaust Emissions, NO_x, Reductants, Fusel oil

ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

YÜKSEK LİSANS TEZİ

SCR Sisteminde Fuzel Yağın İndirgeyici Olarak Düşük Sıcaklarda Kullanımı

Şilen Uğur Hikmet SÜMER BAYRAM

Danışman: Prof. Dr. Ali KESKİN

Otomotiv Mühendisliği Anabilim Dalı

ÖZ

Bu çalışmada, HC-SCR sisteminde Mo-Cu-Ag/TiO_2 katalizörü ve indirgeyici olarak fuzel yağ kullanılarak düşük sıcaklıklarda NO_x dönüşüm oranlarının verimliliği incelenmiştir. Katalizörün yapısal ve kimyasal özellikleri SEM, BET, FTIR ve XRD analizlieri ile belirlenmiştir. Performans testinde, üretilen katalizör ve indirgeyici olarak fuzel yağ kullanılarak 200-300 ºC aralığında, 3 farklı alan hızında (30000 h^{-1},40000 h^{-1}ve 50000 h^{-1}) ve 5 farklı motor yükü altında (1, 2, 3, 4 ve 5 KW) deneyler yapılmıştır. Testler 2 silindirli V-tipi bir dizel motor kullanılarak gerçekleştirilmiştir. Performans testleri sonucunda tüm alan hızı değerlerinde ve motor yüklerinde en yüksek NO_x dönüşüm verimleri, en yüksek test sıcaklığı olan 290 °C'de elde edilmiştir. Tüm testler arasında elde edilen en yüksek NO_x dönüşüm oranı 290 °C'de 1 kW'da 30000 h^{-1}'de %85,94 olarak bulunmuştur. Egzoz gazı sıcaklığındaki 200'den 290 °C'ye artış, NO_x dönüşüm verimliliğini olumlu yönde etkilemiştir.

Anahtar Kelimeleri: SCR, Egzoz Emissions, NO_x, İndirgeyiciler, Fuzel yağ

GENİŞLETİLMİŞ ÖZET

Çevre kirliliği, bugün gezegenimizde insanlığın ve diğer canlıların karşılaştığı en ciddi sorunlardan biridir. Çevre kirliliği, çevre, insan faaliyetlerinin zararlı ürünlerini etkisiz hale getiremediğinde ortaya çıkar. Doğal kaynakların kullanım oranı doğanın kendini yenileme kapasitesinden yüksek olduğunda su, toprak ve hava kirliliği oluşmaya başlar. Her türlü kirlilik arasında hava kirliliği ciddi bir noktada dururken, temiz hava sağlıklı bir yaşam için temel ihtiyaçtır.

Kentsel nüfusun hızlı büyümesi, artan sanayileşme, artan enerji ve motorlu taşıt talepleri gibi hava kirliliğini kötüleştiren bazı bileşenler vardır. Dünyamız hava kirliliğinin artması sonucunda küresel ısınma gibi bazı olumsuz etkilerle karşı karşıya kalmaktadır. Küresel ısınmanın geniş kapsamlı, uzun süreli ve birçok durumda Dünya gezegeni için yıkıcı sonuçları olması beklenmektedir. Küresel ısınma, insan faaliyetleri sonucu atmosfere salınan sera gazlarından kaynaklanmaktadır. Bu gazların önemli bir bölümünü dizel motorlu taşıtların saldığı emisyonlar oluşturmaktadır. Bu emisyonlar içerisinde çevre ve insan sağlığı açısından büyük zaralara neden olan NO_x emisyonları, küresel ısınma ve iklim değişikliğinin ana kaynakları arasında üst sıralarda yer almaktadır. NO_x emisyonları en çok dizel motorlu taşıtlardan salınmaktadır.

NO_x emisyonlarının azaltılmasına yönelik sıkı standartlar ve kurallar uygulanmaktadır. Tüm emisyonların sıfıra indirilmesi amacıyla elektrikli araçlara geçiş hızlanmış olsa da Dizel motorların kullanım alanı çok geniş olup kullanımının uzun süre devam etmesi beklenmektedir. Bu durum gözetildiğinde emisyonların azaltılması konusundaki ar-ge çalışmalarının devam etmesi bir ihtiyaçtır.

NO_x emisyonlarının azaltması için en etkili yöntem seçici katalitik indirgeyici (SCR) sistemidir. Bu sistemde bir indirgeyici vasıtasıyla NO_x emisyonları, su ve azota (N_2) dönüştürülmektedir. Amonyak ise SCR sistemlerinde indirgeyici olarak kullanulan maddelerin en başında gelmektedir. Amonyak,

AdBlue olarak adlandırılan ve %33 üre çözeltisi ($(NH_2)_2CO$) ile %67 saf sudan (H_2O) oluşan çözeltinin egzoz gazına püskürtülmesiyle elde edilmektedir. NO_x emisyonları dönüşümünün en verimli olduğu egzoz gazı sıcaklıkları 350-450 ºC olup, 250 ºC'nin altındaki sıcaklıklarda verimlilik azalmaktadır. Buna ek olarak amonyak birikmesi katalizör yüzeylerinde gözlemlenmektedir.

SCR sisteminin düşük sıcaklıktaki dönüşüm verimliliği arttırmak için indirgeyici olarak HC'ler kullanılır. Bu aynı zamanda sistemin maliyetini egzoz içinde bulunan yanmamış HC'ler ve dizel yakıtının indirgeyici olarak değerlendirmek yoluyla düşürmektedir. İçinde oksijen bulunduran bazı hidrokarbonlar NO_x dönüşüm oranlarını ciddi seviyede artırır. Bunlara örnek olarak; Metanol, propanol ve etanol verilebilir. Özellikle katalist olarak gümüş katkılı seramik yapıların ($Ag\text{-}Al_2O_3$) ve indirgeyici olarak hidrokarbonların kullanıldığı SCR sistemlerinde (HC-SCR) dönüşüm oranları yüksektir. HC-SCR sistemlerinde katalizör olarak Gümüş haricinde birçok metal kullanılmıştır. Bunlara örnek olarak; demir (Fe), paladyum (Pd), platin (Pt), Kobalt (Co), bakır (Cu), rodyum (Rh) verilebilir. Pt içeren katalizörler yüksek performanslı katalizörler olup düşük egzoz gazı sıcaklıklarındaki NO_x dönüşüm oranlarını ciddi seviyede azaltmışlardır.

Çalışma kapsamında, özel olarak tasarlanmış SCR test sisteminde Mo-Cu-Ag/TiO_2 katalizörü ve indirgeyici olarak fuzel yağ kullanılarak düşük sıcaklıklarda NO_x dönüşüm oranlarının verimliliği test edilmiştir. Katalizöre ait analizler yapılmış ve test düzeneğinde değişik motor yükleri, alan hızları ve egzoz gazı sıcaklıklarındaki NO_x dönüşüm oranlarına olan etkileri deneysel olarak araştırılmıştır. Katalizör Çukurova Üniversitesi'nde Otomotiv Mühendisliğine ait laboratuarda üretimiştir. Katalizör, bir desteğin öncü çözeltilerle emdirilmesi, kurutma, kalsinasyon ve buharlaştırmayı içeren emdirme yöntemi kullanılarak hazırlandı. Bu yöntem kapsamında ilk olarak Silindirik Kordiyerit istenilen boyutlara dilimlenir. Daha sonra yüzey alanını arttırmak için 90 ºC'de %50 sıcak oksalik asit çözeltisi ile 3 saat muamele edilir. Sonrasında asitliği gidene kadar

distile su ile yıkanır. Daha sonra 110 ºC'de 1 saat etüvde kurutulup, 550 ºC'de kül fırınında 3 saat kalsine edilerek kordiyerit için ön işlem işlemi tamamlanır. Katalizör hazırlama için, 21,5 g amonyum hepta molibdat 12,6 g bakır nitrat trihidrat ve 500 ml'ye 17.53 g oksalik asit eklenir. Damıtılmış su, bir ultrasonik karıştırıcı ile 1 saat karıştırılır. İçine 50 gr TiO_2 eklenerek bu işleme devam edilir. Daha sonra manyetik karıştırıcı yardımıyla suyu çıkana kadar 90 ºC'de karıştırmaya devam edilir. Karışımın suyu alındıktan sonra etüvde 110 ºC'de 1 saat kurutulur. Sonrasında kül fırınında 550 ºC'de kalsine edilir. Bu işlemden hemen sonra öğütülerek katalizör tozu elde edilir. Elde edilen bu katalizör tozundan 40 g alınır ve 500 ml arıtılmış suya eklenir. Bu çözeltiye 2.55 g AgNO3 ilave edilerek, ultrasonik karıştırıcı yardımıyla karıştırılarak Mo-Cu-Ag/TiO_2 katalizör çözeltisi hazırlanır. Hazırlanan çözeltiye yukarıda belirtilen ön işlemden geçirilmiş kordiyerit daldırılır. Kordiyerit malzemenin kapalı gözenekleri yeniden açmak için üflenir. Daha sonra 120 ºC'de 1 saat etüvde kurutulup 550 ºC'de kül fırınında kalsine edilerek Mo-Cu-Ag/TiO_2 katalizör sentezi tamamlanır.

Katalizörün kimyasal ve yapısal özelliklerinin belirlenmesi için XRD, SEM, BET ve FTIR analizleri gerçekleştirilmiştir. SCR egzoz performans test sisteminde, 200-300 ºC sıcaklık aralığında, 3 farklı alan hızında (30000 h^{-1},40000 h^{-1} ve 50000 h^{-1}) ve 5 farklı motor yükü (1, 2, 3, 4 ve 5 KW) altında deneyler yapılmıştır ve testler sırasında önceden üretilmiş olan katalizör kullanılmıştır. Testler sırasında V-tipi ve 2 silindirli bir dizel motor kullanılmıştır. Performans testleri sonucunda tüm alan hızı değerlerinde ve motor yüklerinde en yüksek NO_x dönüşüm verimleri, en yüksek test sıcaklığı olan 290 °C'de elde edilmiştir. Tüm testler arasında elde edilen en yüksek NO_x dönüşüm oranı 290 °C'de 1 kW'da 30000 h^{-1}'de %85.94 olarak bulunmuştur. Egzoz gazı sıcaklığındaki 200'den 290 °C'ye artışın, NO_x dönüşüm verimliliğini olumlu yönde etkilediği gözlemlenmiştir.

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Finally, I would like to dedicate this study to the loving memory of my father, Özkoç Sümer, who died during the tragic Covid-19 pandemic in 2020 together with millions of victims across the globe due to this disastrous illness. Devastating loss of him resulted in losing my chance to graduate in 2020 and also losing 2 years to finalize this study. Daddy, I didn't give up! Finally, I am now completing my study to contribute to the literature as the daughter of the biggest individual science enthusiast I have ever known.

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LIST OF ABREVIATIONS AND NOMENCLATURE

C	: Celsius
Mo	: Molybdenum
MoO_2	: Molybdenum dioxide
Cu	: Copper
Cu_2O	: Copper oxide
Ag	: Silver
$AgNO_3$	: Silver Nitrate
Ag_2O	: Silver oxide
Au	: Gold
Al	: Aluminium
Ce	: Cerium
C_3H_6	: Cyclopropane
CH_4	: Methane
TiO_2	: Titanium dioxide
V_2O_5	: Divanadim pentaoxide
$Ag\text{-}Al_2O_3$	: Silver–aluminum mixed oxide catalyst
Al_2O_3	: Aluminium oxide
Fe	: Iron
$(NH_2)_2CO$	: Urea
Pt	: Platinum
Pd	: Palladium
Co	: Cobalt
Rh	: Rhodium
$AgNO_3$	: Silver Nitrate
IPCC	: Intergovernmental Panel on Climate Change
NASA	: National Aeronautics and Space Administration
GHG	: Greenhouse Gases

HC : Hydrocarbon

kW : Kilowatt

kV : Kilo Volt

KB : Kilobyte

V : Volt

AC : Alternative Current

DC : Direct Current

kHZ : kilo hertz

ml : milliliter

mm : millimeter

L : Liter

XRD : X-ray Diffraction

EDS : Energy-dispersive X-ray spectroscopy

BET : Brauner– Emmett – Teller

FTIR : Fouirer Transform Infrared Spektrofotometre

DOC : Diesel oxidation catalyst

SCR : selective catalytic reduction

NO_x : Oxides of Nitrogen

SOx : Sulfur Oxides

PM : Particulate matter

CO : Carbon monoxide

CO_2 : Carbon dioxide

ECV : Electric Commecial Vehicle

HEV : Hybrid Electric Vehicle

N_2 : Nitrogen

H_2O : Water

DI : Diesel

COHb : Carboxyhemoglobin

THC : Total hydrocarbon

NO	: Nitric Oxide
NO_2	: Nitrogen Dioxide
N_2O	: Nitrous Oxide
NH_3	: Ammonia
NMHC	: Non-methane hydrocarbons
US	: United States
SOF	: Soluable organic fraction
VOC	: Volatile organic compounds
EGR	: Exhaust gas recirculation
DEF	: Diesel exhaust fluid
DPF	: Diesel particulate filter
TWC	: Three-way catalytic converter
LNT	: Lean NO_x trap
BaO	: Barium oxide
BMO	: Base-metal-oxide
$BaCO_3$	: Barium carbonate
$(Ba(NO_3)_2)$	: Barium nitrate
H_2	: Hydrogen
H_2N	: Amino group
HNCO	: Isocyanic acid
SV	: Space Velocity
EURO	: European
$((NH_4)6Mo_7O_{24}.4H_2O)$	: Ammonium molybdate tetrahydrate
$(Cu(NO_3)_2.3H_2O)$	: Copper nitrate trihydrate
$(2Al_2O_3\text{-}5SiO_2\text{-}2MgO)$	: Alumina Magnesium Silicate
Mo-Cu-Ag/ TiO_2	: Molybdenum -Copper-Silver-Titanium dioxide

1. INTRODUCTION

Environmental pollution is a serious problem humans and other life forms face on Earth today. Environmental pollution occurs when the environment fails to neutralize harmful products of human activity. Water, land, and air pollution begin when the rate of natural resource use exceeds nature's capacity to recover itself.. In this case, pollutants are considered as contaminants which are harmful for every form of life. Among all kind of pollution, air pollution stands at a serious point while the clean air is the main need for a healthy life (Muralikrishna, 2017).

According to Mishra (2003), there are some certain worsening ingredients to air pollution such as fast urban population increase, intensifying industrialisation, expanding energy and vehicle demand. As a result of air pollution increase, we face some negative effects such as global warming. It is anticipated that the effects of global warming will be extensive, persistent, and frequently devastating for Earth. Some of the serious consequences can be listed as increasing average temperatures, extreme weather events, ice melt, increasing ocean levels and acidification and also destroying ecosystems. Global warming is originating from greenhouse gases released into the atmosphere through human activities. The Intergovernmental Panel on Climate Change (IPCC) report from September 27, 2013, emphasizes that there is a connection between human activities and global warming. Global warming is a real phenomenon that has been brought on by human activity, according to more than 197 major scientific organizations. (Anonymous 6).

The greenhouse gases that occur due to human activities are carbon dioxide, methane, nitrous oxide, and fluorinated gases (Resitoglu et al., 2014). Figure 1.1. shows the trends of major greenhouse gases in years.

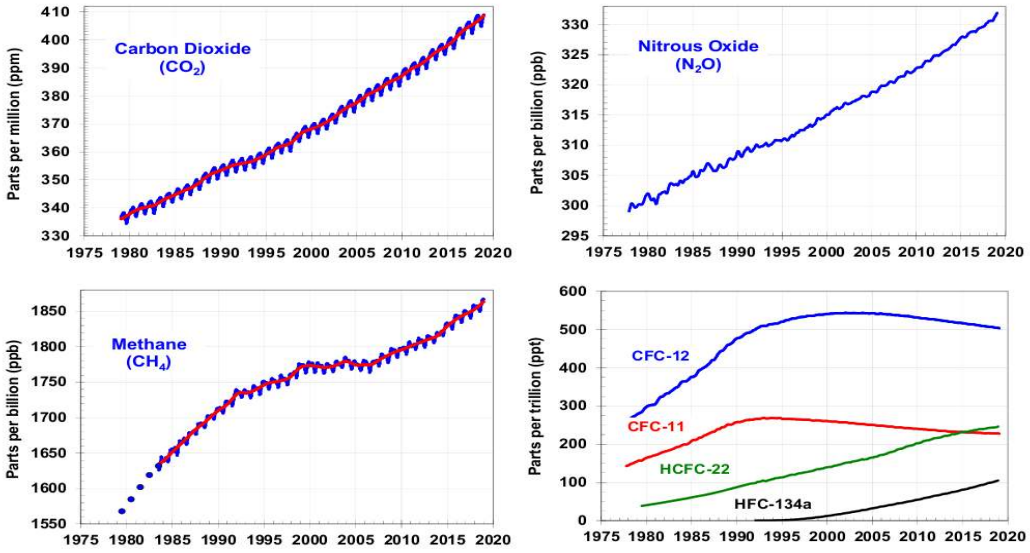


Figure 1.1. Major greenhouse gas trends (Anonymous 1)

Global greenhouse gas emissions are based upon different sectors of the economy. There are two types of emissions produced by humans: those brought on by the burning of fuels for energy, and those brought on by other processes. Burning fuel results in approximately two thirds of greenhouse gas emissions. (Anonymous 1).

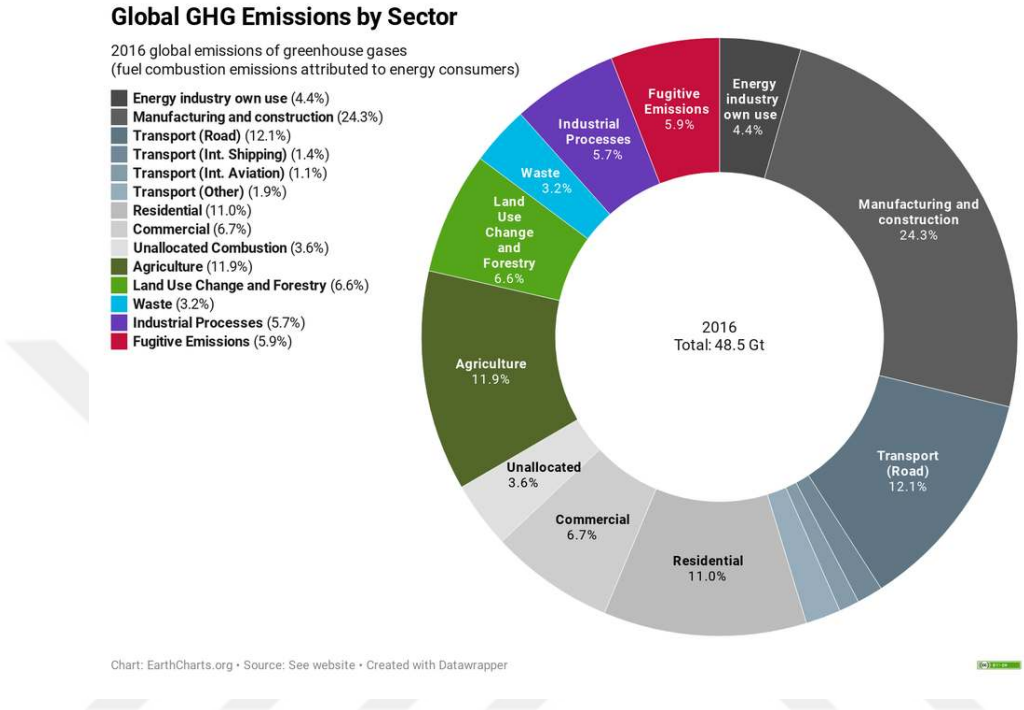


Figure 1.2. Global greenhouse gas effects by sector (Anonymous 1)

According to NASA, in 2010 transportation was the second-largest net source of air pollution in the world (Anonymous 2). Transportation is still one of the biggest contributors to air pollution today. The exhaust gas of the motor vehicles is destroying our clean air and threatening our health as well as our lives. Every year, approximately 60 million vehicles are being manufactured and By 2030, 1.3 billion automobiles are anticipated to be in use worldwide (Piumetti et al., 2015). The problem will get worse day by day according to the expected figures and an unhealthy air composition will be inevitable in years.

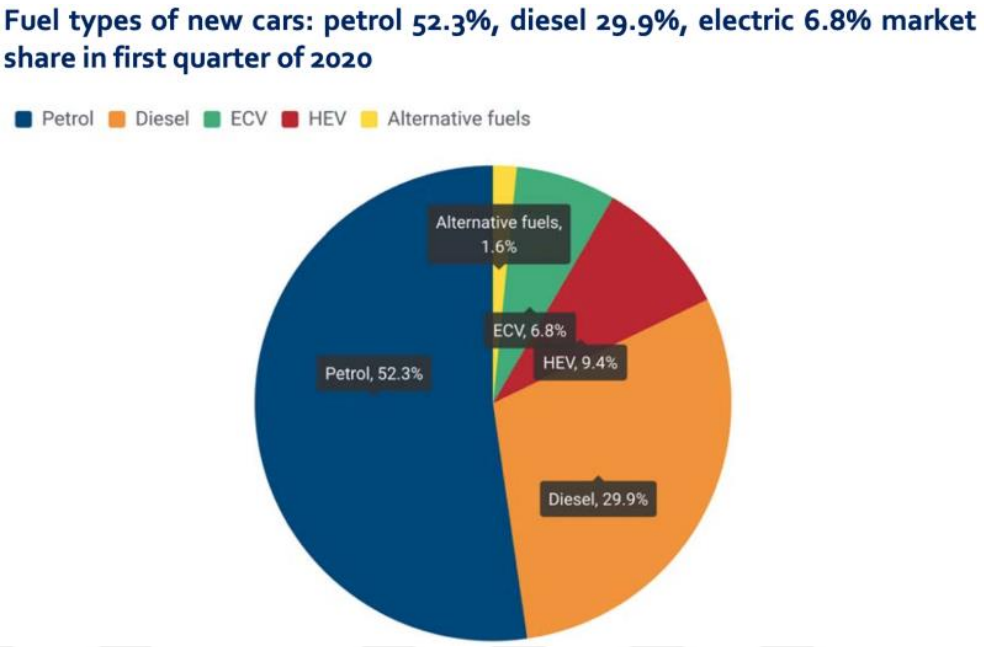


Figure 1.3. Fuel types of new cars in 2020 (Anonymous 4)

Figure 1.3. shows today's market share by fuel types of new vehicles in 2020. The interest in diesel engines has risen dramatically since they were launched after gasoline engines. Diesel engines are preferred for several reasons such as having high efficiency, durability, and reliability and they are also very promising for lower operational costs. Although diesel engines have many advantages, they have some disadvantages, too. Unfortunately they have a significant impact in air pollution worldwide because of unhealthy exhaust emmisions (Resitoglu et al., 2014). Many dangerous pollutants, such as unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), or particulate matter, are present in diesel exhaust gas compositions (PM). Diesel exhaust gas composition is depicted in Figure 1.4.

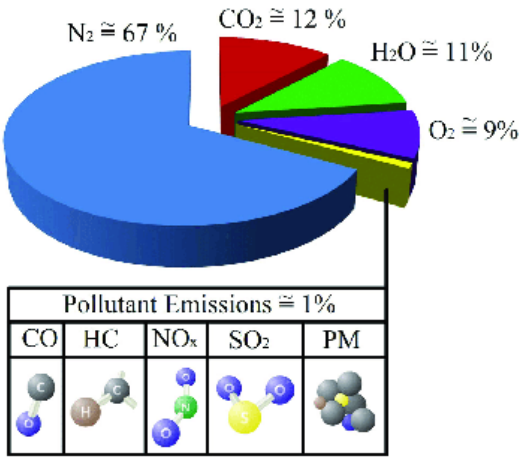


Figure 1.4. The composition of diesel exhaust gas (Resitoglu et al., 2014)

The majority of pollutants are released into the atmosphere as a result of a variety of less-than-ideal combustion processes, including incomplete fuel combustion, mixture component reactions under high temperatures and pressure, lubricating oil and oil additive combustion, and combustion of non-hydrocarbon components of diesel fuel, like fuel additives and sulfur compounds. Common pollutants from the composition of diesel exhaust gas include unburned hydrocarbons (HC), carbon monoxide(CO), nitrogen oxides (NO_x) or particulate matter (PM) (Anonymous 5). As a threatening pollutant from the exhaust composition, NOx's role in the production of nitric acid results in acid rain, acidified lakes, and seas. This acidification affects negativelty the formation of ground level ozone as well as destroying the ozone in the stratosphere which are both very harmful. The estimation of NO_x emmitted to the atmosphere is over 30 million tonnes annually (Al Cheikh Mohamad Ahmad, 2019). For this reason, scientists have been performing a significant number of researches and experiments to reduce NO_x emission by developing clean vehicle and fuel technologies and this mission is well supported by tightened emission standards and regulations worldwide. (Anonymous 3).

2. DIESEL ENGINES AND EMISSIONS

2.1 Diesel engines

The engineer Rudolf Diesel applied for a patent for a "new rational heat engine" on February 27, 1892, at the Imperial Patent Office in Berlin. He received the DRP 67207 patent, dated February 28, 1892, for a "Working Method and Design for Combustion Engines," on February 23, 1893. This was an important first step towards so called “Diesel Engines” (Mollenhauer and Tschoeke, 1997). Adolphus Busch created the first industrial engine in 1898 with the assistance of Diesel in a facility in St. Louis, Missouri, in the United States. After that, in 1899, Diesel's Augsburg facility started producing diesel engines (Anonymous 7). Nowadays, An important instrument in modern society's daily existence is the diesel engine. It produces electrical power, is used for numerous agricultural, building, and industrial processes, and powers a large portion of our land and sea transportation (Lloyd and Cackette, 2001).

An example of an internal combustion engine is the diesel engine. Combustion of diesel engines consists of 4 strokes. Air is first injected into the cylinder, where it is compressed between 14 and 25 times by the piston until it reaches a temperature that will ignite the fuel. The fuel typically (in a modern engine) is sprayed into the cylinder by an electronic fuel-injection system after the air has been compressed, and the fuel quickly ignites and explodes without the need for a spark plug. The power that propels the vehicle on which the engine is attached is generated by the controlled explosion that forces the piston to push back out of the cylinder. The exhaust gases are forced out through an exhaust valve when the piston returns to the cylinder, and the cycle continues (Anonymous 7).

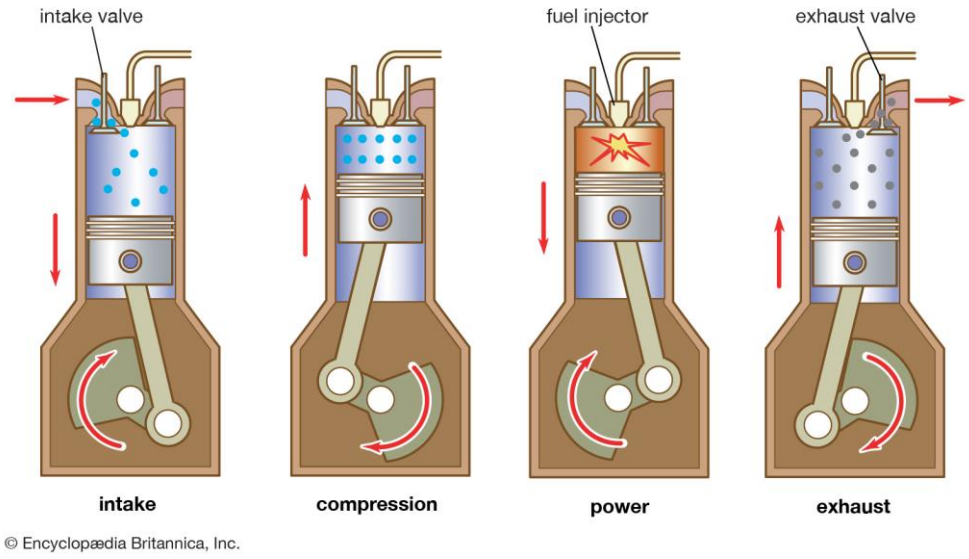


Figure 2.1. Four-stroke diesel engine (Anonymous 8)

2.2. Emissions from Diesel engines

Combustion is a chemical reaction. Whatever oxygen is present in the ground-level air is used while burning diesel fuel. The reactant is referred to as this oxygen. Diesel fuel undergoes oxidation when oxygen interacts with it. In this oxidation process, water and CO_2 are produced (carbon dioxideThe combustion process does not produce any toxic byproducts, like water or carbon dioxide. Because of this, if these two gases were the only ones produced when fuel is burned in an engine cylinder, the process would be referred to as perfect combustion. When the combustion of an HC fuel is imperfect, harmful pollutants are created. As a result of imperfect combustions, several harmful substances are emitted to the atmosphere. Most harmful substances can be listed as carbon moNO_x ide, hydrocarbons, particulate matter and oxides of nitrogen (Bennett, 2010).

2.2.1. Carbon monoxide

The most prevalent type of fatal air poisoning worldwide is caused by carbon monoxideIt is extremely poisonous and forms carboxyhemoglobin (COHb) when combined with hemoglobin, which prevents oxygen from reaching tissues. Carboxyhemoglobin levels of 50% or more can cause seizures, comas, and even death. Natural processes that result from photochemical reactions in the troposphere, which produce around 5 x 1012 kilograms of carbon monoxide per year, are the main source of this gas. Volcanoes, forest fires, and any other types of combustion are additional sources of CO in nature. Therefore, it is crucial to prevent the release of such dangerous and lethal poisonous gases by raising knowledge of potential causes and finding ways to reduce the risk of exposure. (John and Feyisayo, 2013).

2.2.2. Hydrocarbons

Hydrocarbons are poisons that belong to the burned or partially burned fuel class. A significant issue in urban areas is air pollution, which is largely caused by hydrocarbons. Long-term exposure to hydrocarbons increases the risk of developing cancer, liver illness, lung disease, and asthma. Therefore, the substance is followed by the authorities with regulations (Anonymous 9). Two primary sources of HC are found in DI engines, according to the research. One is caused by the amount of fuel in the sac and the holes in the injection nozzle, and the other is because fuel was premixed under conditions where it was leaner than the lean limit. In order to reduce the HC from the lean limit and sac volume sources, respectively, ignition delay reduction and sac volume reduction are both effective (Greeves et al., 1977).

2.2.3. Particulate Matter

Due to their health effects, diesel particles have become a huge concern in the past years. Particles have the ability to pass through cell membranes, enter the circulation, and even go to

the brain. According to certain studies, particles can also cause inheritable mutations. Top emitters can be considered as construction engines, agriculture engines and forestry engines. Because these engines have a lengthy lifespan, it takes a lot longer to reduce emissions effectively, which means that their relative contribution to overall particle emissions will rise in the future. As a result, significant efforts are made to limit emissions, and the laws are tightening (Burtscher, 2005).

2.2.4. Oxides of Nitrogen

Lean air-to-fuel ratios during diesel combustion result in extremely low emissions of total hydrocarbons (THC) and carbon monoxide (CO). On the other side, higher nitrogen oxides (NO_x) generation is a result of the high combustion temperature. Under the influence of daylight, NOx and HC combine to generate photochemical oxidants. NO also reacts with oxygen to form nitrogen dioxide (NO_2) and it has long-term consequences on the respiratory system and lung function, particularly in kids (Tzamkiozis et al., 2009). The primary cause of atmospheric pollution, accounting for 20% of all NO_x emissions worldwide, is NO_x produced by internal combustion engines. (Zhao et al., 2017). As stated by Al Cheikh Mohamad Ahmad (2019), diesel engines hold most of the contribution to NO_x emissions (about 85%) comparing to gasoline engines and nitrogen dioxide (NO_2), nitrous oxide (N_2O) and nitrogen oxide (NO) are all forms of NO_x gases that are found in the environment. According to Reis et al. (2009), stated that 90–95% of NO_x emissions were seen in the form of NO. In addition to that, The two mechanisms known as the thermal and quick mechanisms were principally responsible for NO formation. More than 90% of the emissions from vehicle transportation are caused by the thermal mechanism, which is active above 1600ºC.

3. EMISSIONS REGULATION AND CONTROL

3.1. Emissions standards regulations:

The majority of vehicle types, such as cars, trucks (lorries), locomotives, tractors and similar machinery, barges, but not seagoing ships and airplanes, are subject to regulations in the European Union regarding emissions of nitrogen oxides (NOx), total hydrocarbon (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO), and particulate matter (PM). There are many standards for each type of vehicle. By operating the engine at a standardized test cycle, compliance is assessed. New regulations do not apply to vehicles already on the road, but non-compliant vehicles cannot be marketed in the EU. Although available technology is taken into account when developing the standards, no specific technologies are required in order to achieve the requirements. Current or upcoming standards must be met by newly released models, but minor lifecycle model modifications may still be offered with pre-compliant engines.

The legal framework is made up of a number of directives that each amend Directive 70/220/EEC from 1970. The standards, their effective dates, their scope of application, and which EU directives serve as the standard's definition are included in the table below.

Euro 1 (1992):
For passenger cars—91/441/EEC.
Also for passenger cars and light lorries—93/59/EEC.
Euro 2 (1996) for passenger cars—94/12/EC (& 96/69/EC)
For motorcycle—2002/51/EC (row A)—2006/120/EC
Euro 3 (2000) for any vehicle—98/69/EC
For motorcycle—2002/51/EC (row B)—2006/120/EC
Euro 4 (2005) for any vehicle—98/69/EC (& 2002/80/EC)
Euro 5 (2009) for light passenger and commercial vehicles—715/2007/EC
Euro 6 (2014) for light passenger and commercial vehicles—459/2012/EC and 2016/646/EU. The original directive on emission limitations, 70/220/EEC, has been replaced by these limits. (Anonymous 10).

Road traffic is a significant source of urban air pollution, although traffic management plans may be able to lessen the harm it causes to the environment. Reducing the prevalence of the car and boosting the percentage of personal travel by environmentally friendly forms of public transportation are common proposals that tend to win approval. Notably, the Royal Commission on Environmental Pollution (1994) anticipated for a rise in the percentage of passenger kilometers transported by public transportation from 12% in 1993 to 20% in 2005,

and to 30% by 2020. The majority of the fleet is often made up of passenger cars, and when it comes to emission testing, they have undoubtedly gotten the most attention (Boulter and Cox, 1999). Table 3.1. shows the change of regulation standards for diesel passenger cars through the years.

Table 3.1. European emission standards for diesel passenger cars (Category M)*, g/km (Anonymous 10).

Tier	Date (Type Approval)	Date (First Registration)	CO	THC	VOC	NO_x	$HC+NO_x$	PM	PM [#/km]
Diesel									
Euro 1†	July 1992	January 1993	2.72 (3.16)	-	-	-	0.97 (1.13)	0.14 (0.18)	-
Euro 2	January 1996	January 1997	1.0	-	-	-	0.7	0.08	-
Euro 3	January 2000	January 2001	0.66	-	-	0.50	0.56	0.05	-
Euro 4	January 2005	January 2006	0.50	-	-	0.25	0.30	0.025	-
Euro 5a	September 2009	January 2011	0.50	-	-	0.180	0.230	0.005	-
Euro 5b	September 2011	January 2013	0.50	-	-	0.180	0.230	0.0045	6×10^{11}
Euro 6b	September 2014	September 2015	0.50	-	-	0.080	0.170	0.0045	6×10^{11}
Euro 6c	-	September 2018	0.50	-	-	0.080	0.170	0.0045	6×10^{11}
Euro 6d-Temp	September 2017	September 2019	0.50	-	-	0.080	0.170	0.0045	6×10^{11}
Euro 6d	January 2020	January 2021	0.50	-	-	0.080	0.170	0.0045	6×10^{11}

3.2. Emissions control systems:

Currently, it is possible to employ a few technologies to minimize the diesel exhaust emissions from existing engines as well as from both new engines and automobiles. This is a list of the main technologies. (Manufacturers of Emission Controls Association, 2007)

3.2.1. Diesel Particulate Filters (DPFs):

The diesel engine now has diesel particulate filters (DPFs) on par with fuel injectors. In Europe, the US, and Japan, nearly all brand-new diesel vehicles already have or soon will have DPFs. They are widely used in new Japanese vehicles, and since January 2007, all new HD truck engines in the US have included them (Johnson 2009). DPFs are capable of reducing PM by up to, and in some circumstances by more than, 90%. High efficiency filters are very successful in reducing the carbon proportion of particulates, which some health professionals believe may be the most dangerous part of PMParticle filters can be made to cut emissions of hazardous hydrocarbons by more than 90%. Diesel particulate filters, as their name suggests, filter engine exhaust to remove particulates from diesel exhaust. They can be included into diesel engines that are stationary or in cars. Engineers who design filter systems must include a method of burning off or eliminating collected particulate matter because a filter can fill up over time. When exhaust temperatures are appropriate, the only practical way to get rid of accumulated particulate matter is to burn or oxidize it inside the filter. The filter is "regenerated"

by burning off the material that has become stuck there. "Passively regenerated" filters are those that regenerate by the utilization of exhaust heat that is already present. Such regenerable filters cannot be applied in all circumstances. "Actively regenerated" filters are those that require some form of energy input, such as the infusion of diesel fuel into an upstream DOC. To ensure that filter regeneration happens under all vehicle operating situations, new vehicle applications of DPFs often combine passive and active regeneration systems. To reach filter regeneration conditions on demand, active regeneration systems use a variety of engine controls (Manufacturers of Emission Controls Association, 2007).

3.2.2. Diesel oxidation catalyst (DOC):

Diesel oxidation catalysts reduce the mass of diesel particulate emissions by converting carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide (CO_2) and water while having little effect on nitrogen oxides NO_x). Up to 90% of the soluble organic fraction (SOF) of diesel particles will be removed using an oxidation catalyst. Because this section of the particle contains several substances that health professionals are concerned about, it is crucial to destroy SOF. Therefore, depending on the components that make up the total particle, diesel oxidation catalysts can lower overall particulate emissions by 25 to 50%. Along with generating large reductions in CO and HC, they also lessen diesel smoke and eliminate the unpleasant smell of diesel exhaust. The amount of particles, however, has not changed, and problems related to the consequences of ultra-fine particulates have not been resolved. All diesel vehicles sold in Europe since 1996 have been equipped with DOC technology, however only a small percentage of heavy-duty vehicles have series-production catalysts. To enhance NO_2 levels or "clean-up" any bypass of injected reductant used for NO_x reduction, DOCs are also used in conjunction with NO_x adsorbers, $DeNO_x$ catalysts, DPFs, or selective catalytic reduction (SCR) (Keskin and Emiroglu, 2016).

3.2.3. Three-way catalytic converter (TWC):

An important after-treatment device to reduce harmful engine exhaust emissions is the three-way catalytic converter (TWC). Despite efforts to minimize car exhaust emissions using a variety of technologies, TWC was determined to be the most effective method. No other technology could control all pollutants like hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) prior to the TWC. TWC usually involves active catalytic components that support the oxidation of CO and unburned HC as well as the reduction of NO_x. Whereas Rh (Rhodium) is utilized as a reducing catalyst for the reduction of NO_x, Pt (Platinum) and Pd (Palladium) are used as oxidation catalysts. Apart from precious metal catalysts, economical mixture based upon chromium, copper, nickel, manganese, etc. have additionally been tested but were unable to accomplish comparative efficiency (Rathod et al., 2018).

3.2.4. Lean NO_x Trap (LNT):

Conventional gasoline engines with three-way catalysts performing at stoichiometric conditions are quite effective at decreasing NO_x. Yet, because diesels burn with too much air, it is harder to convert NO_x to nitrogen in the stream of exhaust gases. One of the two primary NO_x after-treatment technologies is the lean NO_x trap. The reduction/oxidation process is commonly catalyzed by a mixture of Pt/Rh-group metals, and the storage capacity is provided by either base-metal-oxide (BMO) or an adsorbent. Barium oxide (BaO) and barium carbonate ($BaCO_3$) are common adsorbers. Engine exhaust NO emissions are changed into NO_2 by an oxidation catalyst. Since NO_2 combines with the BMO to create barium dinitrate ($Ba(NO_3)_2$) during lean engine operation, this is then stored on the LNT. Since the trap has a limited capacity for trapping, periodic regeneration of the trap is necessary under all driving conditions. For a brief period of time, the engine is driven rich to allow extra hydrocarbon (HC), carbon monoxide (CO), or hydrogen (H_2) to react with the Pt/Rh group metals and the NO_x that is generated as the nitrate breaks down. The technology is difficult since LNTs are sensitive to sulfur and only perform at their best within a narrow temperature range. Additional technical difficulties include determining the best times for storage and purging, preventing NO_x 3 "slippage" during purging processes, and creating effective control systems. In particular, insufficient purging lowers trapping effectiveness whereas too little purging results in a fuel penalty. (Alimin et al., 2009).

3.2.5. Exhaust Gas Recirculation (EGR)

EGR, as its names indicate, involves returning some engine exhaust to the charging intake (or intake manifold in the case of naturally aspirated engines). An intercooler reduces the temperature of the recirculated gases in the majority of systems. Lowering the combustion temperature in the engine prevents NO_x generation because the cooled recirculated gases, which have a larger heat capacity and less oxygen than air, have a lower oxygen concentration than air. EGR comes in two varieties. Before to the turbocharger, high pressure EGR collects exhaust gas and reroutes it back into the intake air. After the turbocharger and a diesel particulate filter, low pressure EGR captures the clean exhaust and sends it back to the intercooler. With a low-pressure EGR system, diesel particulate filters are almost always used to avoid excessive amounts of particulate matter from being returned to the engine, which would hasten the wear on the engine and turbocharger. In some instances, high pressure EGR loops with catalysts have been added by engine manufacturers to lower PM levels which are fed back through the combustion process. EGR systems usually recirculate between 25% and 40% of the combustion air to reduce NO_x emissions by more than 40% while also lowering combustion temperatures (Manufacturers of of Emission Controls Association, 2007). A schematic of a low-pressure EGR+DPF system is shown in Figure 3.1.

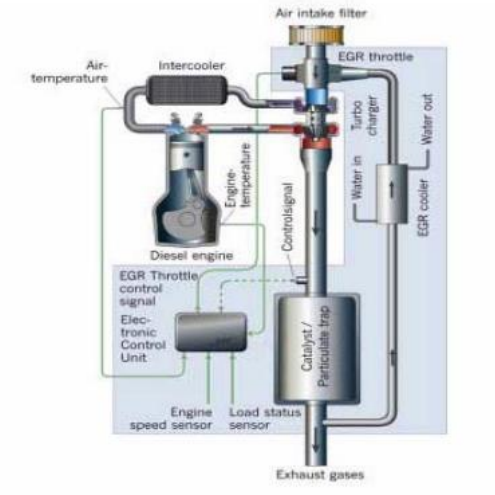


Figure 3.1. Low Pressure Exhaust Gas Recirculation (EGR) + DPF

One of the best methods for lowering NO_x emissions from internal combustion engines currently available is exhaust gas recirculation (EGR). Yet, there are fines associated with the use of EGR. For diesel engines, these include deteriorating particulate emissions and increased specific fuel consumption. Particularly at high loads, EGR exacerbates the trade-off between NOx and particle emissions. The durability of the engine and the quality of the lubricating oil can both be negatively impacted by the use of EGR (Ladommatos et al., 1998).

3.2.6. Selective Catalytic Reduction (SCR):

SCR technology has been applied effectively for more than 20 years to lower nitrogen oxide emissions from stationary diesel engines, maritime vessels, and coal, oil, and gas-fired power plants. The NO_x reduction reaction can occur in an oxidizing environment thanks to SCR technology. Since the catalytic reduction of NO_x with ammonia (NH_3) as a reductant takes place selectively to the oxidation of NH_3 with oxygen, it is referred to as "selective." The choosing of a particular catalyst type depends on the temperature of the exhaust environment. The primary reductant source for mobile source applications is aqueous urea, which quickly hydrolyzes to create ammonia in the exhaust stream (Keskin et al, 2016). This aqueous urea chemically reacts with NO_x to release nitrogen, water vapor and a tiny amount of carbon dioxide to the air which are natural ingredients of atmosphere.

Nowadays, a registered trademark named as AdBlue under VDA company is being used as diesel exhaust fluid (DEF). Urea which is the active material of Adblue is extracted from natural gas. It is made of 32,5% of urea and 67,5% of water. This is the perfect blend to ensure the lowest freezing point at -11°C. If the vehicle is parked under -11°C, fluid freezes. However when the engine starts, fluid starts to melt again. All components of the system is heated in order to ensure the fluid flow perfectly. DEF is a non-separable part of the system and has to

exisit always in the tank, otherwise system locks the vehicle and prevent the ignition (Anar and Bayram, 2018). Figure 3.2 shows an illustration of selective catalytic reduction system.

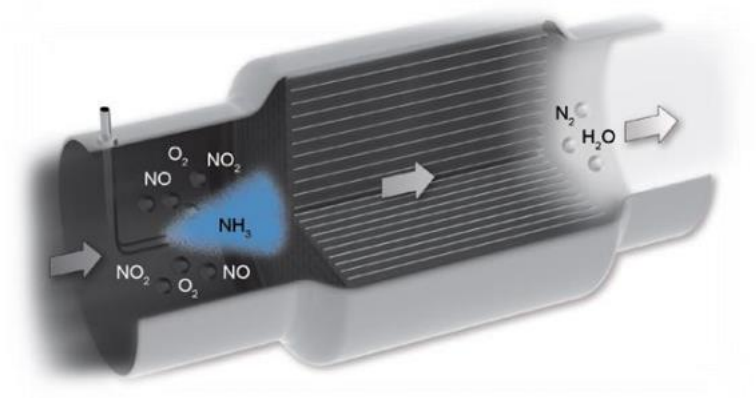


Figure 3.2. Selective catalytic reduction system (Anar and Bayram, 2018)

DEF is sprayed into the exhaust gas stream before the SCR catalyst in an automotive urea-based SCR system. The DEF that was injected becomes heated by the hot exhaust gas, which causes a reduction agent to be created. The solution that was injected initially evaporates due to the fact that water is more volatile than urea. According to the reaction below, the urea evaporates and decomposes in the second step to produce ammonia and isocyanic acid:

$$H_2N - CO - NH_3 \rightarrow NH_3 + HNCO \quad (1)$$

The final stage involves isacyanic acid being hydrolyzed in the gas phase to produce an extra mole of ammonia and carbon dioxide as a byproduct:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (2)$$

The reaction of NO_x gases then consumes ammonia to produce nitrogen. In this respect, the moles of ammonia and NO_x produced by fuel combustion must be equivalent in order for a reduction mechanism to work effectively. Otherwise, the SCR system's effectiveness is harmed by the introduction of insufficient ammonia. To ensure the injection of enough DEF to produce the necessary amount of ammonia is the primary design goal for an effective urea-based SCR system (Kuternowski et al, 2020).

Although urea-SCR is an effective way to reduce NO_x emissions, there are still some drawbacks, such as expensive installation costs, ammonia leaks, and urea that freezes. Due to this circumstance, additional reductants should be taken into account (Hyerim, 2015).

Hydrocarbon SCR (HC-SCR)

Lean burn and diesel technologies hold significant promise for reducing fuel usage and, consequently, carbon dioxide emissions. On the other hand, these technologies have trouble reducing NO_x emissions and result in higher particulate matter emissions. A large range of strategies are now being developed to control NO_x emission. Hydrocarbon-selective catalytic reduction (HC-SCR) is a modern technology that may be promising. By using fuel as a reducing agent, this technology eliminates the requirement for an additional reducing agent to be mounted on the vehicle's board, similar to the additional tank in urea SCR. In addition to all of these benefits, this approach does not require high temperature sulfur regeneration like NO_x storage catalysts. (Petersson et al., 2005).

To sum up, the fundamental benefit of the HC-SCR process is that the fuel itself can be employed as the reducing agent, eliminating the necessity for a storage tank for reductant. Nevertheless, the HC-SCR technology is still in its infancy and cannot be used to reduce NO_x in vehicles with diesel engines. Finding effective NO_x removal catalysts for lean engines that give conversions of more than 80% while employing on-board generated hydrocarbons as the reductant would require more research. Future challenges will include solving this issue, which would constitute a significant advance in NO_x reduction technologies for the automobile sector (Sharifvaghefi, 2011).

Reductants for HC-SCR

Aqueous urea solution used as ammonia source in SCR systems of heavy duty vehicles is kept in a vehicle-mounted external tank. Use of this tank in light duty vehicles is quite difficult. Using the fuel as a reductant in hydrocarbon SCR can eliminate the tank-related negativity (Keskin, 2019).

Several efforts have been undertaken to date to uncover the mechanism of HC-SCR, the pathway can be summed up as follows: Nitrogen oxides + hydrocarbons + oxygen → ad-NO_x + ad-CxHyOz → organo-NO_x compounds (R−ONO + R−NO_2) → −NCO + −CN → nitrogen (Xu et al.,2018)

Efficiency of HC-SCR system can be optimized by using parameters like suitable catalytic materials, suitable reductants and suitable HC / NO_x rate, suitable temperature range, etc (Piumetti et al., 2015).

Generally, NO_x reducing activity increases with a rise in the number of hydrocarbons with carbon. According to the study about effects of alkanes on the activity of Ag-Al_2O_3 catalyst reducing NO to N_2 in the HC-SCR system, the greatest performance was attained with the use of n-octane, the lowest was methane and ethane (Popovych et al., 2016).

A significant amount of NOx transformations correlated with C content. Ranking of the reductants' proven efficiency for the SCR of NO_x over Ag-Al_2O_3 is offered as follows: C4> C3> C2> C1(Candemir, 2019).

Some oxygenated hydrocarbons provides remarkable conversion rates. They can be listed as ethanol, acetone and propanol. These oxygenated hydrocarbons enables above 80% NO_x conversion at 250°C-400°C (Sitshebo, 2010).

Methane, propane, ethane, butane, pentane, n-octane, cyclohexane, propene, benzene, methylcyclohexane, toluene, and cumene were among the hydrocarbons examined as reductants for HC-SCR, according to Guangyan (2017).

Catalysts for HC-SCR

Many studies including various catalysts have been published for the HC-SCR approach, however it is exceedingly challenging to identify a catalyst that can be used under diesel conditions for NO reduction. In the literature, Pt, Rh, and Ag catalysts have received the most attention; among them, Ag is believed to provide the maximum NO conversion. Ag supported on c-Al_2O_3 catalyst is an effective catalyst for reducing NO during the lean-burn combustion of diesel fuel(Tezsevin et al., 2015). Using Cu/ZSM-5 catalysts, NO reduction by HC-SCR in an oxidizing environment has also been observed. Tests conducted have shown that Cu/ZSM-5 is not a viable catalyst for the HC-SCR process under realistic exhaust conditions, primarily because of sulfur exposure's quick deactivation, the diesel exhaust's poor hydrothermal stability, and the inhibitory effects of water. Subsequent studies showed that platinum group metals were particularly effective for HC-SCR at low temperatures (i.e. 200-350 °C). A high hydrothermal stability and resistance to water and SO_x poisoning are also demonstrated by studies on Pt-based catalysts. The oxidation of the reducing agent (a hydrocarbon) by oxygen at higher temps causes a relatively narrow temperature window for NO reduction, and the significant production of N_2O is another negative for these catalysts. (Sharifvaghefi, 2011).

Table 3.2. Catalytic performances of several materials towards the HC-SCR reaction

Catalyst	Reductant	Catalytic performances
Cu/ZSM-5	C3H6	Maximum conversion: 33% (370 °C)
		Conversion higher than 20% (320–450 °C)
Co/Al2O3	CH3OH	Maximum conversion: 40% (370 °C)
		Conversion higher than 20% (>290 °C)
Ag/Al2O3	C2H5OH	Maximum conversion: 31% (460 °C)
		Conversion higher than 20% (>370 °C)
Pt/Al2O3	C3H6	Maximum conversion: 41% (215 °C)
		Conversion higher than 20% (200–270 °C)
Pt/ZSM-5	C3H6	Maximum conversion: 33% (240 °C)
		Conversion higher than 20% (220–270 °C)

Factors to take into account while selecting an HC-SCR catalyst

A catalyst must be hydrothermally stable and maintain its activity at low temperatures and in the presence of SO_x in order to function under the conditions of a diesel reaction. Zeolite-based catalysts are unsuitable for NO_x reduction because of their instability in hydrothermal environments. Moreover, due to N_2O production and the limited temperature range of operation, Pt and Rh-based catalysts are not suitable. (Tezsevin et al., 2015).

3.3. Objective of the study

The purpose of this study was to experiment the consequences of the Mo-Cu-Ag/TiO_2 catalyst as a reductant with Fusel oil on the NO_x percentages in a diesel engine coupled to a test that is loaded with a HC-SCR and DOC.

A by-product of the fermentation of alcohol is fusel oil. It is made up of numerous alcohols, mainly aliphatic alcohols of the C3, C4, and C5 types. For every 1000l of ethyl alcohol, the distillation yields approximately 1l of acetaldehyde and 5l of fusel oil. Raw fusel oil is a dark-reddish, rather viscous liquid with a strong, foul smell. Due to these characteristics, fusel oil's direct usage as a solvent has been extremely constrained. It is burned in several regions to power processing plants (Küçük and Ceylan, 1997). Several businesses and scientists throughout the world are interested in fusel oil as an alternative fuel. With less NOx, fusel oil can be utilized as a clean, high-efficiency spark-ignition fuel. Due to the fact that it directly affects the engine's output power and has a lower energy value than petroleum and gasoline, fusel oil is regarded as the biggest barrier to the direct use of pure fuel (Anonymous 11). Therefore, in this study a new workplace for fusel oil will be experimented by aiming to reduce NO_x level. Experiments were held under different conditions such as different engine loads and space velocity.

4. LITERATURE REVIEW

This section will review and summarize earlier relevant work with a focus on NO_x reduction and Hydrocarbon Selective Catalytic Reduction.

According to Granger et al, bimetallic Ag–Au catalyst, has superior conversion rates when supported on alumina that had been produced using the sequential impregnation process when pre-processed in hydrogen at 250 °C comparing to the pretreatment at 500°C in hydrogen or air. They also showed that bimetallic AgAuAl catalyst had higher SCR activity comparing to AuAl and AgAl catalysts after ageing (Pavan,2015).

In a study by Ström et al., the effects of silver and indium-containing catalysts were studied over ethanol, dimethyl ether, acetic acid, ethane and ethane on NO_x conversion in SCR. Significant differences were observed among the reductants studied for NO_x reduction. In use of dimethyl ether as reductant, In / Al_2O_3 catalyst was determined to increase SCR activity comparing to Ag / Al_2O_3 catalyst.

Ag-based catalysts were created by Evdou et al. utilizing the dry impregnation method. These Ce- or Ag-supported g-alumina catalysts were investigated for the selective catalytic reduction (SCR) of NO_x using a variety of reductants such as C_3H_6, CH_4 and CO. Among C_3H_6, CH_4 and CO used as reducing agents, C_3H_6 performed at the best for reducing activity (Iliopoulou et al.,2004).

Wang et al. used two different catalysts containing palladium with different pores. They investigated the effects of NO on selective catalytic reduction. They concluded that the NO conversion rate (95%) of Pd / V_2O_5 / TiO_2 / SBA-15 catalyst was higher (although it had a lower surface area) than the NO conversion rate (84%) of the Pd / V_2O_5 / TiO_2 / MCM41 catalyst.

Diesel engine with V-SCR catalyst in the study by Liu et al., vanadium and tungsten emissions from exhaust emission control systems have been investigated. Commercially vanadium and tungsten emission among the catalyst systems used started at 500ºC and the temperature. Depending on the increase of the temperature, it has increased exponentially. Measurements using reactor and motor testing were similar, although the results are obtained with the motor test was usually higher in measurements made at all temperatures. It was concluded that this was caused by particle and vapor phase emissions in the engine exhaust system.

In a study by Kelly et al., the use of first, second and tertiary amines as reductants has been investigated instead of NH_3 in a typical small NH_3-SCR. The effect of temperature change was investigated parametrically in the study.With the use of amine species, it has been observed that the measured NO_x conversion rates are close to the rates obtained with NH_3. The maximum NO_x conversion rate was measured around 375ºC with all three amines.

Abu-Jrai and Tsolakis experimentally studied the effects of H_2 and CO gases on SCR system. In experiments using real exhaust gas, catalyst alumina (Al_2O_3) with 1% Pt added was used. Tests were carried out between 200 to 300ºC temperatures. The maximum reduction rate was achieved at 260ºC and was around 60%.

The effects of hydrogen addition in HC-SCR using different reducers at low temperatures were investigated by Gu et al. Engine tests have been carried out in both laboratory and real conditions. It was determined that the NO_x reduction efficiency with HC-SCR increased by adding hydrogen in laboratory environment. It was determined that the highest NO_x reduction efficiency was 43% with the use of heptane at 315ºC in the absence of hydrogen. By adding hydrogen, the highest NO_x reduction efficiency (58% at 315ºC) was obtained with dodecane. It has been determined that the NO_x reduction efficiency increases with hydrogen, the chain length and structure of the fuels are important, and it has been concluded that long chain saturated hydrocarbons provide the highest NO_x reduction efficiency with hydrogen addition. In engine tests, diesel fuel was used as a reductant and it was determined that the NO_x reduction efficiency was 79% at 315ºC and 76% at 245ºC. It is concluded that as the chain length of saturated hydrocarbons increases, the NO_x reduction efficiency increases.

Lopez et al. built two buses and tested them using different fuels and different technologies. They found that the EGR + DPF technology performed better in terms of CO_2 and NO_x emissions with the use of SCR + urea technology while EGR + DPF technology performed better in terms of CO and PM emissions. When B20, B100 and diesel fuel were compared, they found that the use of B20 and B100 fuel increased fuel consumption and produced more NO_x emissions but less PM.

Komatsu et al. investigated the effect of catalysts containing platinum group in HC-SCR on NO_x conversion at low temperatures. Mesopore materials were used as the main structure in the study. It has been observed that the catalysts were very active at 150-200ºC and that problems such as hydrothermal aging and SO_x deactivation did not occur in the catalysts.

5. MATERIALS AND METHODS

Throughout the section, all materials, methods and instruments used for the experiment are defined and explained in details.

5.1. Mo-Cu-Ag/TiO_2 Catalyst preparation:

The catalyst was prepared using the impregnation method that includes impreganating a support with precursor solutions, drying, calcination and evaporation. Firstly, the Cylindrical Cordierite was sliced to desired dimensions as shown in Figure 5.1. Secondly, it is treated with 50% hot oxalic acid solution at 90 ºC for 3 hours to increase the surface area. Then it is washed with distilled water until its acidity is gone. After that, it is dried in an oven at 110 ºC for 1 hour and calcined in an ash furnace at 550 ºC for 3 hours and the pre-treatment process for cordierite is completed. For catalyst preperation, 21.5 g ammonium molybdate tetrahydrate ($(NH_4)6Mo_7O_{24}.4H_2O$) (made of 0.025 M Molybdenum (Mo), 0.075 M Copper (Cu) and 0.2 M oxalic acid, 12.6 g copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and 17.53 g oxalic acid are added to 500 ml. Distilled water to be stirred via a Sonic Vibra-Cell VC 750 ultrasonic mixer (Figure 5.8) for 1 hour. This process is continued by adding 50 g TiO_2 into it. Then, with the help of magnetic stirrer, stirring is continued at 90 ºC until the water is removed. When the water of the blend is removed, it is dried in an oven at 110 ºC for 1 hour. After that, it is calcined in an ash furnace at 550 ºC. Right after this process, it is ground to obtain catalyst powder. 40 g of this obtained catalyst powder is taken and added into 500 ml. distilled water. Adding 2.55 g of $AgNO_3$ to this solution, Mo-Cu-Ag/TiO_2 catalyst solution is prepared by mixing with the aid of an ultrasonic mixer. Above mentioned pre-treated cordierite is immerced to the prepared solution. The closed pores of the cordierite material are blown to re-open. Then, it is dried in an oven at 120 ºC for 1 hour and calcined in an ash furnace at 550 ºC, and the Mo-Cu-Ag/TiO_2 catalyst synthesis is completed.

5.1.1. Cordierite Specifications:

In the preparation of the catalyst, a ready cordierite ($2Al_2O_3$-$5SiO_2$-2MgO) with a monolith honeycomb as a support was used (Figure 5.1) with the following dimensions: 103x130mm and a 400 cpsi square pores. The monolith differentiates from the others with its remarkable hydrothermal stability, thermal expansion rate, and low cost. (Wang et al., 2016).

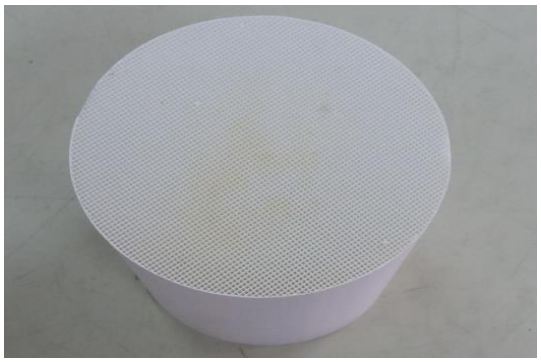


Figure 5.1. Monolith honeycomb Cylindrical Cordierite

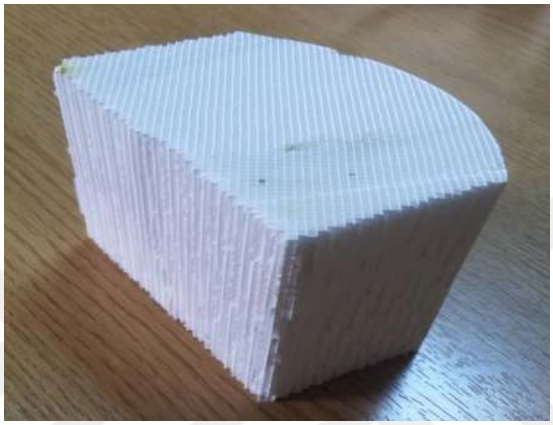


Figure 5.2.Cut cordierite to be used in the catalyst preparation

Figure 5.3. Silver, Copper, and distilled water

5.2. Catalyst characterisation equipments and technical properties:

This section explains the technical specifications of the machines used to analyse the catalysts.

5.2.1. X-ray diffraction(XRD):

X-ray diffraction is a method used to study the atomic and molecular structure of a crystal and is based on the diffraction of the rays in an X-ray beam of crystalline atoms in

various directions specific to the crystal. By measuring the angles and amplitudes of these diffracted beams, a crystallographer can obtain a three-dimensional image of the density of electrons in the crystal. From this electron density, the average positions of the atoms in the crystal can be determined along with chemical bonds, irregularities in the crystal structure and some other information. The X-RAY DIFFRACTOMETER (XRD) used in this thesis is the PANalytical EMPYREAN XRD (Figure 5.4) available in the Cukurova univeristy's central research laboratories.

Figure 5.4. The PANalytical EMPYREAN XRD

Table 5.1 shows the technical specifications of the machine.

Table 5.1. The PANalytical EMPYREAN XRD

Tube	X-Ray tube,CU-Ka
Voltage range[kV]	20-50
Flow range[MA]	5-60
Goniometer diameter[mm]	480
Goniometer geometry	Perpendicular,therta-therta, and alfa-1
Smallest size of step	0.0001°(θ/2θ).
Scanning speed	0.0001°/minute
Angle-to-angle passing speed	500°/minute
Maximum angle	111< 2 θ <168°
Detector	high-speed pixel-based
Maximum counting capacity	1x106 signal/sec
Minimum pixel space	70 micron x 70 micron
Fixed snapshot in angular field	4° (2θ)
Mapping	2D
Model	Bragg-Brentano optic model
Collimator	Cross-slit

5.2.2. B.E.T. Analysis

Brunauer-Emmett-Teller (BET) Surface Area Analysis is a technique that proves determining measures of the surface area,micro and macro pores size, and pores size distribution by physical adsorption method in solid and powder samples at low pressures and with high-resolution.The device used in the experiments was the KELVIN 1042 which is available at the Cukurova univeristy's central research laboratories, shown in Figure 5.5:

Figure 5.5. KELVIN 1042

Table 5.2. KELVIN 1042 technical properties

Gas volume measurement interval	0.005-20cc
Specific are that can be measured(SSA)	0.01 m^2/g
Pore size[nm]	2-200
Ability	Can work with 6 sample in one cycle
Degassing Temperature	35-350°C
Analyses period	15 minutes(single point)

5.2.3. SEM analysis:

SEM (scanning electron microscope) is a type of electron microscope that obtains images by scanning the sample surface with a focused electron beam. Electrons interact with atoms in the sample, producing different signals that contain information about the topography and composition of the sample surface. The electron beam scans the surface with raster scanning and the position of the beam is matched with the detected signal to create an image. In this thesis, FEI Quanta 650 Field Emission SEM(Figure 5.6) available at the cukurova university's central research labarotory was used.

Figure 5.6. FEI Quanta 650 Field Emission SEM

The technical properties of the device are: Microscop's resolution; in high vacuum,in 30kV 1.2nm(SE),in 1KV 3nm(without slowing down the electron)(SE),in Low vacuum,30kV 2nm(SE); high vacuum SE and four department BSE detector that can be summoned back;high vacuum incolumn SE and BSE detector;X-Ray energy distribution spectrometery;GSED (for ESEM mode)detector;STEM detector that can be called back;BSE detector that can work in low vacuum; voltage of acceleration, 100V-30kV;probe flow,100nA;amplification:6-1.000.000 x;camera navigation.

5.2.4. FT-IR Analysis

FT-IR stands for Fouirer Transform Infrared Spektrofotometer. Infrared (IR) absorption spectroscopy is a type of vibrational spectroscopy; IR rays are absorbed by the vibrational movements of the molecule. Fast and high resolution spectra are obtained without the need to scan each wavelength separately. It gives results in a short time even with a small amount of samples. FT-IR device is used in many branches of science such as agriculture, environment, biochemistry, food and beverage, toxicology, material analysis, optical materials and polymers. For this study a Jasco, FT7IR-6700 was used which is available at Cukurova University Labs.

5.3. Technical properties of the devices used in catalyst preparation:

Throughout this section the properties and technical specifications of all the devices used in catalyst preparation are explained.

5.3.1. Ultrasonic Processor:

The technical properties of the vibra-Cell V750 ultrasonic processor which was used to stir the distilled water for 1 hour during catalyst preparation are given in Table 5.3 and also a photo can be found in figüre 5.7.

Table 5.3. Vibra-Cell V750 ultrasonic processor technical properties

	Net power output	750 watts
Power supply	Frequency	20 KHz
	Dimensions (H x W x D)	235 x 190 x 340mm
	Weight	6,8 kg
Sealed converter	Part No	Piezoelectric lead zirconatetitanate cry
	Diameter	63,5 mm
	Length	183 mm
	Weight	900 g
	Cable Length	1,8 m
Standard probe	Tip Diameter	13mm with threaded end replacable tip
	Processing capability	10 ml to 250 ml
	Length	136 mm
	Weight	340 g
	Material	Titanium alloy Ti-6A-4

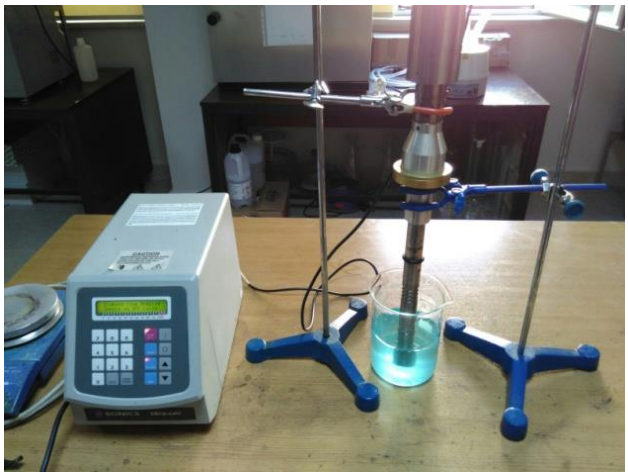


Figure 5.7. vibra-Cell V750 ultrasonic processor

5.3.2. Sintering Oven:

The sintering process of the catalyst was done using the Protherm furnace Model PLF 110/6 (figure 5.8) with the following specifications: Maximum Temperature: 1100(°C); Continuous Operating Temperature (°C):1050; Volume (L):7.0; Inside Measurements (HxWxD) (cm): 14x20x25; Outside Measurements (HxWxD) (cm): 65x55x58; Power:1350W; voltage:220v; Phase:1

Figure 5.8.Protherm furnace Model PLF 110/6

5.3.3. Drying Oven:

During the catalyst preparation, drying of the catalyst at 110°C for 1 hour was done using the Memmert BAIC oven UNB 500 with the technical specifications shown in Table 5.4:

Table 5.4. Memmert BASIC oven UNB 500 Specifications

Model	UNB 500
Chamber width A[mm]	560
Chamber height B[mm]	480
Chamber depth C[mm]	400
Oven width D[mm]	710
Oven height E[mm]	760
Oven depth F[mm]	550
Chamber volume[litre]	108
Weight[kg]	50
Power[W]	2000
Max number of trays	5
Max.load per tray[kg]	30
Total load per oven[kg]	60
Ambient conditions	Ambient temperature 5°C to 40°C
Setpoint temperature range	20° C to nominal temperature
Setting accuracy	0.5°C
Indication resolution	0.5 °C
Nominal voltage[V]	AC 230

5.4. NO_x emissions measurement test system:

In this section, the properties of the NO_x measurement system are explained.

5.4.1. Performance test system overview:

To test the effects of Fusel oil as a reductant and Mo-Cu-Ag/TiO_2 catalyst on the efficiency of NO_x reduction, an AKSA diesel engine available at the automotive department's laboratory was used. For loading the engine, a 10kW electric loading system (Figure 5.14) was used. The test system generally comprises of an engine, a loading system, and a specifically designed performance test bench. To determine the exhaust gas flow rate aboard the system, an orifice plate was mounted onto the exhaust system. In order to adjust the exhaust gas temperatures, a heater was also mounted to the system. Temperatures were measured using k-type thermocouples temperature sensors installed one before DOC, and one after DOC in the exhaust system. NO_x emissions reduction rates were monitored using two Continental model NO_x sensors. To extract data from these two sensors, a program was coded in accordance with the CAN J1939 protocol, and using a PCAN-USB, the data extracted was recorded into the computer. To ensure the NO_x reduction in the SCR system, the process of reductant spraying was composed of a multi-point (6 pores) injector and a pump that were controlled using a microprocessor hardware and software. Reductant spraying was monitored electronically using a matlab Simulink program on the computer that took measures of the spraying flow rates, an Arduino MEGA 2560 microprocessor (figure 5.11), and I/O carts. The space velocity of the gas flow; space velocity [SV (h^{-1})] is the ratio of exhaust-gas volumetric flow [Vf (m^3/h)] to catalyst volume [Vc (m^3)] (Reşitoglu, 2015) was measured using a manometer with an orifice plate.

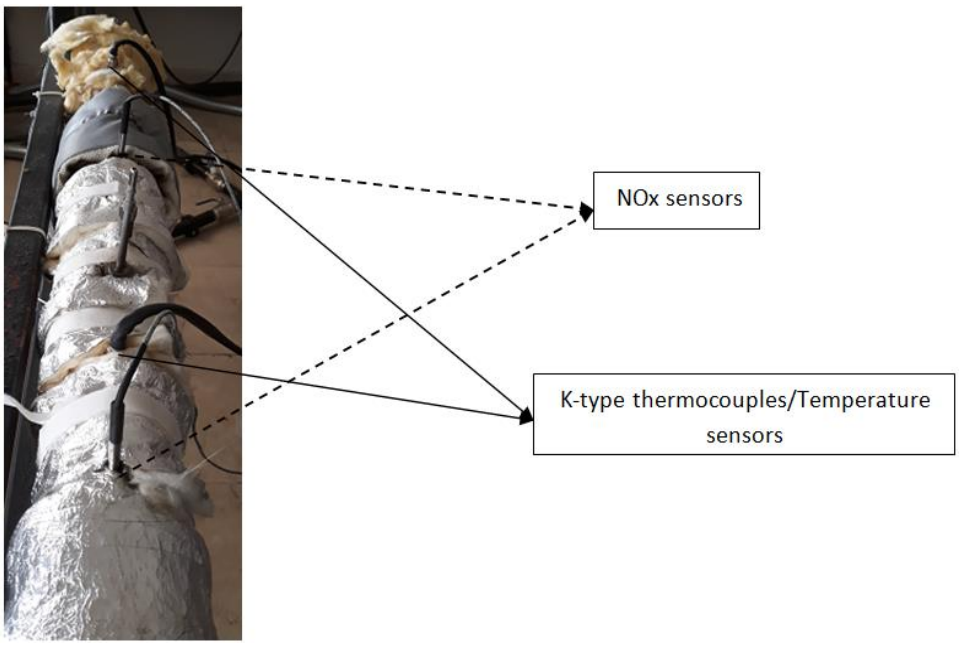


Figure 5.9. Exhaust pipe showing the NO_x sensors and the K-type thermocouple

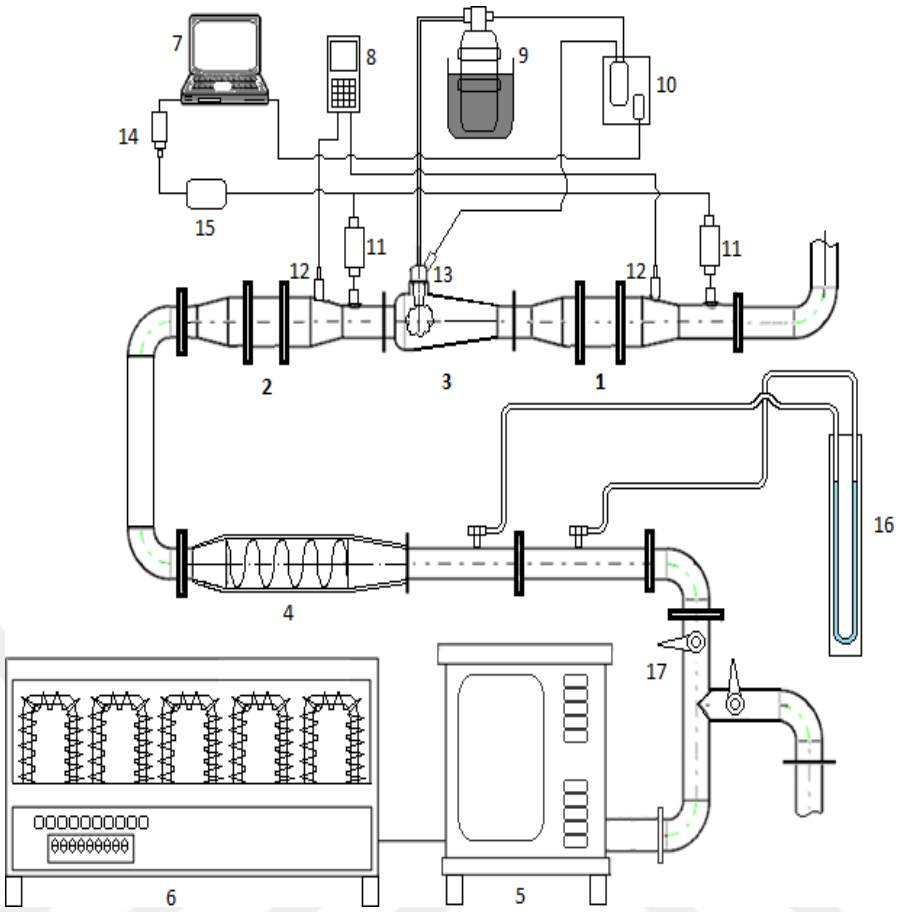


Figure 5.10. Layout of the experiment (Al Cheikh Mohamad Ahmad, M., 2019)

Figure 5.10. Layout of the experiment schematic view of the test bench is as follows: 1-SCR (Selective Catalytic Reduction Catalyst), 2-DOC (Diesel Oxidation Catalyst), 3-Mixing Chamber 4-Exhaust Gas Heating Furnace, 5-Diesel Engine, 6-Power Loading Unit, 7 -SCR Control Unit, 8-Thermometer Datalogger, 9- Reductant Liquid, 10- Injector Spray Control Unit, 11-NO_x Sensor, 12-Temperature Sensor, 13-Injector, 14-NO_x Data Converter, 15-24V Power Supply, 16 -Debi meter (Thin-plate orifice method), 17-Valves).

5.4.2. Test system components technical properties:

This section explains the technical properties of the appliances used for test performance results.

NO_x Sensors

The main aim of the experiment is to measure the NO_x emissions rates to check if the reductant and the catalyst worked well or not. The NO_x gas emissions changed according to the engine working conditions. In the experiment setup, Two NO_x sensors were placed one before the SCR catalyst and one after the SCR catalyst; the first sensor was used to measure the NO_x

emissions before spraying the reductant, and the second sensor was placed to measure the NO_x emissions after the reductant spray. In this way, the effects can be realized. The sensor communication was done according to CAN J1939 protocol.

Arduino MEGA 2560

Arduino MEGA 2560 was uploaded with a program and used together with matlab simulink on the computer to control the pump flow and speed of the reductant spraying. The technical specifications are shown in table 5.5.

Table 5.5. Arduino MEGA 2560 Specifications

Microcontroller	**ATmega2560**
Operating voltage	5V
Input voltage(recommended)	7-12V
Input Voltage(limits)	6-20V
Digital I/O pins	54(of which 14 provide PWM output)
Analog Input pins	16
DC current per I/O Pin	40Ma
Dc current for 3.3V Pin	50Ma
Flash memory	256kb of which 8KB used by bootloader
Spam	8KB
EEPROM	4KB
Clock Speed	16MHZ

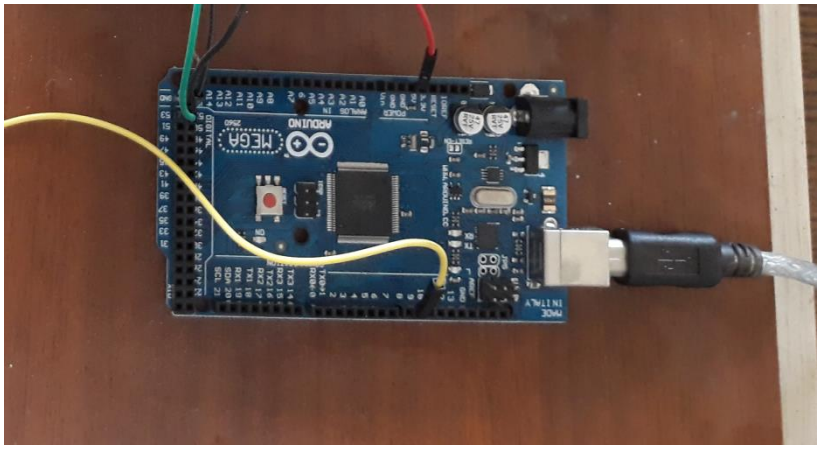


Figure 5.11. Arduino MEGA 2560

Pump

A gasoline pump was used in the experiments to spray fusel oil with a multi-points (six pores) reductant injector. The pump is connected to an Arduino MEGA 2560 to monitor and adjust the flow of the spray.

Engine

An AKSA A2CRX08 2-cylinder V-type diesel engine with a bore of 80mm and a stroke of 79mm was used for the experiments. The technical specifications of the engine are shown in table below:

Table 5.6. AKSA A2CRX08 technical properties

Model	APD 12EM
Prime frequency(Hz)	50
prime power(KVA)	8.8
Stanby power(KVA)	9.6
Nominal voltage(V)	230
Nominal flow(A)	38
R.P.M(r/min)	3000
PHASE	1p
Power factor($\cos\varphi$)	1
Warning mode	Brushless capacitor
Oil capacity	2.3
Water capacity	6.4
Fuel tank capacity	15
Fuel consumption(L/h)	4
Battery voltage	12V DC
Dimensions(mm)	L=1158 W=775 H=1017
Cylinder volume(cm^3)	794
Stroke(mm)	79
Cooling mode	Water
Compression ratio	23/1

Orifice plate and menometer

A manometer and an orifice plate were mounted to the system and connected to the exhaust pipe to calculate the hourly space velocity in the light of Bernouillie's equation. The manometer is filled with water and the desired space velocity corresponds to a certain water level difference which is adjusted with a manual valve on the exhaust pipe.

Emissions measuring equipment

An MRU DELTA 1600-V was used in order to be able to measure exhaust gas emissions from the engine. Measuring ranges and the technical properties of the device as follows:

- CO : 0 ... 10 %
- CO_2 : 0 ... 20 %
- O_2 : 0 ... 22 %
- NO : 0 ... 4.000 ppm
- NO_2 : 0 ... 1.000 ppm
- CxHy : 0 ... 20.000 ppm
- Display : 10 - lines, backlit graphical display
- Weight:appr. 10 kg
- Dimensions : 530x490x310 mm

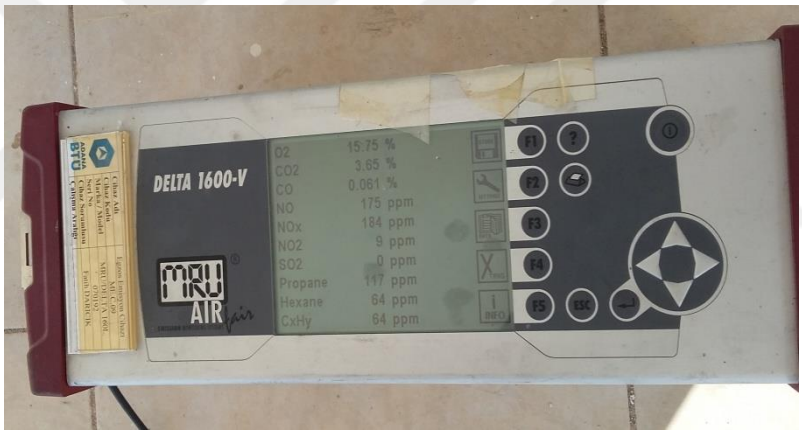


Figure 5.12. MRU DELTA 1600-V

Thermocouple thermometer

To measure the temperatures during the experiments a KJTRSE thermocouple thermometer logger 9682 was used with following specifications:

- K temperature range and Accuracy: 200-1370°C;(0.3% rdg +0.7°C)
- J temperature range and Accuracy:200-760°C;(0.3% rdg +0.7°C)
- T temperature range and Accuracy:200-390°C;(0.3% rdg +0.7°C)
- R temperature range and Accuracy:0-1760°C;(0.3% rdg +0.7°C)
- S temperature range and Accuracy:0-1760°C;(0.3% rdg +0.7°C)
- E temperature range and Accuracy:200-736°C;(0.3% rdg +0.7°C)
- Resolution:0.1°C
- LCD size(mm,HxW): 26(H)x45(W)mm

- Operating temp: 0-50°C
- Operating RH%: Humidity<80%
- Storage temp: 20-50°C
- Storage RH%: Humidity<90%
- Dimension(mm,LxWxT): 170x70x40(H)mm
- Weight: 210g
- Battery:AAA batteryx4pcs or 9v adaptör

Figure 5.13. KJTRSE thermocouple thermometer logger 9682

Electric Loading system

The motor was loaded using a 10kW loading system available at the automotive laboratory (Figure 5.14). This system allows to load the engine at different levels starting from 1kW to 10kW. So that, experiments can be held under different engine load conditions.

Figure 5.14. Electric loading system

6. RESULTS AND DISCUSSION

During this chapter, the performance outcome of the experiments and laboratory tests to analyse Catalyst qualifications (SEM, BET, XRD and FTIR) are presented and interpreted.

6.1. Catalyst Characterization results

6.1.1. SEM analysis Results

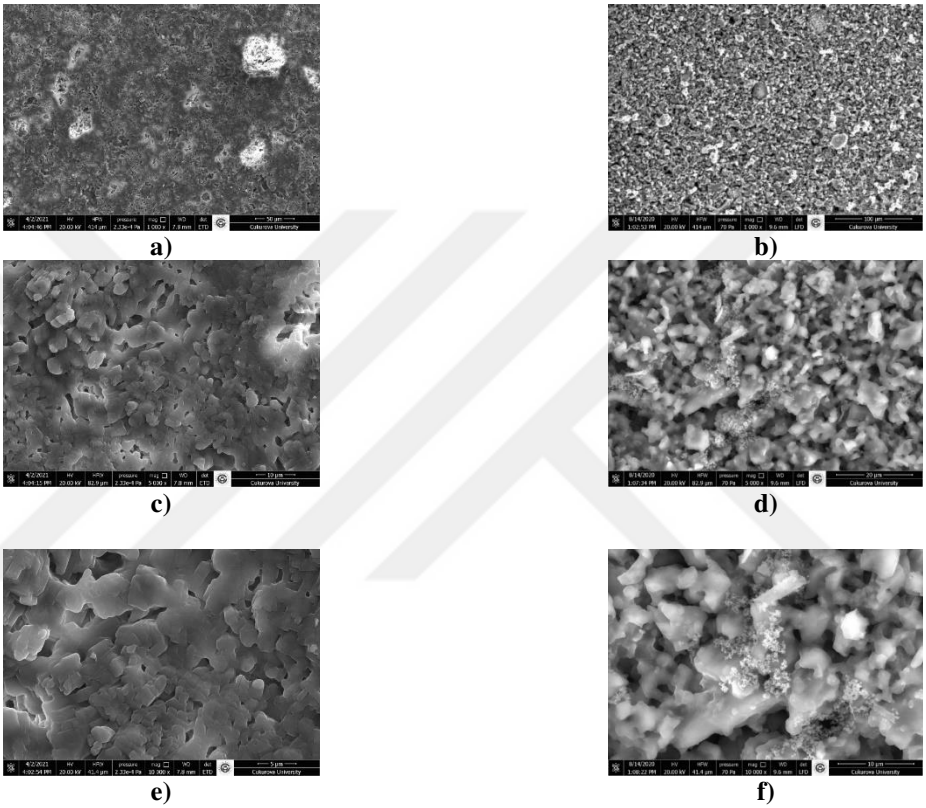


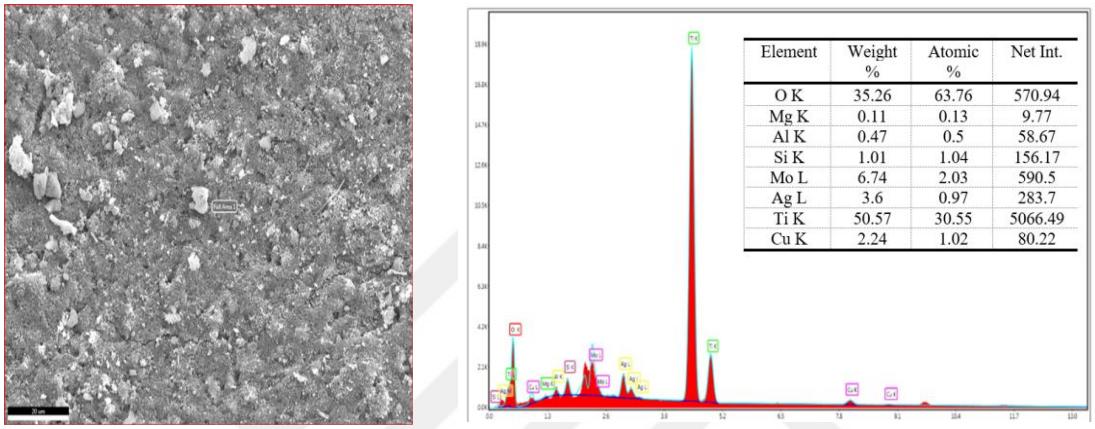
Figure 6.1. SEM pictures of a barren cordierite (a:1000x, c:5000x and e:10000x) and Mo-Cu-Ag/TiO_2 /Cordierite catalyst (b:1000x, d:5000x and f:10000x)

Figure 6.1 shows the morphological features of the catalyst and the blank cordierite as measured by SEM images at 1000x, 5000x, and 10000x magnification.

The SEM photos demonstrate the rough and porous surface of the blank cordierite. Images of the catalyst revealed that, following the coating process, no pore obstruction was caused by the cordierite monolith coated in catalytic active ingredients. Additionally, the cordierite had an unevenly distribution of the active catalytic coating elements. Active catalytic elements were observed in grouped forms on the coated cordierite surface. The catalyst's attachment to a porous surface might get extrapolated according to the SEM picture at 10000x magnification seen in Figure 6.1.f. The images show how copper, silver, molybdenum, and titanium nanoparticles are clearly dispersed on the surface of the cordierite carrying conformation. The morphological makeup of the nanoparticles of active ingredients was distinctive and asymmetrical. The presence

of evenly disseminated small particles contributes to the catalyst's increased functionality. Figure 6.1 demonstrates that the coating procedure worked out well.

The complete surface area of the catalyst was scanned by energy-dispersive X-ray spectroscopy (EDS) analysis in given SEM picture of the produced catalyst at 2500x magnification shown in Figure 6.2. After coating, Ag, Mo, Ti, and Cu metal peaks were seen on the cordierite structure's surface. The weight and atomic proportions of the components in the study region are displayed in Figure 6.2.



Element	Weight %	Atomic %	Net Int.
O K	35.26	63.76	570.94
Mg K	0.11	0.13	9.77
Al K	0.47	0.5	58.67
Si K	1.01	1.04	156.17
Mo L	6.74	2.03	590.5
Ag L	3.6	0.97	283.7
Ti K	50.57	30.55	5066.49
Cu K	2.24	1.02	80.22

Figure 6.2. Energy-dispersive X-ray spectroscopy of the catalyst

The outcomes of the EDS analysis imply that the components that are catalytically active are spread across the surface.

6.1.2. BET Analysis results

An essential factor that describes the catalyst's activity is its surface area. Greater number of catalyst-active sites are created when the catalyst's surface zone increases, improving the distribution of its active components. Table 6.1. displays the findings of the BET study. The surface area of Mo-Cu-Ag/TiO_2 /Cordierite catalyst measured by BET was acquired as 42.002 m^2/g. Cordierite's initial substrate has a very small surface area and around 0.5 m^2/g (Shigapov et al. 1999). After the acid pretreatment method, the cordierite substrate's BET surface area significantly enhanced. As a result, it was discovered that the catalyst's BET surface area was about 98.81% greater than that of the cordierite. Also, the Langmuir surface area, micropore volume, and micropore area of Mo-Cu-Ag/TiO_2 /Cordierite catalyst were found as 53.726 m^2/g, 14.661 mm^3/g, and 41.608 m^2/g, respectively.

Table 6.1. BET analysis of Mo-Cu-Ag/TiO_2 /Cordierite catalyst

Catalyst	BET Surface Area, (m^2/g)	Micropore Volume, (mm^3/g)	Micropore area, (m^2/g)	Langmuir Surface Area, (m^2/g)
Mo-Cu-Ag/TiO_2 /Cordierite	42.002	14.661	41.608	53.726

6.1.3. XRD Analysis:

In order to find the active phase on Mo-Cu-Ag/TiO_2 /Cordierite catalyst, XRD pattern technique has been used. The XRD pattern of the catalyst is given in Figure. 6.3.

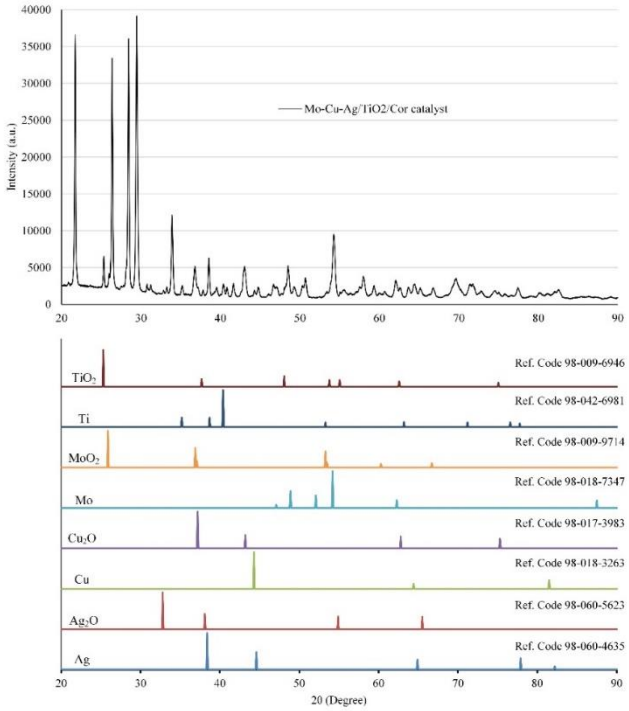


Figure 6.3. XRD patterns of the catalyst

The peaks of Ag_2O, Ag, Cu, Cu_2O, Mo, MoO_2, Ti, and TiO_2 phases were found. The diffraction peaks were detected as follows;

Ag_2O phase 2θ= 32.8°, 38.07°, 54.9°, 65.5° (Ref.98-060-5623),
Ag phase 2θ= 38.37°, 44.6°, 64.91°, 77.99° (Ref.98-060-4635),
TiO_2 phase 2θ= 25.29°, 37.79°, 48°, 53.87°, 55.03° (Ref.98-009-6946),
Ti phase 2θ= 35.25°, 38.68°, 40.38° (Ref98-042-6981),
Cu phase 2θ= 44.29°, 64.43°, 81.52° (Ref.98-018-3263),
Cu_2O phase 2θ= 37.23°, 43.25°, 62.83° and 75.35° (Ref98-017-3983),
Mo phase 2θ= 48.91°, 52.03°, 54.2°, 62.3°, 87.5° (Ref.98-018-7347),
MoO_2 phase 2θ= 25.98°, 36.91°, 37.06°, 53.3° (Ref.98-009-9714).

6.1.4. FTIR Analysis

To determine the chemical and structural composition of the Mo-Cu-Ag/TiO_2/Cordierite catalyst, FTIR analysis was conducted. The FT-IR spectra of the Mo-Cu-Ag/TiO_2 /Cordierite catalyst were investigated between 450-4000 cm^{-1} and is given in Figure. 6.4.

The vibration band at 450 cm^{-1} might mean the presence of Ag/TiO_2 nanoparticles (Rajangam et al. 2020). The FT-IR absorption spectrum at 3423 cm^{-1} might be related to Ag_2O (Shume, Murthy, and Zereffa 2020). The stretching mode of Ti-O-Ti can be used to explain the appearance of bands at 450-800 cm^{-1} (Devi, Venckatesh, and Sivaraj 2014). Cu-O stretching may be responsible for the peak at 482 cm^{-1} and the band at 579 cm^{-1}, as well as the Cu-O stretching vibration. The presence of the Cu_2O phase may be indicated by the active mode that was detected in the region of 605 to 660 cm^{-1} (Ethiraj and Kang 2012). The band at 1092 cm^{-1} may be attributed to the H-O-H, whereas the band at 3423 cm^{-1} may be attributed to stretching of the O-H. (Kayani et al. 2015). There is a chance that the bands seen at 579 cm^{-1} and 768 cm^{-1} correspond to the stretching vibrations of O-Mo and O-Mo-O, respectively. (Zhang et al. 2017). Hence, the results of the FTIR spectrum provide proof that the produced catalyst contains nanoparticles of catalytic elements.

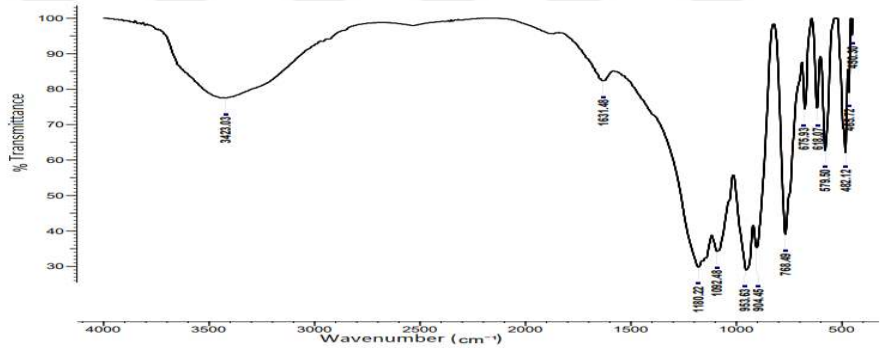


Figure 6.4. FTIR spectrum of the Mo-Cu-Ag/TiO_2 /Cordierite catalyst

6.2. NO_x conversion rates

In this chapter, the outcome of the test engine experiments with Mo-Cu-Ag/TiO_2 /Cordierite as a catalyst and temperature, spraying ratios, loading and space velocity were all taken into consideration while discussing fusel oil's performance as a reductant agent and how it affected NO_x conversion rates.

The NOx conversion rates in the study's trials were acquired at 5 various engine loads (1 kW, 2 kW, 3kW, 4kW and 5kW), 3 different space velocities (30000 h^{-1}, 40000 h^{-1} and 50000 h^{-1}), and 10 different exhaust gas temperatures (200°C – 300°C). Figures 6.5.-6.9. displays NOx conversion rates for test results from 1 kW to 5 kW engine load, correspondingly, at various temperatures and space velocities.

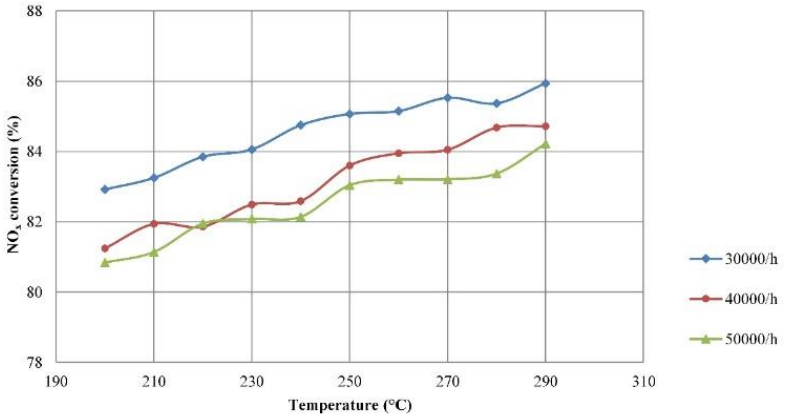


Figure 6.5. NO_x conversions of catalyst at 1 kW

Under 1kW engine load (Figüre 6.5.), the highest NO_x transformaton ratio was seen at 30000 h^{-1} space velocity around 290°C and it was seen that conversion rates rising by the rise of temperature.

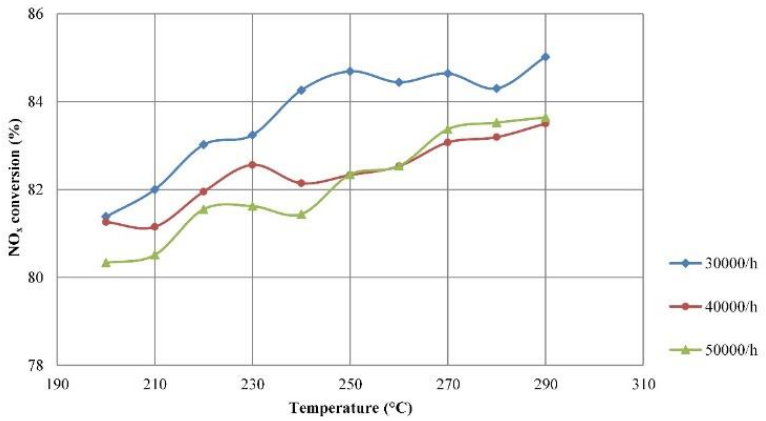


Figure 6.6 NO_x conversions of catalyst at 2 kW

Under 2kW engine load, same tendency was observed. The rise in temperature resulted in higher conversion rates. Again the maximum conversion rate was seen at 30000 h^{-1} space velocity. However, maximum conversion rate observed below the maximum of 1kW engine load tests.

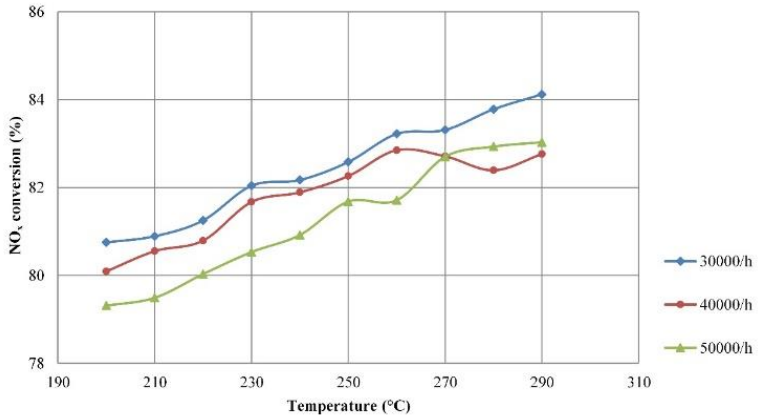


Figure 6.7 NO_x conversions of catalyst at 3 kW

Under 3kW engine load, same pattern has been observed. On the other hand, at 270°C, same conversion rates was seen on 40000 h^{-1} and 50000 h^{-1} space velocities. Above 270°C at 40000 h^{-1} space velocity, conversion rates performed below 50000 h^{-1} space velocity. However overall, max conversion rate was observed at 30000 h^{-1} space velocitiy again.

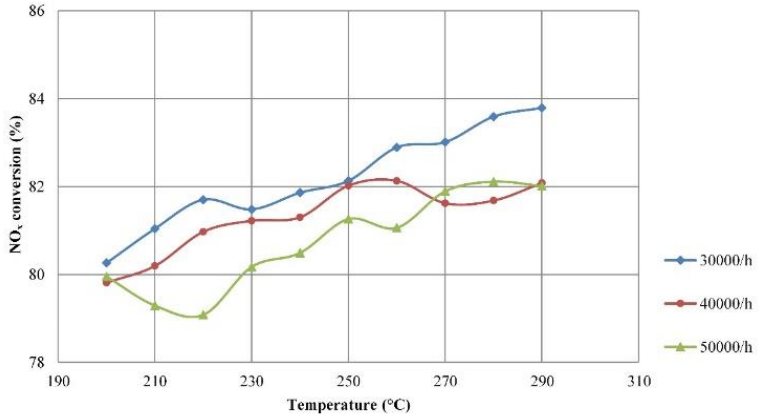


Figure 6.8. NO_x conversions of catalyst at 4 kW

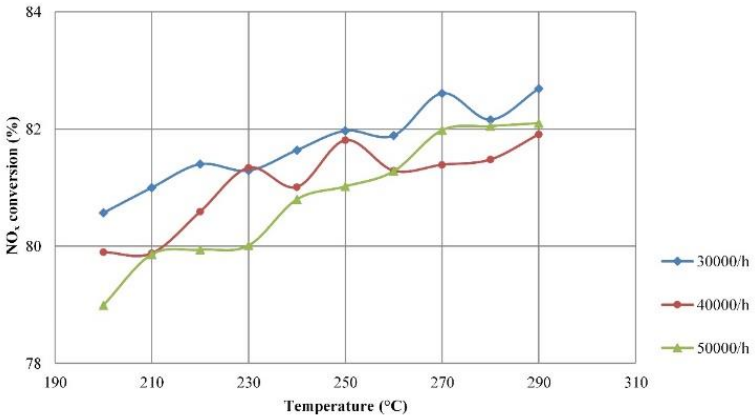


Figure 6.9. NO_x conversions of catalyst at 5 kW

Under 4kW and 5kW engine loads, max conversion rates were observed at max temperature level of the test range. Under 4kW engine load, at 50000 h^{-1} and 40000 h^{-1} space velocities, conversion rates fell behind the rates of 30000 h^{-1}.

6.2.1. Temperature effect:

It was discovered in all of the experiments that NOx conversion rates increased as temperature rose. According to this outcome, the highest NO_x transformation rates were detected at 290 °C under all the space velocity values and engine loads. The catalytic activity which had a positive effect on NO_x conversion, was increased by the increase of exhaust gas temperature. Only at 40000 h^{-1} space velocity, transformation rates fluctuated with the rise of temperature.

6.2.2. Space Velocity Effects

Regarding Space Velocity values, the NO_x conversion efficiency under all the engine loads was seen as 30000 h^{-1}>40000 h^{-1}>50000 h^{-1}. Figure.6.5. shows that under the engine load of 1 kW, the NO_x conversion rates at 290 °C were acquired as 85.94% at 30000 h^{-1}, 84.72% at 40000 h^{-1}, and 84.22% at 50000 h^{-1}. This demonstrates that NO_x conversion rates have been seen to be roughly related to space velocity. Under all engine loads, maximum efficiency has been always observed at 30000h-1. The least successful and fluctuating space velocity value was 50000h-1 which always falls behind the other space velocity values and resulted in unbalanced NO_x conversion rates.

6.2.3. Engine loading effects

The minimum NO_x conversion rate has been seen as 78,99% at 5kW engine load and the maximum NO_x conversion rate has been seen 85.94% at 1 kW engine load. It has been observed that the NO_x conversion reduced with a rise in engine load in all experiments conducted at the same temperature and space velocity. It is known that HC and CO emissions show extra reducing characteristics in SCR reactions. Table 6.2. demonstrates that HC and CO emissions fall as loading rises. The NO_x conversion rates may have decreased as engine load rose because the concentration

of these pollutants in the exhaust gas decreased. Also, as indicated in Table 6.2, it was seen that the HC:NO_x ratio declined at various engine loads, and it has been noted that this circumstance has a detrimental impact on the NO_x conversion ratios.

Table 6.2. Exhaust gas products for different engine loads (without emission control system)

Engine load	NO_x (ppm)	NO_2 (ppm)	C_xH_y (ppm)	CO (%)	O_2 (%)	CO_2 (%)	HC:NO_x
0 kW	184	9	64	0.061	15.75	3.65	0.347
1 kW	263	16	64	0.048	14.93	4.27	0.243
2 kW	344	17	63	0.039	14.14	4.88	0.183
3 kW	387	16	63	0.033	13.73	5.11	0.162
4 kW	380	14	63	0.032	13.47	5.44	0.165
5 kW	375	12	63	0.033	13.05	5.73	0.168

6.2.4. Presence of H_2O

According to Zhang et al. (2019); Ahmad et al. (2020), the NO_x conversion for Ag-based catalysts is adversely impacted by the presence of water in the exhaust gas and reductant. Zhang et al. (2019) observed and declared that the maximum NO_x transformation ratio of Ag-Fe/Al-PILC catalyst was 82% at 22000 h^{-1} at 250 °C with the reductant as C_3H_6. Ahmad et al. (2020) observed the top NO_x conversion rate of Ag-Cu catalyst as 62.75% with the reductants as ethanol-water blends at 20000 h^{-1}. Even though fusel oil includes around 10% H_2O, the NO_x transformation ratio provided common outcomes of the other studies where H_2O not used. Keskin and Akar (2020) says that the top NO_x transoformation ratio of ANP-TVC-TVM hybrid catalyst when ethanol, n-propanol, and n-penthanol reductants are present at 300 °C at 30000 h^{-1} were 88.2%, 85.8%, and 82%, respectively.

6.3. Conclusion and recommendations

6.3.1. Conclusion

This experiment was carried out to investigate the NO_x reduction with fusel oil as the reducing agent and Mo-Cu-Ag/TiO_2 /Cordierite catalyst for the SCR system. Oxalic acid was used to increase the surface area of the cordierite substance, the carrying structure. The produced catalyst's BET surface area was increased by 98.81%. The XRD analysis revealed spikes of nanometal materials having catalytic capabilities. It was determined from the XRD results that there was a significant interaction between the cordierite and these components. Results from SEM/EDS were used to ascertain whether catalytic components were present on the cordierite surface. The cordierite's morphological structure did not significantly change after the coating process. Performance testing revealed that at 290 °C, the maximum test temperature, the best NO_x conversion efficiencies in all space velocity values and engine loads were accomplished. Of all the tests, the highest NO_x conversion rate achieved was found to be 85.94% at 290 °C at 1 kW at 30000

h^{-1}. The increase from 200 to 290 °C, the NO_x conversion efficiency was positively influenced by the exhaust gas temperature. It can be inferred that the various nano metallic catalysts could be a better approach on the catalytic activity at low temperatures in the case of using fusel oil as the reductant agent for SCR systems.

6.3.2. Recommendations

In Turkey, unfortunately aftertreatment emissions are only partially studied scientifically. As Turkey couldn't catch up with combustion engine and aftertreatment systems production, the popular electric vehicle investments are more being considered and supported by the government. However, the bigger combustion engines are being used widely in diferent areas like marine, heavy commercial vehicles and industrial areas which is a proof that we should still consider the negative effects and outputs. Hence, any literature update would encourage more effective ways to reduce NOx emissions from diesel engines. The findings of this thesis may be used as a guide for future studies on aftertreatment emissions restrictions. Future studies may find it more important to use waste materials like fusel oil, as well as to use fusel oil as the reducing agent, the NO_x reduction behavior of various catalysts can be researched by scientists.

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