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PRIMJENA SELEKTIVNE KATALITIČKE REDUKCIJE NA DVOTAKTNE SPOROOKRETNE BRODSKE DIZELSKE MOTORE

THE SELECTIVE CATALYTIC REDUCTION (SCR) APPLICATION ON TWO STROKE SLOW SPEED MARINE DIESEL ENGINES

SAŽETAK

Sustavnim pristupom problematici sprječavanja onečišćenja atmosfere iz brodskih sporookretnih dizelskih motora, a u skladu s novoprihvaćenim međunarodnim normama, nametnula se potreba za analizom trenutno dostupnih metoda redukcije štetnih plinova iz kojih bi se potom sintetiziralo ekološki prihvatljivo i ekonomski isplativo rješenje.

Slijedom toga u radu je sažet pregled glavnih onečišćivača atmosfere iz sporookretnih brodskih dizelskih motora, izvor i razlog njihovog nastajanja, te pojašnjeni problemi vezani za selektivnu katalitičku redukciju. Ukratko je objašnjena sama kemijska reakcija koja se odvija u reaktoru, kao i najčešće metode vezane za smanjenje NOx-a.

Kako moderne generacije motora rade s vrlo niskim temperaturama ispušnih plinova pojavljuje se problem naslaga amonijevog sulfata na nižim režimima rada motora. U radu je dan pregled i rezultati istraživanja provedenog u Japanu 2009. godine koje pokazuje da je moguće koristiti SCR i na nižim temperaturama bez značajnijih smanjenja performansi motora ili reaktora. Zaključno, autori su dali svoje prijedloge i razmišljanja vezana za mogućnost kombiniranja SCR-a s performansama koje mogu postići nove generacije sporookretnih brodskih dizelskih motora s elektroničkom kontrolom.

Ključne riječi: *dušični oksidi (NOx), selektivna katalitička redukcija (SCR), sporookretni dvotaktni brodski dizelski motori, emisija ispušnih plinova*

SUMMARY

A systematic approach to the problem of preventing air pollution from marine slow speed diesel engines, in accordance with the recently adopted international standards, has become necessary for the analysis of currently available methods of reducing emissions from which they would then be synthesized in an environmentally friendly and economically viable solution.

Subsequently, the main atmosphere pollutants from slow speed diesel engines synopsis have been summarized in this paper, the sources and reason of their formation and the problems linked with the selective catalytic reaction (SCR) have been explained too. The chemical reaction in a SC Reactor has been briefly explained, as well as, in general, the methods for the NOx reduction.

Since the modern slow speed diesel engines run with very low exhaust gas temperatures, on low engine loads the ammonium sulfate deposits formation problem have appeared. The paper aims at presenting the review and researching results carried out in Japan in 2009, which approved that the SCR application on board a ship is possible without significantly reducing engine or reactor performances.

The authors have also included their suggestions and considerations linked with new possibilities of SCR performances in combination with modern, electronically controlled, slow speed diesel engines.

Key words: *nitric oxides (NOx), Selective Catalytic Reduction (SCR), slow speed diesel engines, exhaust gas emission.*

1. UVOD

S obzirom na veliku instaliranu snagu sporookretnih dvotaktnih brodskih dizelskih motora i njihov broj u eksploataciji, može se zaključiti da su to motori koji ukupno izgaraju vrlo velike količine goriva, te kao produkt nastaju i velike emisije raznih polutanata. Uz dobro poznate stakleničke plinove, postoje kemijski spojevi koji imaju naročito štetno djelovanje na ozonski omotač. Pored već zabranjenih halona i freona, najveći učinak imaju dušikovi oksidi pod zajedničkim nazivom NOx spojevi.

Glavni onečišćivači atmosfere, dobiveni izgaranjem goriva u dizelskim motorima su dušični oksidi (NOx), sumporni oksidi (SOx), ugljični monooksid (CO), ugljični dioksid (CO_2), neizgoreni ugljikovodici (HC) i krute čestice (PM).

NOx je funkcija maksimalne temperature izgaranja i lokalne koncentracije O_2 u smjesi. Koncentracija O_2 se može smanjiti dovođenjem manje količine svježeg zraka korištenjem dijela količine ispušnih plinova preko tzv. sustava recirkulacije ispušnih plinova (engl. EGR – Exhaust Gas Recirculation). NOx mogu biti smanjeni primarnim ili sekundarnim metodama. Po postojećim Tier II normama za sporookretne brodske dizelske motore, brzine vrtnje manje od 130 min^{-1}, granica je 14,4 g/kWh. Po nadolazećim Tier III standardima (2016. g.) granica se spušta na 3,4 g/kWh.

SOx je funkcija količine sumpora u gorivu, te je smanjenje postotka S u gorivu najučinkovitiji način smanjenja SOx-a. Jedan od načina je ispiranje ispušnih plinova morem, ali se tu pojavljuju problemi skladištenja ili neutralizacije sumporne kiseline, taloga, korozije i sl. Normativi za količinu sumpora u gorivu od 07. 2010. su 1% za ECA (Emision Control Area), 4,5% (3,5% će biti od 1. 1 2012.) globalno. Nadolazeći propisi (2015. do 2020.) propisuju smanjenje na 0,1% u ECA (1. 1. 2015.) i 0,5% globalno (1. 1. 2020., ali samo ako rafinerije mogu zadovoljiti zahtjev što će se provjeriti 2018., inače stupa na snagu 1. 1. 2025.).

CO je produkt nepotpunog izgaranja. Funkcija je pretička zraka i temperature izgaranja, a ovisi i o kvalitete smjese goriva i zraka. Kod 2T sporookretnih motora je udio CO u ispušnim plinovima najčešće vrlo nizak zbog velikog pretička zraka ($\lambda>2$). Značajnije se pojavljuje kod naglih povećanja opterećenja u vremenu zaleta TP (turbopuhala).

1. INTRODUCTION

Considering the large installed capacity of slow speed two-stroke marine diesel engines and their number in service, it can be concluded that these are engines that burn very large amounts of fuel, creating as a product high emissions of various pollutants.

Besides the well known greenhouse gases, there are chemical compounds which have an especially harmful effect on the ozone shield. Apart from the already prohibited Halons and Freons, the greatest destructive influences on the ozone shield have nitrogen oxides, commonly named NOx.

The main earth's atmosphere pollutants, produced by fuel burning in diesel engines are nitrogen oxides (NOx), sulfur oxides (SOx), carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbons (HC) and particulate matter (PM).

NOx is a function of maximum combustion temperature and local oxygen concentration in fuel-air mixture. The O_2 concentration can be reduced by bringing smaller amount of fresh air into the engine cylinder by using the exhaust gas recirculation method (EGR). NOx concentration can be reduced by primary or by secondary methods. According to the existing Tier II regulations for slow speed diesel engines, rotational speed less than 130 rpm, the limit is 14.4 g/kWh. According to new incoming Tier III standards (2016.), this limit will go down to 3.4 g/kWh.

SOx is a function of sulfur quantities in the burned fuel, so the decreasing sulfur percent in fuel oil is the most effective means of reducing SOx in exhaust gases. There is also the SOx reducing method by using exhaust gas scrubbing with sea water, but there are problems of sulfuric acid formation, its neutralization or storage. International regulations for sulfur quantity in heavy fuel are 1% (from July 2010) in Emission Control Area (ECA) and 4.5% globally (3.5% will be from January 2012). The new incoming regulations will come into application from 2015 to 2020 with limits of sulfur in fuel oil of 0.1% (2015.) in ECA and 0.5% globally (from January 2020 but only if refineries can comply with, which should be checked in 2018. The full enter into force will be in 2025.).

CO_2 je produkt potpunog izgaranja i neminovan je u izgaranju, te je funkcija potrošnje goriva. Jedan je od najvećih čimbenika koji utječu na efekt staklenika, a najbolja metoda smanjenja je smanjenje potrošnje goriva.

HC ovise o vrsti goriva i vrsti cilindarskog ulja, a neizbježni su zato što i u najboljem slučaju male količine goriva i ulja ostanu neizgorene.

PM nastaju od djelomično izgorjelog goriva, a ovisi o količini pepela i ostacima katalizatora iz rafinerijskog procesa u gorivu i cilindarskom ulju, količini dovedenog cilindarskog ulja, te količini skinutih, prije nataloženih čestica s površine stijenki prostora izgaranja i cjevovoda ispušnog sustava.

Budući da sporookretni brodski dvotaktni dizelski motori rade s velikim pretičkom zraka, katalizatori koji se rabe u automobilskoj i kamionskoj industriji su neprimjenjivi. Također, sumpor iz teških goriva bi vrlo brzo uništio takav tip katalizatora zbog naslaga koje se stvaraju spajanjem amonijaka i sumpora iz goriva na nižim temperaturama reakcije.

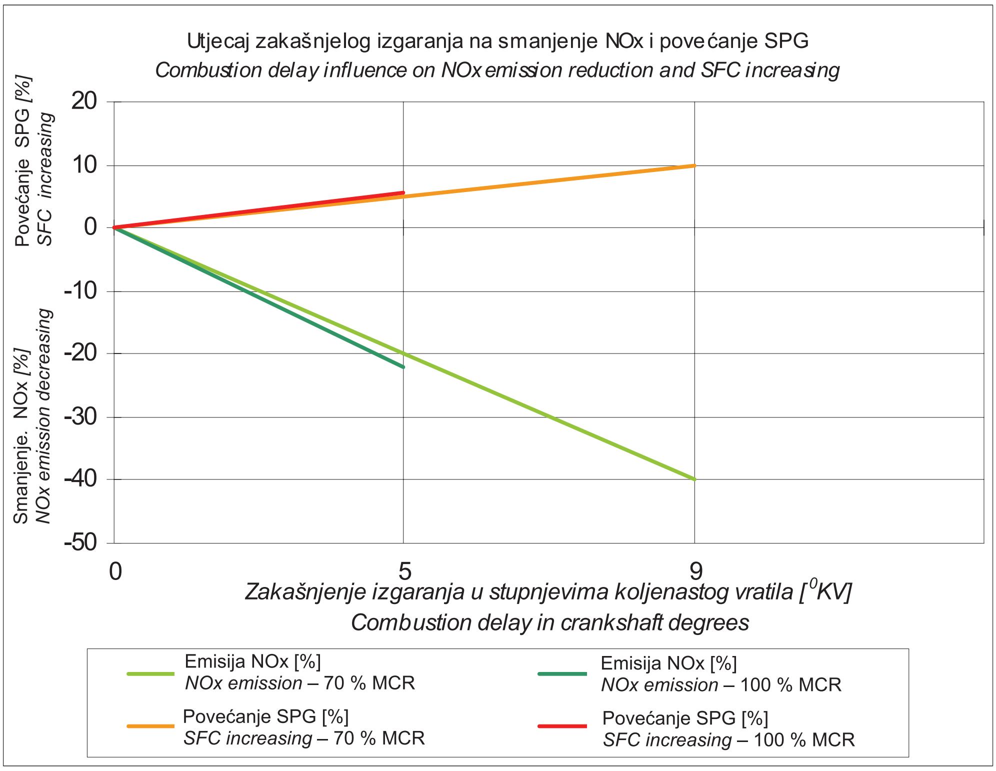
Selektivna katalitička redukcija (SCR) se koristi u svrhu smanjivanja emisije, za atmosferu vrlo štetnih, dušikovih oksida (NOx) koji se stvaraju izgaranjem goriva u motorima s unutarnjim

CO is a product incomplete combustion. It is a function of air fuel ratio (AFR) and combustion temperature but is also dependant of air – fuel mixture quality. In slow speed diesel engines, the CO content into exhaust gases is usually very low or negligible due to high AFR ($\lambda>2$). It can occur significantly during suddenly engine load changing due to turbo blower speed retarding.

CO_2 is a product of complete combustion, it is unavoidable and it is directly connected with fuel oil consumption. It is one of the greatest factors influencing the greenhouse effect and the best reducing method is decreasing the fuel oil consumption.

HC depends on fuel oil and cylinder oil type. They are also unavoidable because, even in the best cases, small amounts of fuel and cylinder oil remain unburned.

PM are produced from partially burned fuel and lube oil and they depend on ash quantities and catalyzing residues from fuel and lube oil refinery process, on the delivery of cylinder lube oil and on the quantity of the removed, before precipitated particles from the combustion space wall surface and exhaust system pipeline.



Slika 1. Ovisnost povećanja SPG-a i smanjenja Nox-a ovisno o zakašnjenju ubrizgavanja [2]
Figure 1 *SFC increasing and NOx reducing depending of combustion delay* [2]

izgaranjem. Stoga, zbog samog procesa izgaranja, odnosno relativno dugog trajanja izgaranja u odnosu na četverotaktne brzookretne dizelske motore, najveće emisije NOx-a nastaju u sporookretnim brodskim dizelskim motorima.

SCR se koristi za obradu ispušnih plinova nakon izlaza iz cilindara motora, a prije njihovog izlaza u atmosferu. Suština je u dodavanju para amonijaka u ispušne plinove visoke temperature koja se mora održavati zbog same kemijske reakcije u području između 300 do 400 ^{0}C. Zbog potrebe za tako visokim temperaturama reakcije ovaj se sustav najčešće ugrađivao prije turbopuhala (Slika 2).

Ako je temperatura kemijske reakcije previsoka (iznad 490 ^{0}C), amonijak izgara i ne sudjeluje u reakciji s NOx-ima. U slučaju preniske temperature (ispod 250 ^{0}C), razina kemijskih reakcija je preniska, a sam katalizator se može zaprljati i oštetiti.

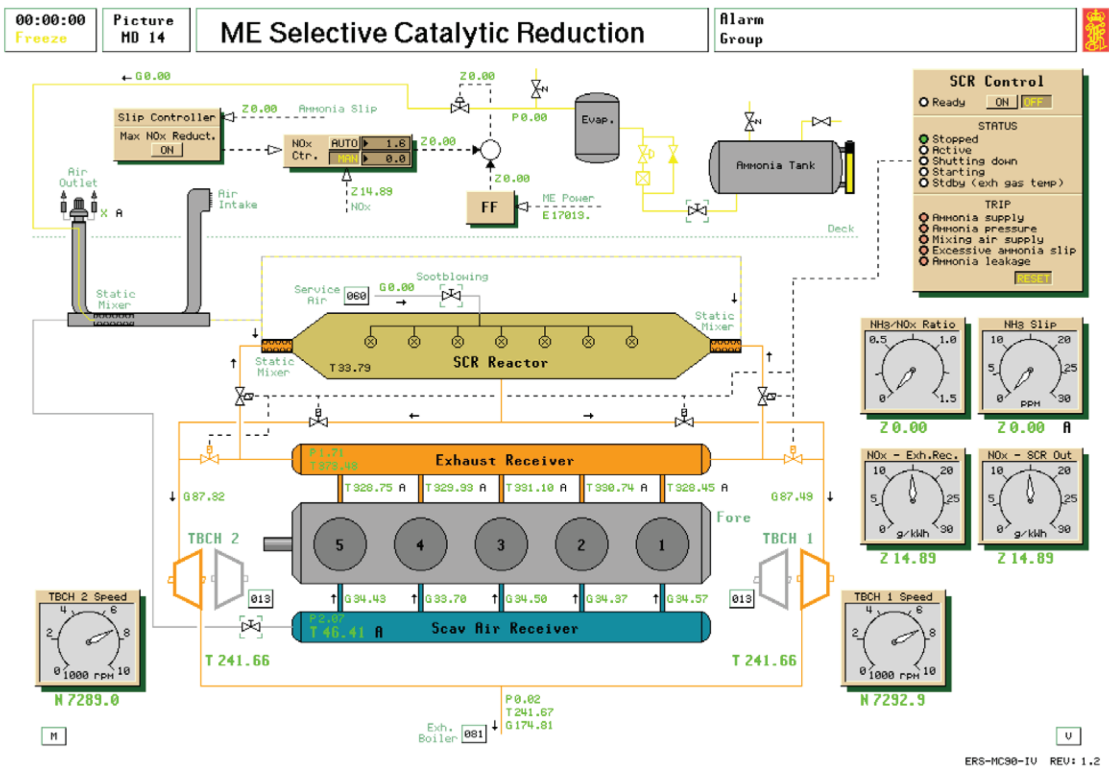
2. METODE ZA SMANJENJE NOX-a

Metode za smanjenje Nox-a mogu se podijeliti na primarne i sekundarne. U primarne me-

Since the two-stroke slow speed marine diesel engines run with huge AFR, the catalysts used in car and truck industries are unusable. Besides, the sulfur from heavy fuels will destroy such type of catalyst due to deposits produced by combining ammonia and sulfur from fuel on lower reaction temperatures.

Selective Catalytic Reduction (SCR) is used for reduction purpose of the, for the atmosphere very harmful, NOx emissions produced by fuel combustion in internal combustion engines. Therefore, due to the combustion process itself and the relatively long combustion duration as compared to the four-stroke high speed diesel engines, the greatest NOx emissions are produced in two-stroke low speed marine diesel engines.

SCR is used for the exhaust gases treatment after the engine cylinder outlet, and before their exit into the atmosphere. The bottom line is in the addition of the ammonia gases into the high temperature exhaust gases that must be maintained because of the chemical reactions ranging from 300 to 400 ^{0}C. Because of the need for such high reaction temperatures, this system has been usually incorporated before the turbochargers (figure 2).



Slika 2. Prikaz sustava selektivne katalitičke redukcije [1]
Figure 2 *Selective catalytic reduction system* [1]

tode spadaju način izgaranja (mogu smanjiti NOx za 10 do 50%), npr.: smanjenje maksimalnog tlaka izgaranja, kontrola kvalitete zraka za izgaranje, prilagodba sapnice rasprskača i ubrizgavanja goriva, emulzija vode i goriva, ubrizgavanje vode ili ovlaživanje zraka i dr.

U sekundarne metode spadaju one koje smanjuju NOx izvan prostora izgaranja, odnosno nakon cilindra, jer najčešće nemaju veći utjecaj na performanse motora, a stupanj smanjenja NOx se kreće i do 95% što je slučaj kod SCR-a koja je trenutno i najučinkovitija metoda smanjenja emisije NOx-a.

2.1. Utjecaj smanjenja maksimalnog tlaka izgaranja

Smanjenjem, maksimalnog tlaka izgaranja (p_{max}) smanjuje se maksimalna temperatura izgaranja, te su manje i lokalne maksimalne temperature procesa koje su najveće u područjima oko mlaza goriva. Visoka temperatura je uz uvjet dovoljnog vremena glavni preduvjet stvaranja Nox-a, te se njezinim smanjenjem smanjuje i stvaranje Nox-a. Nedostatak je što se smanjenjem temperature u područjima neposredno iza GMT-a smanjuje toplinska iskoristivost goriva, odnosno povećava potrošnja goriva. Ovisnost specifične potrošnje goriva (SPG) i smanjenja Nox-a o zakašnjenju ubrizgavanja prikazana je na slici 1 [2].

2.2. Kontrola kvalitete zraka za izgaranje

Parcijalni tlakovi kisika i dušika u zraku mogu se promijeniti količinom dovedenog zraka u cilindar ili promjenom omjera kisika i dušika. Količina ovisi o tlaku ispirnog zraka, odnosno brzini vrtnje turbopuhala. Omjer se može mijenjati recirkulacijom ispušnih plinova, odnosno EGR-om. Uz 15%-tnu recirkulaciju ispušnih plinova, koncentracija O_2 u smjesi zraka i ispušnog plina koja ulazi u (puni) cilindar pada s 21% na približno 18%, što ima značajan utjecaj na smanjenje emisije NOx-a.

2.3. Prilagodba sapnice rasprskača i ubrizgavanje goriva

Ispitivanja su pokazala značajan utjecaj oblika i tipa sapnice rasprskača kao i načina ubrizgavanja na emisiju Nox-a [9]. Način ubrizgavanja određuje profil izgaranja kojim se može

If the temperature of the chemical reaction is too high (above 490 ^{0}C), ammonia burns and does not participate in the reaction with NOx. In case of too low temperatures (below 250 ^{0}C), the level of the chemical reaction is too low, and the catalyst can contaminate and damage.

2. THE NOX REDUCING METHODS

The methods for reducing NOx can be divided into the primary and secondary ones. Primary methods affect the combustion (NOx can be reduced by 10 to 50%), and are for example: reducing the maximum combustion pressure, controlling the combustion air quality, the fuel oil nozzle adjustment and fuel injection, fuel and water emulsions, water injection or humidification of air, etc. The secondary methods are those that reduce NOx emissions beyond the combustion space, and after the cylinder. They usually have a greater impact on the engine performance, and the degree of NOx reduction ranges up to 95% in the case of SCR, which is currently the most effective method of reducing NOx emissions.

2.1. The effect of reducing the maximum combustion pressure

Reducing the maximum combustion pressure (p_{max}), the maximum combustion temperature is reduced, and the local maximum temperatures of the process, that are the highest in spaces surrounding the fuel injection, are lower. High temperature, conditioned with a sufficient time, is a major prerequisite to create NOx, and by its reduction decreases the creation of the NOx. The disadvantage is that the reduction of the temperature in spaces right behind the TDC reduces the thermal fuel efficiency and increases the fuel oil consumption. The specific fuel consumption (SPG) and the NOx reduction depending on the injection delay are shown on Figure 1 [2].

2.2. Combustion air quality control

Oxygen and nitrogen partial pressure in the air can be changed by the quantity of air fed into the cylinder or by changing the oxygen and nitrogen ratio. The combustion air amount deznačajno smanjiti emisija NOx-a uz zadržavanje potrošnje goriva u sadašnjim granicama. Za spuštanje NOx-a na razinu koju propisuju najnovije Tier III norme ovakva strategija, bez nekog od dodatnih načina smanjivanja, nije dovoljna.

2.4. Emulzija vode i goriva (FWE)

Utjecaj vode na smanjenje stvaranja NOx-a tijekom izgaranja ovisi o tipu i vrsti motora, ali općenito se može reći da 1% vode u gorivu smanjuje produkciju NOx-a za 1% [2].

S obzirom na volumetrijski kapacitet visokotlačne pumpe, u standardnim izvedbama sporookretnih brodskih dvotaktnih dizelskih motora dozvoljava se miješanje do 20% vode u gorivo na punom opterećenju motora. S obzirom na izgaranje, istraživane su emulzije goriva i vode s omjerima do 50:50% [2]. Izgaranje ovako velikih količina vode s gorivom zahtijeva i dodatne modifikacije motora, prvenstveno sustava goriva i prostora izgaranja, te takvi motori ne spadaju u standardne izvedbe. Miješanje goriva i vode izvodi se prije recirkulacijskog kruga (prije tanka mješača).

Količina dodane vode ovisi o željenom smanjenju emisije Nox-a. Za brodove koji koriste ovakav sustav potreban je i poseban zaštitni sustav da u slučaju nestanka električne energije (black out) omogući ponovno pokretanje GM-a. Naime, zaštitni sustav treba omogućiti nastavak stabilnog miješanja goriva i vode jer bi u suprotnom trebalo prebaciti na gorivo bez vode.

2.5. Ubrizgavanje vode ili ovlaživanje zraka (DWI i HMI)

Direktno ubrizgavanje vode u cilindar motora vrši se pomoću posebne sapnice ili pomoću sapnice za ubrizgavanje goriva. Rezultat je isti kao kod FWE sustava s time što je emulzifikacija (FWE) jednostavnija, te je manja potrošnja vode (koristi se ista sapnica). Nedostatak je abrazivno djelovanje na sapnicu i njezin kraći vijek trajanja.

Kod ovlaživanja zraka potrebno je naglasiti da previše vode u ispirnom zraku može prijevremeno uništiti cilindar. Stoga se nakon rashladnika zraka ugrađuju odvajači kapljica, iako ovakav način još nije našao veću primjenu na sporookretnim brodskim dizelskim motorima.

pends on the scavenging air pressure or turbocharger speed. The ratio can be modified by exhaust gas recirculation (EGR). With a 15% exhaust gas recirculation, the O_2 concentration in the mixture of air and exhaust gas which enters into the cylinder is falling from 21% to about 18%, thus having a significant impact on reducing the NOx emissions.

2.3. Fuel valve nozzle adjustment and fuel injection type

Tests have shown a significant influence of the fuel oil nozzle shape and type as well as of the fuel injection type on NOx emissions [9]. The fuel oil injection method determines the combustion profile, which can significantly reduce the NOx emissions while maintaining the fuel oil consumption in the current limits. To lower the NOx to the level prescribed by the latest Tier III standards such a strategy, without any additional reducing ways, is not enough.

2.4. Fresh Water Emulsification

The influence of water on reducing the NOx formation during the combustion stage depends on the engine type, but, generally speaking, it can be said that one per cent of water in the fuel reduces the production of the NOx by one per cent [2]. Thanks to the fuel injection pump volumetric capacity, in the two-stroke slow speed marine diesel engine standard versions, the mixing of up to 20% of water in the fuel at full engine load is allowed. As regards combustion, fuel and water emulsion were investigated with a ratio of up to 50:50% [2]. The combustion of such large amounts of water in the fuel requires additional engine modifications, primarily the fuel oil system and combustion space, and such engines are not included in the standard version. Fuel and water mixing is performed before the fuel recirculation circuit (before the mixing tank). The amount of the added water depends on the desired reduction of the NOx emissions. To enable the ME restarting, for ships that use this system, a special safety system is compulsory in case of the power failure (black out). However, the safety system should provide a continuous and stable mixing of fuel and water, otherwise, the transfer to the fuel oil without water should be necessary.

2.6. Kumulativni efekt

Kada se koriste samostalno, prethodno spomenuti načini smanjenja NOx-a ne mogu udovoljiti Tier III normama, ali u kombinaciji imaju značajan efekt i mogu smanjiti NOx za više od 80% u odnosu na Tier II norme. Treba naglasiti da neke od metoda, osim metoda smanjenja temperature izgaranja vodom i smanjenja NOx-a posebnim sapnicama, nisu u potpunosti ispitane.

2.7. Selektivna katalitička redukcija (SCR)

SCR je isprobana i najučinkovitija metoda za značajno smanjenje NOx-a bez većeg utjecaja na specifičnu potrošnju goriva (SPG). Na stacionarnim postrojenjima je u uporabi od 1980. U dizelskim motorima za komercijalna teretna i putnička vozila to je jedina ekonomski isplativa, a za okoliš prihvatljiva tehnologija koja smanjuje emisije NOx na razinu vrlo blizu nule. SCR tehnologija je dizajnirana da omogućuje reakciju NOx-a u oksidirajućem okruženju (uz prisustvo O_2 kao neophodnog kemijskog elementa). Selektivna je, jer smanjuje samo razinu NOx-a koristeći amonijak (NH_3) kao neophodni element unutar sustava katalizacije. Izvor amonijaka je obično urea koja je već u primjeni kod kamionskih i motora autobusa, a poznata pod nazivom "tekućina za ispušne sustave" (engl. Diesel Exhaust Fluid ili 'AdBlue').

U tehnologiji smanjenja NOx-a kod kopnenih vozila rezultati su vrlo dobri. NOx se smanjuju do 90% uz paralelno smanjivanje HC i CO od 50 do 90%, te PM od 30 do 50%. U kombinaciji s filtrom za krute čestice PM se mogu i dodatno smanjiti.

Amonijak je u vodi dobro i ravnomjerno otopljen, te se isparavanjem ponovo odvaja i potom oksidira uz pomoć kisika i visoke temperature ispušnih plinova.

Osnovna kemijska reakcija koja se odvija u reaktoru može se opisati sljedećim izrazima:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$

SCR samostalno, bez drugih metoda, može smanjiti NOx za više od 90%. Kako je za proces oksidacije neophodan kisik, sporookretni dvotaktni dizelski motori su pogodni za ovakav sustav, zbog velikog pretička zraka s kojim rade.

2.5. Direct water injection or scavenging air humidification (DWI or HMI)

A direct water injection (DWI) into the engine cylinder can be done with special nozzles or with fuel oil nozzles. The result is the same as by the FWE system, but the emulsification (FWE) is simpler and the water consumption is less (the same nozzle is used). The disadvantage of this method is the abrasive effect to the nozzle and its short lifetime.

In the case of scavenging air humidification, it should be noted that too much water in the scavenging air can prematurely destroy the cylinder. Therefore, the mist catchers should be installed after the scavenging air coolers, and this method has not found greater application in two-stroke slow speed marine diesel engines.

2.6. Cumulative effect

The previously mentioned ways for the NOx reduction, when used alone, can not meet the Tier III standards, but in combination have a significant effect and can reduce NOx by more than 80% compared to the Tier II standards. It should be noted that some of the methods, except the method of reducing combustion temperature by water and that of reducing NOx by special nozzles, have not been fully tested

2.7. Selective catalytic reduction (SCR)

SCR is a well proven and efficient method for a significant NOx reduction with no significant impact on the specific fuel consumption (SFC). For stationary installations it has been in use since 1980. In diesel engines for commercial trucks and passenger cars, it is the only economically viable and environmentally friendly technology that reduces the NOx emissions to a level very close to zero. The SCR technology is designed to allow the reaction of NOx in the oxidizing environment (in the presence of O_2 as an essential chemical element). It is selective because it reduces only the level of the NOx using ammonia (NH_3) as a necessary element within the catalysis. The ammonia source is usually urea, which is already in use in truck and bus engines, and known as Diesel Exhaust Fluid or Ad Blue.

The results obtained in the NOx reducing technology by land vehicles are very good. NOx

Ako je temperatura previsoka (> 490°C), NH_3 izgori prije nego što stigne reagirati s NO i NO_2. Na nižim temperaturama (< 250°C), razina kemijske reakcije je slaba, ostaje određena količina NH_3 koji nije sudjelovao u reakciji (NH_3 slip), te dolazi do kondenzacije amonijevog sulfata koji uništava katalizator tako što se taloži na njegove stijenke.

Količina NH_3 ubrizgana u ispušni plin kontrolira se računalom ili PLC-ejem na osnovi usporedbe zadane vrijednosti, te opterećenja motora. Opterećenje se uzima kao glavni parametar funkcije koja opisuje stvaranje NOx-a. Funkcija koja opisuje količinu stvorenih NOx-a ovisno o opterećenju motora određuje se na probnom stolu za vrijeme ispitivanja motora. Ta funkcija je uprogramirana u procesor koji upravlja doziranjem urea otopine. Doziranje urea otopine se konstantno podešava na osnovi stvarne količine NOx-a (osjetnik je smješten u ispušnom vodu prije izlaza ispušnih plinova u atmosferu). Ovakav način kontrole se koristi zbog tromosti reakcije u reaktoru koja bi nastala kada bi se doziranje vršilo samo na osnovi ovisnosti količine urea otopine u ovisnosti o količini NOx-a. Tada bi se pojavila prekomjerna odstupanja u koncentracijama NOx-a ili bi u ispušnim plinovima koji izlaze u atmosferu zaostao amonijak. Osjetnik za mjerenje NOx-a je integralni dio opreme za doziranje NH_3 (urea otopine), a sve je spojeno na kontrolno-upravljački panel koji se nalazi u kontrolnoj kabini strojarnice. U sklopu nadzora nalazi se analizator kisika, uređaj za alarm količine NH_3, te kontrolni memorijski zapis o stanju i performansama sustava.

Stupanj snižavanja NOx-a ovisi o količini dodanog amonijaka (izražava se omjerom NH_3/NOx). Na većim NH_3/NOx omjerima veća se količina NOx-a smanjuje, ali u isto vrijeme postoji opasnost od povećanje količine "neiskorištenog" amonijaka (NH_3 slip). Poželjno je da je koncentracija neiskorištenog NH_3 u ispušnim plinovima što manja, jer postoji opasnost da se na stijenkama izmjenjivača topline utilizatora stvori talog u obliku amonijak-vodik sulfata (NH_4HSO_4), koji je vrlo tvrd i može predstavljati veliki problem vezano uz izmjenu topline, trajnost cijevi i sl.

Sustav SCR s glavnim dijelovima prikazan je na slici 2. [1].

is reduced up to 90% with a parallel reduction of HC and CO by 50 to 90% and PM by 30 to 50%. In combination with a particulate matter (PM) filter, the PM can be further reduced.

Ammonia is well and evenly diluted in water and it is separated again by evaporation and then it oxidizes by means of oxygen and high temperature exhaust gases.

The basic chemical reaction that takes place in a reactor can be described by the following terms:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$

SCR alone, without other methods, can reduce NOx by more than 90%. As for the oxidation process oxygen is needed, slow speed two-stroke diesel engines are suitable for such a system, due to the large air fuel ratio.

If the temperature is too high (> 490oC), NH_3 burns out before it reaches to react with NO and NO_2. At lower temperatures (< 250oC), the level of the chemical reaction is weak, a certain amount of NH_3, which was not involved in the reaction (NH_3 slip), remains and the condensation of the ammonium sulfate occurs which destroys the catalyst by depositing on its wall.

The NH_3 amount injected in the exhaust gas is controlled by a computer or by a PLC-operation based on the comparison of the set point and the engine load. The engine load is taken as the main parameter of a function that describes the NOx creation. The function that describes the amount of the generated NOx, depending on the engine load is determined on the test bed during the engine trial. This function is programmed into a processor that controls the dosage of the urea solution. The dosing of the urea solution is continuously adjusted based on the actual amounts of NOx (the sensor is located in the discharge line before the exit of the exhaust gases into the atmosphere). This control method is used because of the inertia of the reaction in the reactor, which would occur if the dosage is made only on the basis of the quantity of the urea solution, depending on the amount of the NOx. Then, excessive variations in the concentrations of the NOx will appear or the ammonia will remain into the exhaust gases emitted into the atmosphere. The NOx measuring sensor is an integral part of the

Doziranje amonijaka u ppm je automatizirano na osnovi usporedbe zadanog parametra količine NOx-a u g/kWh i stvarne vrijednosti za količinu NOx-a. Protok amonijaka može se smanjivati (do 0,01 g/kWh/s) ili povećavati (do 0,02 g/kWh/s) određivanjem željene brzine. Maksimalna količina dodanog amonijaka je ograničena, budući da višak dovodi do pojave viška amonijaka u ispušnim plinovima uslijed nepravilnih kemijskih reakcija, a zaostaju i NOx-i koji se nisu neutralizirali.

Amonijak se dovodi u obliku vodene otopine pod tlakom. Cijeli sustav za dovod amonijaka mora zadovoljiti sigurnosne standarde, budući da je amonijak eksplozivan i opasan za ljudski organizam. Cjevovodi imaju duple stijenke uz detektore i nadzor propuštanja.

Primjena SCR-a ima i određene troškove, odnosno znatno se povećava početna investicija, a isto tako i troškovi eksploatacije. Primjer izračunavanja troškova u primjeni SCR-a prikazan je u tablici 1. Ako se analiziraju istraživanja [10] do [20] moguće je izračunati isplativost ugradnje SCR-a. Komparacijom ovih istraživanja može se zaključiti da početna investicija ugradnje SCR-a ovisi o vrsti i starosti broda te instaliranoj snazi i tipu motora (četverotaktni ili dvotaktni). Intervali u kojima se kreću cijene ugradnje SCR-a su od 40 do 100 US$/kW, dok se operativni troškovi kreću od 3 do 4 US$/MWh. Ako se za primjer uzme brod s GM snage 20 MW, specifične potrošnje 160 g/kWh, koji godišnje radi 7.000 radnih sati, početna investicija se kreće od 0,8 do 2 mil. US$, dok operativni troškovi iznose od 420.000 do 560.000 US$/god. Primjer utjecaja pojedinih čimbenika na troškove SCR-a prikazan je u tablici 1. [20].

U tablici je vidljivo kako na troškove veliki utjecaj ima i gorivo. Upotreba teškog goriva s velikom količinom sumpora smanjuje trajanje reaktora povećavajući troškove zbog potrebe za češćom zamjenom ili regeneracijom reaktora. Također, uz cijenu uree od 400 US$/toni te saznanja da je potrošnja uree od 7 do 10 % potrošnje goriva, za prije dani primjer od 20 MW godišnje, na ureu se potroši oko 760.000 US$/god. Na gorivo, uz iste uvjete, po cijeni goriva od 550 US$/t potroši se oko 14 mil. US$/god (za 25.344 t/god). Ako to izrazimo ekvivalentno u potrošnji po kWh može se reći da motor sa SCR-om ekvivalentno troši više goriva za oko 8 ÷ 10 g/kWh od motora bez SCR-a (168 ÷ 170 g/kWh).

NH_3 feeding equipment (urea solution) and everything is connected to the control panel located in the engine control room. Within the control system there is the oxygen analyzer, a device for the NH_3 quantity alarm and a control memory record of the condition and performances of the system.

The degree of the NOx reduction depends on the amount of the added ammonia (expressed as a ratio NH_3/NOx). At higher NH_3/NOx ratios, a greater quantity of the NOx is reduced, but at the same time there is a risk of the increasing amount of the unused ammonia (NH_3 slip). It is desirable that the concentration of he unused NH_3 in the exhaust gases as small as possible, because there is a problem with the ammonia-hydrogen sulfate (NH4HSO4) deposits creation, which is very strong and can be a great problem with the heat transfer, pipes durability, etc. The SCR system with the major components is shown in Figure 2 [1].

The ammonia dosage in ppm is automated based on the comparison of the default parameters of the NOx in [g/kWh] and the actual NOx value. The flow of ammonia can be reduced (up to 0.01 g/kWh/s) or increased (up to 0.02 g/kWh/s) by determining the desired speed. The maximum amount of the added ammonia is limited, since the excess leads to excess of ammonia in the exhaust gases resulting due to the irregular chemical reactions and not neutralized NOx also remained.

The ammonia is supplied under pressure in the form of aqueous solutions. Since ammonia is explosive and dangerous to human beings, the whole system for supplying ammonia must meet safety standards. Pipelines have a double wall with leak detectors and surveillance.

The SCR application includes certain costs, and significantly increases the initial investment, as well as the exploitation costs. The example of the SCR application cost calculation is shown in table 1. If researches [10] and [20] are being analyzed, it is possible to calculate the SCR installation profitability. By comparing these studies, it can be concluded that the initial investment of the SCR installation depends on the type and age of the ship and the installed engine power and type (four- or two-stroke). The SCR installation price intervals vary from 40 to 100 US$/kW, while the operating costs vary from 3 to 4 US$/MWh. For example, if the

Tablica 1. Utjecaj pojedinih čimbenika na troškove SCR-a [20]
Table 1 *The influence of some factors on the SCR cost [20]*

	MALI BRODOVI *SMALL SHIPS*		SREDNJI BRODOVI *MEDIUM SHIPS*		VELIKI BRODOVI *LARGE SHIPS*		
	GM / *ME*	PM / *AE*	GM / *ME*	PM / *AE*	GM / *ME*	PM / *AE*	
kW	3.000	2.000	10.000	5.000	20.000	15.000	
Fiksne investicije / *Fixed investment* (15 god/*yr)* €	135.000	90.000	350.000	175.000	755.000	453.000	
Operativni troškovi za HFO > 1,5 % S / *Operating costs for HFO > 1,5 % S*	Promjena reaktora svake 2,5 godine. / *Exchange of the reactor every 2,5 years.*						Regeneracijom reaktora troškovi su 60% nove investicije. / *Regeneration reactor costs are 60% of new investment.* Idealno za gorivo s 1,5%S. / *Ideal for fuels with 1.5 % S.*
Operativni troškovi za HFO < 1,5 % S / *Operating costs for HFO < 1,5 % S*	Promjena reaktora svakih 5 godina. / *Exchange of the reactor every 5 years.*						
Operativni troškovi za MDO / *Operating costs for MDO*	Promjena reaktora svakih 20 godina. / *Exchange of the reactor every 20 years.*						
Operativni troškovi / *Operating costs*	- Nema dodatne potrošnje goriva. / *No additional fuel consumption.* - Potrošnja uree = 7,5 % potrošnje goriva (urea 0,3 €/l). / *The consumption of urea = 7,5 % of fuel consumption (urea 0,3€/lit).*						
Troškovi održavanja / *Maintenance costs*	6 čišćenja u 1.000 radnih sati (150 €/čišćenju). / *6 cleaning in 1.000 running hours (150 € / cleaning).*						

3. DALJNJI RAZVOJ SCR-a

U Europi većina motora koji imaju prilagođen SCR rade s temperaturama ispušnih plinova od 300 ^{0}C i više, pa se ne pojavljuju problemi s niskim temperaturama. Dvotaktni sporookretni brodski dizelski motori bili su, i ostali, toplinski strojevi koji rade s najvećim toplinskim stupnjem iskoristivosti. Ovi tipovi motora danas rade na temperaturama ispušnih plinova ispod 300 ^{0}C, a novije generacije ovih motora s elektroničkom regulacijom ubrizgavanja i regulacijom «timinga» ispušnog ventila mogu imati temperature ispuha ispod 250 ^{0}C. Niže temperature ispušnih plinova smanjuju izgubljenu toplinu, pa je manja i potrošnja goriva. Tako je manja i emisiju CO_2.

Da bi se zadržale performanse i dobro stanje katalizatora, postrojenja sa SCR-om na kopnu rade u povoljnijem okruženju, s niskosumpornim gorivima, te u uvjetima visokih temperatura. Postoje sustavi SCR-a instalirani na brodove sa sporookretnim dvotaktnim motorima kao pogonskim strojem. Oni su do sada uvijek bili smješteni prije TP-a, u područje viših tempera-

ship with the installed ME of 20 MW, with the specific fuel consumption of 160 g/kWh and with 7,000 running hours per year is taken into consideration, the initial investment varies from 0.8 to 2 million US$, while the operating costs amount from 420,000 to 560,000 US$/year. An example of the individual factors impact on the SCR cost is shown in table 1 [20].

The table shows that the fuel oil has a major impact on the SCR costs. The use of heavy fuel oil with high sulfur content reduces the duration of the reactor thus increasing the costs due to the need for a more frequent replacement or regeneration of the SCR reactor. Assuming the above mentioned example, the urea price of 400 US$/t, and the fact that the urea consumption is from 7 to 10% of the fuel consumption, the urea expenses amount to US$ 760,000 per year. Under the same conditions and at the fuel price of 550 US$ / t, fuel oil costs are about US$ 14 million / year (for 25,344 t / year). If expressed in equivalent consumption per kWh we can say that the engine with the SCR, consumes equivalently more fuel for about 8 ÷ 10 g / kWh as compared to the engine without a SCR (168 ÷ 170 g / kWh).

tura (Slika 2), čime se smanjuje iskoristivost TP-a, a time i cijelog motora (veća potrošnja goriva). U slučajevima manjih snaga (nižih temperatura) otvara se mimovodni ventil koji zaobilazi reaktor i dovodi ispušni plin direktno na TP čime se štiti reaktor od naslaga i uništenja. Drugim riječima upotreba SCR-a na ovakvim pogonima moguća je samo na stabilnim, stacionarnim većim opterećenjima. Kod promjena opterećenje (npr. tijekom manevra) primjena SCR-a je opasna po trajnost samog reaktora. Problem je što se NOx ne stvara samo na velikim opterećenjima već i na nižim, npr.: kad brod plovi smanjenom brzinom uz obalu, kod dolaska u i odlaska iz luke, prolaska kroz kanal, rijeku i slično.

Jedan od načina povećanja temperature potrebne za kemijsku reakciju pri snižavanju NOx-a prikazan je na slici 3. [5]. Shematski je prikazan SCR u koji se ugljikovodici (HC) i amonijak (NH_3) dovode preko cjevovoda za ubrizgavanje. Cjevovod je perforiran u svrhu raspršivanja, a smjese se zagrijavaju pomoću zagrijača. Zagrijani ugljikovodici dolaze u kontakt s kisikom (O_2) u ispušnom plinu uzrokujući samozapaljenje, te formiraju zonu izgaranja blizu samih sapnica. Izgaranjem na visokoj temperaturi u zoni izgaranja stvaraju se OH radikali koji kemijski reagiraju s dušikom (N_2) iz dovedenog amonijaka (NH_3). Reakcijom se stvaraju plinovi tzv. amini radikala (NH_2) koji imaju redukcijska svojstva s obzirom na smanjenje NOx-a. NOx se u kontaktu s amino-radikalima smanjuje razlaganjem na N_2 i vodenu paru.

Dovođenjem N_2 i (ili) vodene pare omogućuje se podešavanje smjese HC i NH_3 u svakoj koncentraciji. Temperatura miješanja NH_3 i HC je do 600 ^{0}C ili više. Poželjno je da bude 700 ÷ 1000 ^{0}C (još pogodnije 800 ÷ 900 ^{0}C) [5]. To su temperature na kojima se stvaraju OH radikali (iz HC) te amina radikala (iz NH_3).

Gotovo sva istraživanja idu u smjeru načela prikazanog i objašnjenog na slici 3., ali s drugačijim načinima postizanja dovoljno visoke temperature.

Na novim generacijama sporookretnih dvotaktnih brodskih dizelskih motora povećanje temperature ispušnih plinova može se provesti drugim profilom ubrizgavanja u kombinaciji s promjenjivim trenutkom otvaranja ispušnog ventila. Rezultati ispitivanja [4] pokazali su da je regeneracija reaktora i vraćanje na prvobitne

3. FURTHER SCR DEVELOPMENT

In Europe, most engines with the adapted SCR run with the exhaust gas temperatures of 300 ^{0}C or more, so they do not have problems with low temperatures. Two-stroke slow speed marine diesel engines were and have remained thermal machines that operate with the highest degree of thermal efficiency. Today, these types of engines operate at exhaust gas temperatures below 300 ^{0}C, and new generations of these engines, with electronic fuel injection control and exhaust valve timing control, may have the exhaust temperatures below 250 ^{0}C. Lower exhaust gases temperatures mean less heat loss, and less fuel consumption. Thus, the CO_2 emissions are also lower.

In order to maintain performances and good condition of the catalyst, the ashore SCR plants work in a more favorable environment, with low sulfur fuels, and in high temperature conditions. There are SCR systems installed on board ships propulsion plants with two-stroke slow speed marine diesel engines. SCR has so far always been placed before the TC, in the higher exhaust gas temperature area (Fig. 2), thus reducing the efficiency of the TC and of the entire engine as well (more fuel oil consumption). In the case of less power (lower temperature), a bypass valve is open which bypasses the reactor and directs the exhaust gas circulation directly to the TC which protects the reactor from the debris and destruction. In other words, the use of the SCR on these plants is possible only on stable, stationary larger loads. When the load changes (e.g. during the maneuver), the SCR application is threatening the durability of the reactor. The problem is that the NOx creates not only at high loads but at lower ones too, for example, when the ship is operating at a reduced speed along the coast, on entering and leaving a port, passing through the canal, river, etc.

One of the ways to increase the temperature required for the chemical reaction in reducing the NOx is shown in Figure 3 [5]. The SCR, in which the hydrocarbons (HC) and ammonia (NH_3) are induced by injection pipelines, is schematically given. The pipeline is perforated in order to obtain a spray and the mixture is heated by using a heater. The heated hydrocarbons come into contact with oxygen (O_2) in the exhaust gas causing self-ignition and the combustion zone is formed very close to the nozzle.

performanse moguća, te da je regeneraciju reaktora moguće izvoditi kad god je to potrebno. Također, ispitivanje s dvije vrste goriva pokazalo je da se kod MDO s manjim postotkom S (0,07%) povećavaju performanse katalizatora na manjim opterećenjima što je dokazalo povezanost performansi s količinom S u gorivu [4].

4. ZAKLJUČAK

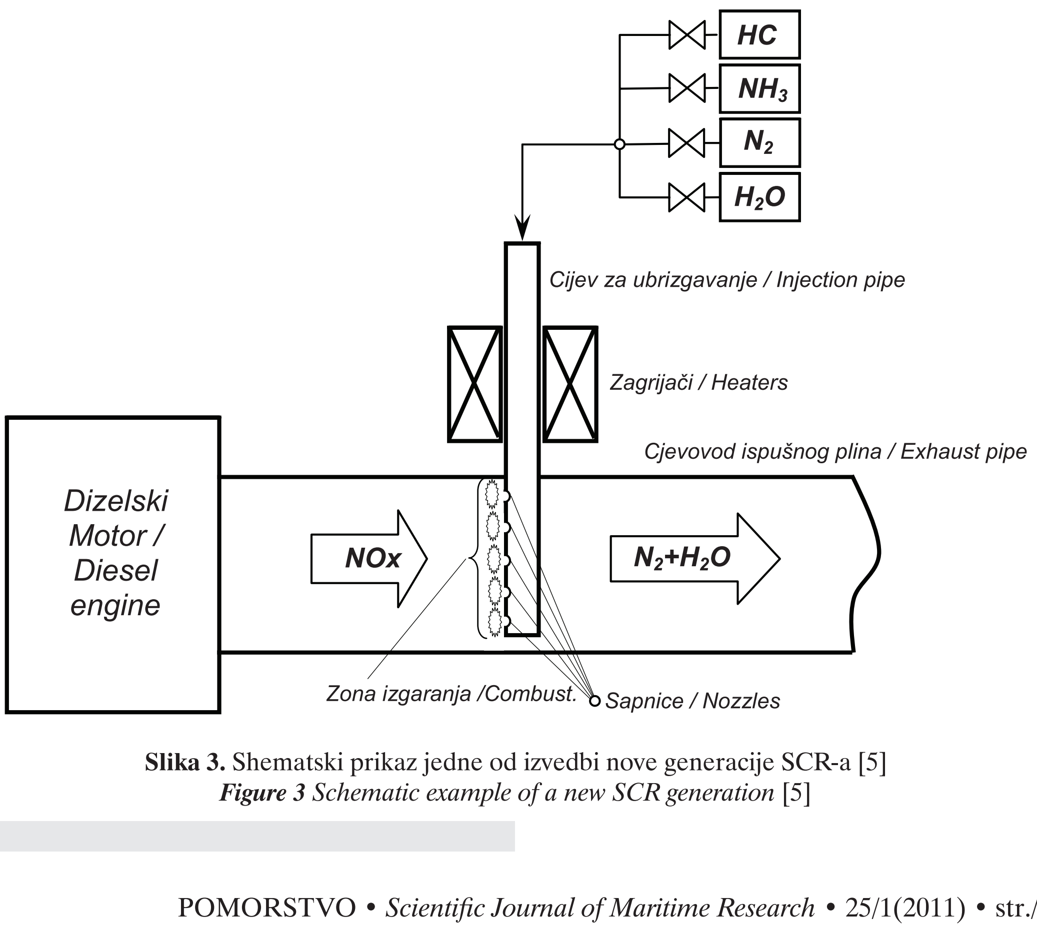
Nadolazeći propisi vezani za smanjenje onečišćivača atmosfere iz dizelskih motora i generatora pare s brodova zahtijevaju veliki tehnološki pomak na ovim toplinskim strojevima. U radu je iznesen kratki pregled metoda koje su danas u uporabi i razvoju, s posebnim osvrtom na trenutno najučinkovitiji, a to je SCR. Izloženi su problemi, te obrađena neka od rješenja. Iznijeta su i razmišljanja koja bi mogla pridonijeti razumijevanju ove teme, te možda pomoći pri daljnjem rješavanju problema.

Može se zaključiti da budućnost nosi velike tehnološke promjene u primjeni svih, pa tako i velikih sporookretnih brodskih dizelskih motora. One će se manifestirati u potpunom prevladavanju elektroničke kontrole ubrizgavanja i kontrole upravljanja ispušnim ventilom uz primjenu nekih od prethodno spomenutih tehnologija.

In the combustion zone, by combustion at high temperature, the OH radicals are produced which chemically react with the nitrogen (N_2) from the fed ammonia (NH_3). The gases are generated by reaction, the so called amine radicals (NH_2), having reduction properties due to the reduction of the NOx. The NOx is reduced in contact with the amine radicals, decompositioning into N_2 and water vapor.

By bringing N_2 and (or) water vapor, it is possible to adjust the mixture of HC and NH_3 in each concentration. The mixing temperature of NH_3 and HC are up to 600 ^{0}C or more. It is desirable to be 700 ÷ 1000 ^{0}C (more favorable 800 ÷ 900 ^{0}C) [5]. These are the temperatures at which OH radicals are formed (from HC) and amine radicals (from NH_3).

Almost all researches have gone in the direction of the principles presented and explained in Figure 3, but with different ways in achieving a sufficiently high temperature. For a new generation of the two-stroke slow speed marine diesel engines, the exhaust gas temperature increase can be achieved with another injection profile in combination with a variable exhaust valve opening. Test results [4] have shown that the reactor regeneration and the return to the original performance are possible, and that the



Slika 3. Shematski prikaz jedne od izvedbi nove generacije SCR-a [5]
***Figure 3** Schematic example of a new SCR generation* [5]

Za očekivati je da će se profilom ubrizgavanja u kombinaciji s EGR-om (primarnim metodama) nastojati postići maksimalna iskoristivost motora, a zatim nekom od sekundarnih metoda, od kojih je najučinkovitija SCR pokušati udovoljiti novim normama za NOx. Problemi s niskim temperaturama su djelomično riješeni, a razvoj će ići i dalje tako da je SCR, prema sadašnjim saznanjima, tehnologija koja za sada nema zamjenu.

Ipak, treba istaknuti da će cijena goriva imati značajan utjecaj, a za očekivati je da ona neće pasti već vjerojatno konstantno rasti. Kada bi cijena goriva pala, mogla bi se proporcionalno smanjiti iskoristivost motora podizanjem temperatura ispušnih plinova korištenjem velike fleksibilnosti elektroničke kontrole ubrizgavanja i ranijim otvaranjem ispušnog ventila. Time bi se proširilo područje primjene SCR-a na veća radna područja motora bez korištenja prije opisanih metoda. Produžilo bi se razdoblje čišćenja (regeneracije) SCR-a, a za pretpostaviti je da bi se produžilo i vrijeme trajnosti inače vrlo skupog SCR-a.

Jedno od rješenja za goriva s većim postotkom sumpora je ugradnja pročistača (engl. scrubbera) prije SCR-a, ali se tada pojavljuje problem snižavanja temperature. Ovaj problem moguće je riješiti ugradnjom električnih zagrijača ili sustava prikazanog na slici 3 uz dobivanje električne energije iskorištavanjem otpadne topline (turbo generator, plinskoturbinski generator i sl.) što ne bi povećalo SPG.

POPIS KRATICA

SCR – Selektivna katalitička redukcija
EGR – Tehnologija recirkulacije ispušnih plinova
FWE – Tehnologija miješanja goriva i vode
DWI – Tehnologija direktnog ubrizgavanja vode
HMI – Tehnologija ovlaživanja zraka
SPG – Specifična potrošnja goriva
ECA – Područja s posebnom kontrolom štetnih emisija
PM – Krute čestice
TP – Turbopuhalo

reactor regeneration can be carried out whenever it is necessary. On the other hand, testing with two fuel oil types has shown that the MDO with a smaller percentage of S (0.07%) increases the performance of the catalyst at lower loads, thus proving the performance correlation with the amount of S in the fuel [4].

4. CONCLUSION

The upcoming regulations related to the reduction of atmospheric pollutants from diesel engines and boilers from ships require a technological shift on these thermal engines. This paper aims at presenting a brief overview of the methods that are now in use and under development, with a special reference to the currently most effective method named the SCR. The problems have been exposed and some of the solutions discussed over. Opinions that could contribute to the understanding of this topic and, maybe, help to resolve some of the further problems have been presented.

It can be concluded that the future is bringing a great technological change in the application of all engines, the large two-stroke slow speed marine diesel engines included. They will be manifested in a complete overcoming of the fuel injection electronic control and exhaust valve timing control with the use of some of the previously mentioned technologies.

It is to be expected that, with the injection profile in combination with the EGR (primary methods) we will try to achieve the maximum engine utilization and then, by using one of the secondary methods, of which the most effective is the SCR, we will try to meet new standards for the NOx. Problems with low temperatures have been partially resolved, and the development will go further on, so that the SCR, according to the already existing knowledge, represents the technology that has no replacement.

However, it should be noted that fuel prices have a very important influence, and it is to expect that they will not fall, but probably grow constantly. Should fuel prices fall, engine efficiency could be proportionally reduced by raising the temperature of the exhaust gases by using the high flexibility of the fuel injection electronic control and by an earlier timing of the exhaust valve opening. This would broaden the SCR application area at higher engine operating ranges, by not using the previously described methods. The SCR cleaning (regeneration) period would be extended and this means that the shelf life of the otherwise very expensive SCR should be extended too.

One of the solutions for fuels with higher sulfur content is to install a special type of a scrubber prior to the SCR, but then the temperatures reduction problem appears. But the problem can be easily solved by installing electric heaters or the system presented in figure 3, and producing electric power by exploiting waste heat (turbo generator, gas turbine generator, etc.) which would not increase the SFC..

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