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ULOGA ADITIVA U POBOLJŠANJU SVOJSTAVA DIZELSKIH GORIVA

Sažetak

Proizvodnja dizelskoga goriva bez primjene različitih aditiva praktično nije zamisliva. Golem napredak motorizacije, trajni razvoj oblikovanja dizelskih motora, jačanje zahtjeva zaštite okoliša te sve veća konkurencija na tržištu motornih goriva, postavljaju zahtjeve na parametre kakvoće dizelskoga goriva, dok u njihovu udovoljavanju aditivi imaju nezamjenjivu ulogu.

Rad navodi osnovne zahtjeve za kakvoćom dizelskoga goriva, opis učinka pojedinih vrsta aditiva te mogućnosti njihove primjene danas, kao i u bliskoj budućnosti.

1. Uvod

Proizvodnja i distribucija dizelskih goriva bez primjene raznih aditiva zasad praktično nije ostvariva. Povećanje zahtjeva za zaštitom okoliša, napredak u razvijanju dizelovih motora i opreme odgovorne za smanjenje koncentracije onečišćavala u ispušnim plinovima, kao i sve veća konkurencija na tržištu motornih goriva, pokretačke su sile parametara kakvoće dizelskih goriva. U postupku unaprjeđenja kakvoće dizelskih goriva, aditivi imaju gotovo nezamjenjivu ulogu. Najveća je njihova prednost što već i u vrlo malim dozama od svega nekoliko stotina mg/kg mogu izmijeniti svojstva dizelskoga goriva do one mjere koja bi inače bila realno ostvariva jedino promjenom proizvodnih tehnologija, uz neizrecivo visoke troškove. U nekim su slučajevima zahtijevana svojstva dizelskih goriva bez primjene aditiva, putem tehnoloških prilagodbi, praktično neostvariva.

2. Zahtjevi kakvoće dizelskih goriva

Pojedinačna se svojstva dizelskih goriva mogu podijeliti u dvije glavne skupine. Prvu skupinu predstavljaju svojstva što ih zahtijeva norma kakvoće - EN 590. Nastanak norme, kao i vrijednosti pojedinačnih parametara kakvoće, mogu se smatrati konsenzusom postignutim od autora norme, koji obično zastupaju sljedeće tri skupine:

- proizvođače automobila (motora),
- predstavnike zaštite okoliša,
- proizvođače motornih goriva.

Njihovi zahtjevi glede parametara kakvoće dizelskih goriva sažeti su u tablici 1.

Tablica 1: Zahtjevi autora normi glede kakvoće dizelskih goriva

Proizvođači automobila	**Zaštita okoliša**	**Industrija nafte**
Cetanski broj Mazivost Sadržaj sumpora Sadržaj poliaromata Svojstva destilacije: Oksidacijska stabilnost Sadržaj FAME Viskoznost Ostatak ugljika (koks) Sadržaj pepela	Sadržaj sumpora Sadržaj poliaromata Svojstva destilacije: - % V/V postignut pri 350°C - Kraj destilacije, ^0C Plamište	Minimalne promjene u odnosu na prethodnu verziju norme

Druga skupina zahtjeva predstavlja složena svojstva, poznata kao primjenska. Za njihovu su formulaciju odgovorne sljedeće strane:

- proizvođači automobila (motora),
- predstavnici zaštite okoliša,
- kupci (vlasnici motornih vozila),
- konkurencija na tržištu motornih goriva.

Tablica 2: Učinak mogućih čimbenika na primjenska svojstva dizelskih goriva

Čimbenik			
Proizvođači automobila	**Zaštita okoliša**	**Korisnici (vlasnici motornih voz.)**	**Konkurencija na tržištu**
Čistoća brizgaljki Ukupni kiselinski broj Korozija željeza Pjenjenje Bez metala (Zn,Cu,Mn,..) Izgled	Ispušne emisije Emisije CO_2 Pjenjenje Sadržaj sastojaka iz obnovljivih izvora	Potrošnja diz. goriva Snaga motora Rad kod niskih temperat. Ubrzanje vozila Vijek motora Vijek skladištenja dizelskog goriva	„Naše je dizelsko gorivo najbolje na tržištu”
Oblici zahtjeva / utvrđivanje primjenskih svojstava			
Svjetska povelja o gorivu	Zakoni, propisi Direktive zaštite okoliša	Predmet tržišnoga zanimanja Ispitivanja motornih benzina u časopisima	Uspoređivanje oglašavanja konkurenata

Za razliku od norme (EN 590) stvorene kao konsenzus između zainteresiranih strana, pri čemu se pojedinačni zahtjevi i njihova ograničenja mogu smatrati minimalnima, strane odgovorne za primjenska svojstva nisu obvezne voditi računa o zahtjevima i mogućnostima ostalih partnera. Radi toga su i sami zahtjevi obično stroži. Zahtjevi vezani uz primjenska svojstva dizelskih goriva prikazani su u tab. 2.

3. Vrste aditiva za dizelska goriva

Pri proizvodnji i distribuciji dizelskih goriva, obično se koriste sljedeći aditivi, kojima se poboljšavanju njihova normirana i korisnička (primjenska) svojstva:

- antioksidanti,
- inhibitori korozije,
- sredstva za deemulgiranje,
- poboljšivači cetanskog broja,
- poboljšivači niskotemperaturnih svojstava,
- ubrizgivački detergenti,
- aditivi mazivosti,
- sredstva protiv pjenjenja,
- antistatički aditivi,
- sredstvo za smanjenje NOx.

Antioksidanti suzbijaju kemijske reakcije nezasićenih ugljikovodika u dizelskome gorivu s kisikom iz zraka, što bi moglo dovesti do raznih kondenziranih visokomolekularnih tvari i smola. Posljedica je njihova djelovanja dugotrajno održavanje radnih svojstava goriva, po mogućnosti kod pohrane. Kao antioksidanti, obično se primjenjuju alkilfenoli, aromatski amini te alkilno-supstituirani aromatski amini.

U slučaju kada dizelsko gorivo sadrži metil estere masnih kiselina (FAME), u skladu s EN 590, do 5 % V/V, ili kada dizelsko gorivo sadrži FAME do 35 % V/V ("žuti biodzel" korišten u Češkoj Republici i Slovačkoj) te većinom kod korištenja zelenog biodizela (100% FAME), navedene vrste antioksidanta nisu dovoljno učinkovite, pa ih je potrebno zamijeniti drugim, prikladnijim vrstama.

Inhibitori korozije svojim polarnim dijelovima molekula prekrivaju metalnu površinu i tako priječe njezin doticaj s tvarima (voda, zrak) koje bi mogle izazvati njezinu koroziju. Izvori vlage u dizelskome gorivu su neki tehnološki postupci, odnosno "disanje" spremnika. Kao inhibitori korozije mogu se koristiti organske kiseline i njihovi aminski derivati.

Sredstva za deemulgiranje poboljšavaju (ubrzavaju) odjeljivanje vode iz dizelskoga goriva, osobito u slučaju kada je ovo prirodno svojstvo ugljikovodičnih goriva umanjeno doziranjem površinski aktivnih aditiva (inhibitora korozije, detergentnih aditiva).

Učinak primjene sredstva za deemulgiranje osobito je važan kod dizelskoga goriva zimske gradacije, jer kod pada temperature okoliša otopljena voda stvara mikro kristale leda, koji djeluju kao kristalne jezgre parafinske kristalizacije, uz susljedno pogoršanje svojstava hladnoga tečenja do te mjere da se smanjuje učinak poboljšivača tečenja (MDFI) i disperzanta parafina (WASA).

Poboljšivači cetanskoga broja, osim povećanja samoga cetanskoga broja (CN) također unapređuju i brzinu te cjelovitost izgaranja, sastav ispušnih plinova, dok ujedno i smanjuju buku motora.

U prošlosti vrijednost cetanskoga broja dizelskoga goriva nije bila tako velika kao ona oktanskoga broja za motorni benzin. Bila je važna samo za osiguravanje minimalne vrijednosti CB od 42, kako bi se nadvladale poteškoće pokretanja motora i spriječile detonacije kod izgaranja, kao i stvaranje veće količine čađe u ispušnim plinovima. Iz tih je razlika tek zanemariva pozornost bila posvećena vrijednosti cetanskoga broja fosilnih dizelskih goriva te se isključivo cetanski indeks, nazvan također i laboratorijskim cetanskim brojem, smatrao dostatnim parametrom. Cetanski je indeks moguće izračunati iz gustoće i 3 destilacijske točke krivulje (EN ISO 4264). Uza sve veću primjenu dizelskih goriva za motore velikih brzina vrtnje, no većinom uz tehnologiju izravnoga ubrizgavanja, kao i zahvaljujući sve strožim granicama emisije ispušnih plinova, preispitano je navedeno mišljenje te proizvođači motora traže još veće vrijednosti cetanskoga broja. Kod dizelskih goriva koja sadrže frakcije dobivene katalitičkim te pretežito termalnim krekiranjem te stoga s visokim udjelom olefina i policikličnih aromata, obilježenih vrlo niskim CB, metode izračuna cetanskoga indeksa daju nepravilne rezultate. Navedene vrste dizelskih goriva valja ispitivati uz pomoć ispitnih motora za utvrđivanje cetanskoga broja (ISO 5165).

Poboljšivači cetanskoga broja mogu povoljno utjecati i na start motora pri niskotemperaturnim uvjetima. Primjena cetanskih poboljšivača omogućuje korištenje komponenti iz postupaka krekiranja i tako povećava proizvodnju dizelskih goriva.

Kao poboljšivači cetanskoga broja, koriste se gotovo isključivo alkilni nitrati. U prošlosti su to bili propil nitrat te prvenstveno amil nitrat. U posljednja je dva desetljeća isključivo mjesto zauzeo 2-etilheksil nitrat. Reakcija dizelskoga goriva na dodavanje poboljšivača cetanskoga broja ovisi o proizvodnoj tehnologiji te na toj tehnologiji utemeljenu cetanskome broju neobrađena goriva, kao što je prikazano na slici 1. Nema informacija o komercijalnoj primjeni drugih vrsta spojeva, kao što su peroksidi i hidroperoksidi.

Slika 1: Mogućnosti povećanja cetanskoga broja putem dodavanja 2-ethilheksil nitrata

Za poboljšanje niskotemperaturnih svojstava, obično se koriste dvije vrste aditiva.

Aditivi depresanti ili poboljšivači tečenja srednjih destilata, MDFI, snižavaju tecište i točku začepljenja hladnog filtra, CFPP, dizelskih goriva. Učinak tih aditiva objašnjava se njihovim ograničavanjem rasta parafinskih kristala. Kao MDFI, obično se koriste kopolimeri alkena (većinom etilenski kopolimer) s alkilnim esterima nižih organskih kiselina: npr. octene ili propionske. Za učinkovitost ovih aditiva važna je također i globalna struktura te molekulna gustoća kopolimera. Odabir pravilnih aditiva ovisi nadalje o svojstvima i tehnologiji proizvodnje temeljnoga dizelskoga goriva (frakcijski i tipski sastav, točka zamućenja).

Utjecaj učinkovitosti različitih aditiva na konačnu točku začepljenja hladnog filtra (CFPP) dizelskih goriva dokumentiran je na slikama 2, 3 i 4.

Aditiv protiv taloženja parafina, WASA, raspršuje stvorene parafinske kristale i tako priječi njihovo taloženje u obliku krute faze na dnu spremnika s gorivom – aditiv kristale drži raspršenima u dizelskome gorivu. Istodobno je rast kristala zapriječen pri smanjenju temperature dizelskih goriva. U nekim slučajevima ovaj disperzantni aditiv ujedno blago smanjuje točku zamućenja dizelskoga goriva. Uporabom ovog aditiva moguće je povećati učinak depresantskoga aditiva te ih se stoga u pravilu koristi zajedno.

Učinak aditiva protiv taloženja parafina moguće je procijeniti uz pomoć nekoliko ispitnih metoda. U našem istraživačkom institutu već dugo koristimo ispitivanje ARAL prema Exxon PTM-4.26 ispitnoj metodi. Ispitivanje oponaša svojstva dizelskoga goriva nakon gašenja motora za vrijeme zimskoga razdoblja. Za vrijeme ispitivanja, uzorak goriva hladi se s temperature od 27℃ na -13 ℃, uz primjenu gradijenta od -1 ℃/10 minuta te se na toj temperat uri ostavlja 16 sati (sl. 5).

Slika 2: Učinak različitih MDFI na CFPP dizelskoga goriva klase F

Slika 3: Učinak različitih MDFI na CFPP arktičkoga dizelskoga goriva klase 1

Slika 4: Učinak različitih MDFI na CFPP dizelskoga goriva klase 2

Slika 5: Temperaturni uvjeti ispitivanja ARAL

Nakon završetka ispitivanja, transparentnost ispitnoga uzorka ocjenjuje se vizualno i određuje količina istaloženih parafina. Nakon što je 80 % količine iz gornjega dijela uzorka goriva odvojeno, ostatak uzorka (20 % količine) koristi se za utvrđivanje CFPP ($CFPP_{AT}$) i točke zamućenja (CP_{AT}). Na temelju vrijednosti CFPP prije ($CFPP_{BT}$) i CP nakon ispitivanja ARAL (CP_{AT}), može se izračunati vrijednost niskotemperaturne operabilnosti (OP) uzorka ispitanog goriva, koristeći sljedeće jednadžbe:

$$OP = 0.4 * CFPP_{BT} + 0.98 * CP_{AT} - 1.2$$

Učinkovitost stupnja obrade WASA prema količini nataloženih parafina za vrijeme ispitivanja ARAL te vrijednost $CFPP_{AT}$ prikazani su na slici 6.

Slika 6: Učinak stupnja obrade WASA na rezultate ispitivanja ARAL

Detergentni aditiv čisti sapnice za ubrizgavanje i održava ih čistima. U slučaju da u dizelskome gorivu nema detergenta, sapnice za ubrizgavanje, koje su u komori izgaranja izložene visokim temperaturama i tlakovima, bivaju onečišćene smolastim talogom, koji se za razmjerno kratko vrijeme pretvara u ugljik. Ugljični se talozi stvaraju u uskim kanalima sapnica (približno desetine milimetra), kao proizvod krekiranja dizelskoga goriva. Onečišćene sapnice ne raspršuju gorivo ispravno, što dovodi do pogoršanja sastava ispušnih plinova, porasta potrošnje goriva te problema s hladnim pokretanjem motora. Neki detergenti aditivi poboljšavaju također i postupak izgaranja, poglavito s gledišta stvaranja ispušnih plinova te njihova sastava.

U Europi se učinkovitost detergentnih aditiva ocjenjuje ispitivanjem na motoru Peugeot XUD 9, prema ispitnoj metodi CEC PF – 023 TBA. Za karakterizaciju učinkovitosti pojedinih aditiva, umjesto smanjenja kapaciteta sapnica koristi se jednodimenzionalni indeks onečišćenja.

Indeks onečišćenja, FI, Peugeot XUD 9 sapnica motora računa se prema sljedećoj jednadžbi:

$$\mathbf{FI} = \frac{V_{BT} - V_{AT}}{V_{BT}} \times 100 \quad (\%)$$

V_{BT} = protok zraka kroz sapnicu prije ispitivanja (l/min)
V_{AT} = protok zraka kroz sapnicu poslije ispitivanja (l/min)

Ukupni indeks onečišćenja hoda računa se kao aritmetički promjer sve 4 sapnice pri hodu od 0,1 mm, pri čemu je prosječna vrijednost hoda igle 0,1 – 0,3 mm (TFI 0,1 – 0,3 mm), odnosno 0,1 – 0,5 mm (TFI 0,1 – 0,5 mm).

Mogućnost poboljšanja detergentnih svojstava dizelskoga goriva detergentnim aditivima prikazana je na slici 7. Kao što se vidi, aditiv označen "Ad" 3 ne poboljšava detergentnost dizelskoga goriva. Rezultati izmjereni nakon primjene "Ad" 3 prikazani su kako bi se dokumentirala činjenica da svi aditivi označeni kao detergentni nisu učinkoviti kod svakog dizelskoga goriva.

Slika 7: Učinak odabranih aditiva na detergentna svojstva dizelskih goriva

<u>Aditiv za mazivost</u> poboljšava maziva svojstva dizelskoga goriva. Potrebu za primjenom objašnjava činjenica kako crpku ubrizgavanja i brizgaljke podmazuje samo dizelsko gorivo. Čak i kod dizelskoga goriva sa sadržajem sumpora od 500 mg/kg, bez aditiva za mazivost trošenje dijelova crpke za ubrizgavanje je znatno, radi čega brže dolazi do njihovog kvara. Uvođenjem dizelskih goriva sa sadržajem sumpora od 50 mg/kg ili čak dizelskih goriva bez sumpora (maks. 10 mg/kg), važnost aditiva za mazivost i smanjenje trošenja znatno raste. (sl. 8, 9 i 10).

U slučaju da dizelsko gorivo sadrži - u skladu s EN 590: 2004 - do 5% vol. metil estera masnih kiselina (FAME), primjena aditiva mazivosti nije potrebna, poradi izvrsnih mazivih svojstava FAME (sl. 11). Dodatak FAME, međutim, utječe na više svojstava dizelskoga goriva. Povišenje gustoće i kinematičke viskoznosti može istodobno biti ograničavajući čimbenik primjene FAME (sl. 12).

Slika 8: Učinak dodatka odabranih aditiva na maziva svojstva dizelskih gor. klase F

Slika 9: Učinak dodatka odabranih aditiva na maziva svojstva arktičkih dizelskih goriva klase 1

Slika 10: Učinak dodatka odabranih aditiva na maziva svojstva arktičkih dizelskih goriva klase 2

Slika 11: Učinak dodatka FAME na maziva svojstva dizelskih goriva

Slika 12: Učinak dodatka FAME na gustoću i viskoznost dizelskoga goriva

Slika 13: Učinak dodatka aditiva na svojstva pjenjenja dizelskih goriva

Aditiv protiv pjenjenja smanjuje pjenjenje dizelskoga goriva, osobito kod točenja goriva crpkama velikog protoka. Stvaranje pjene produljuje vrijeme uzimanja goriva te ugrožava okoliš, prijeteći čak i mogućnošću izazivanja požara. Sklonost pjenjenju procjenjuje se korištenjem francuske norme NF M 07-075, kao volumen stvorene pjene i vrijeme njezina opadanja. Učinak obrade aditiva protiv pjenjenja na smanjenje sklonosti ka pjenjenju dizelskoga goriva prikazan je na slici 13.

Primjenom antistatičkih aditiva, poboljšavaju se svojstva vozivosti dizelskoga goriva te se dodatno smanjuje opasnost stvaranja statičkoga elektriciteta, a time i mogućnost eksplozije pri crpljenju dizelskoga goriva iz cisterni u spremnike benzinskih postaja, a svakako i kod natakanja goriva u automobil. Ne treba isključiti kako će u bliskoj budućnosti primjena antistatičkih aditiva postati obvezatnom.

Sredstvo smanjenja NOx AUS 32, označeno kao "AdBlue", iako se ne dodaje izravno u dizelsko gorivo, nedvojbeno je neophodno za pravilan rad *Selective Catalytic Reduction* (SCR) sustava, koji od 2005. kao mjeru sve češće primjenjuju europski proizvođači kamiona. Što se tiče kemijske strukture toga aditiva, riječ je o 32,5 % otopini uree u vodi. Za ispitivanje njegove kakvoće, koriste se analitičke metode u skladu s normom VDA 2025. Kao što i samo ime govori, sredstvo smanjenja NO_X smanjuje sadržaj NO_X u ispušnim plinovima te se očekuje kako će i potrošnja goriva primjenom sustava SCR biti smanjena za 5–7 %. AdBlue je na benzinskim postajama dostupan u kanistrima, a može ga se natočiti i u zasebni spremnik kamiona, uz pomoć posebnog pribora.

4. Zaključci

Primjena različitih vrsta aditiva postala je dijelom suvremene proizvodnje dizelskih goriva. Sa stajališta učinka, aditivi pomažu osigurati zahtjeve kakvoće europske norme EN 590 (mazivost, oksidacijska stabilnost, niskotemperaturna svojstva, cetanski broj), a potom ispuniti očekivanja proizvođača motora izražena u Svjetskoj povelji o gorivu, ali također i ona korisnika automobila. U nekim slučajevima, aditivi također imaju povoljan ekološki učinak.

Daljnji razvoj aditiva, njihovo složeno ispitivanje te odabir najprikladnijih vrsta i tipova, zahtijeva ogromna financijska sredstva te se njihova primjena svakako nastoji kapitalizirati kao dio marketinških sredstava za osvajanje što je moguće većeg dijela tržišta.

Napomena: Ovaj je rad poduprla Slovačka agencija za istraživanje i razvoj, ugovorni broj APVV-20-037105.

Legenda uz slike u izvornom engleskom tekstu:

Slika 1
Cetane n° = Cetanski broj
Cetane improver = Poboljšivač cetanskog broja

Slika 2; 3; 4
MDFI content = Sadržaj MDFI

Slika 5
Temperature = Temperatura
Duration of test (hour) = Trajanje ispitivanja u satima

Slika 6
% VV of settled paraffins = % VV nataloženih parafina
Before test = Prije ispitivanja
After test = Poslije ispitivanja
CFPP at ARAL test = CFPP kod ispitivanja ARAL
WASA dosage = Dodatak WASE

Slika 7
Total fouling index = Ukupni indeks onečišćenja
Base fuel = Osnovno gorivo

Slika 8; 9; 10
Wear scar diameter = Promjer traga trošenja
Additive dosage = Dodatak aditiva

Slika 11
Wear scar diameter = Promjer traga trošenja
FAME content = Sadržaj FAME

Slika 12
Density at = Gustoća pri
Viscosity at = Viskoznost pri
FAME content = Sadržaj FAME

Slika 13
Foam vanishing time = Vrijeme nestajanja pjene
Foam volume = Količina pjene
Additive dosage = Dodatak aditiva

ROLE OF ADDITIVES IN IMPROVING OF DIESEL FUEL PROPERTIES

Abstract

The production of diesel fuel without the application of various additives is practically not conceivable. An enormous progress in motorization, continuing development in the design of diesel engines, the increase of requirements for environmental protection and growing competition at the motor fuel market create demands on the diesel fuel quality parameters at fulfilment of them the additives play their non-substituted role.

The paper contents the basic requirements as for diesel fuel quality, description of the effects for the individual additive types and the possibilities of their applications nowadays and in the near future.

1. Introduction

The production and distribution of diesel fuels without the application of various additives are at present practically not realistic. The increase of requirement for protection of environment, the progress in development of diesel engines and equipments responsible for reduction of the concentration of pollutants in exhaust gases as well as growing competition on motor fuel market represent driving forces as for qualitative parameters of diesel fuels. At the process of diesel fuel quality improvement the additives play their non-substituted role. The biggest advantage of additives is, that in very low dosage of some hundreds mg/kg they are able to modify diesel fuel properties in such extend, which would be realistic only at alterations in production technologies at abnormal high expenses. In several cases the required properties of diesel fuels without the additive application are through the technological adjustments even practically not achievable.

2. Requirements for Diesel Fuel Quality

The individual properties of diesel fuels can be divided into two main groups.

The first group is represented by those properties which are required by the qualitative standard - EN 590. The genesis of the standard and the values of the individual qualitative parameters can be considered for a consensus of the standard’s authors which, as a rule, represent the following three sectors:

- Automobile (engine) manufacturers,
- Environment protecting representatives,
- Producers of motor fuels.

Requirement of the above mentioned parties as for the diesel fuel quality parameters are summarised in table 1.

Table 1: Requirements of the standard authors on diesel fuel quality

Automobile **manufacturers**	**Environment representatives**	**Oil industry**
Cetane number Lubricity Sulphur content Polyaromatics content Distillation properties Oxidation stability FAME content Viscosity Carbon Residue Ash content	Sulphur content Polyaromatics content Distillation properties: - % V/V recovered at 350°C - Final Boiling Point Flash point	Minimal changes towards previous standard issue

The second group of the requirements represents the complex of properties which are obviously named as the utility properties. For their formulation the parties as follows are responsible:

- Automobile (engine) manufactures,
- Environment protecting representatives,
- Customers (motorists),
- Competition on motor fuel market.

Table 2: Effect of the possible factors on diesel fuel utility properties

Factors			
Automobile manufacturers	**Environment representatives**	**Customers (motorists)**	**Competition on market**
Injector cleanliness Total acid number Ferrous corrosion Foaming No metals (Zn,Cu,Mn,..) Appearance	Exhaust emissions CO_2 emissions Foaming Content of components from renewable sources	Diesel consumption Engine power Operability at low temperatures Vehicle acceleration Engine service life Diesel storage life	„Our Diesel is the best one on the market”
Forms of requiring / determination of utility properties			
World-Wide Fuel Charter	Laws, Acts Environmental Directives	Object of market interest Motor gasoline tests in journals	Benchmarking Advertisement of competitors

As distinct from the standard (EN 590) which was created as a consensus among the participating parties and thus the individual requirements and their limits can be considered as minimal ones, the parties responsible for the utility properties are not obliged to have in mind the requirements and possibilities of the other partners. From this reason the requirements are usually more severe. The requirements as for the utility properties of diesel fuels are presented in table 2.

3. Sorts of Diesel Fuel Additives

At the diesel fuel production and distribution the additives as follows, improving their standardised and utility properties are usually applied.

- Antioxidants,
- Corrosion inhibitors,
- Demulsification agents,
- Cetane improvers,
- Improvers of low-temperature properties,
- Injector detergents,
- Lubricity additives,
- Antifoam agents,
- Antistatic additives,
- NOx reducing agent.

<u>Antioxidants</u> repress the chemical reactions of unsaturated hydrocarbons founded in diesel fuel with air oxygen which could result in various condensed high-molecular substances and gums. The result of their activities is maintenance of the fuel performances for a long time period preferable at the storing. As antioxidants alkyl-phenols, aromatic amines and alkyl substituted aromatic amines are usually applied.

In the case, that diesel fuel contains fatty acids methyl esters (FAME) according to EN 590 up to 5% V/V, or when diesel fuel contains FAME up to 35% V/V ("yellow bio-diesel" used in Czech Republic and Slovakia) and mainly when "green" bio-diesel (100% FAME) is used, above antioxidant types have not sufficient efficiency, so it is necessary to replace them by other, more appropriate types.

<u>Corrosion inhibitors</u> with their polar parts of molecules they cover metallic surface and thereof they prevent the contact between the surface and those substances (water, air) which can cause its corrosion. The sources of humidity contained in diesel fuel are some technological processes or "breathing" of the tanks. As corrosion inhibitors organic acids and their amine derivatives can be used.

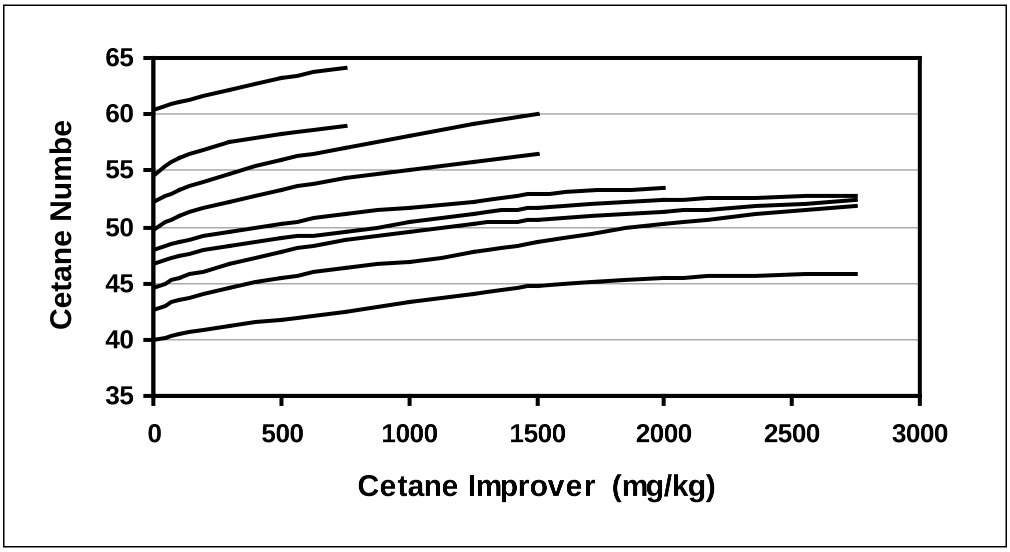
<u>Demulsification agents</u> improve (accelerate) water separation from diesel fuel especially in those cases when this natural property of hydrocarbon fuel is depressed by the dosage of surface-active additives (corrosion inhibitors, detergent additives).

The effect of demulsification agent application is particularly important at winter-grade diesel fuel, because during falling of ambient temperature the dissolved water created micro crystals of ice, which act as crystal nucleuses for paraffin crystallisation with subsequent deteriorating of cold flow properties to such extent, that flow improver (MDFI) and wax dispersant (WASA) effectiveness is depressed.

Cetane improvers, besides the increasing of cetane number (CN) itself they also improve the speed and completeness of combustion process, composition of exhaust gases and reduce the engine noise.

In the past the value of cetane number for diesel fuel had no such an importance as octane number for motor gasolines. It was only important to ensure the minimum CN value of 42 in order to overcome the difficulties at engine starting and preventing the detonations at combustion and the creation of higher amount of soots in exhaust gases. Due to the presented reasons only a negligible attention was dedicated to the cetane number value of fossil diesel fuels and as a rule only cetane index, named also laboratory cetane number, was considered as sufficient parameter. The cetane index can be calculated from density and 3 distillation curve points (EN ISO 4264). With the growing application of high-speed diesel engines, but predominately with direct injection technology and due to the still more strict exhaust emission limits the above opinions were re-evaluated and the engine manufacturers require still higher cetane number values. In the case of diesel fuels containing fractions obtained by catalytic and predominately thermal cracking and therefore with high proportion of olefins and polycyclic aromatics, characterised by very low CN, the methods of cetane index calculation lead to incorrect results. These types of diesel fuels have to be tested using special testing engines for cetane number determination (ISO 5165).

Figure 1: Possibilities of cetane number increasing by 2-ethylhexyl nitrate addition



The cetane improvers can have also positive influence on engine starting at low temperature conditions. The application of cetane improvers enables to utilise the components from cracking processes and thereby increase the diesel fuel production.

As cetane improvers the alkyl nitrates are almost exclusively used. In the past it was propyl nitrate and primarily amyl nitrates. In the last two decades the exclusive post is taken by 2-ethylhexyl nitrate. Response of diesel fuel for the cetane improver addition is depended on its production technology and from this technology resulting cetane number of non-treated fuel, as it is graphically illustrated in Fig. 1. There is no information about the commercial application of other types of compounds as peroxides or hydro-peroxides.

For improvement of low-temperature properties two types of additives are commonly applied.

Depressant additive (Middle Distillate Flow Improver – MDFI) decreases the pour point and cold filter plugging point (CFPP) of diesel fuels. The effect of this additive is explained in such a way that the additive is present at creation of paraffin crystals and so it inhibits the growth of the crystals. As middle distillate flow improvers are commonly used copolymers of alkenes (mostly ethylene copolymer) with alkyl esters of lower organic acids e.g. of acetic or propionic acid.

For the efficiency of these additives is important also the global structure and molecular weight of copolymer. The selection of proper additives depends also on properties and technology of base diesel fuel production (fractional and type composition, cloud point).

The influence of efficiency of various additives on the final cold filter plugging point (CFPP) of diesel fuels is documented on Fig. 2, 3 and 4 respectively.

Dispersant additive (Wax Anti-Settling Additive – WASA) disperses created paraffin crystals and so inhibits the crystals to be settled in the form of solid phase on the bottom of fuel tank – the additive keeps the crystals dispersed in diesel fuel. At the same time the growth of crystals is inhibited at the decrease of diesel fuel temperature. In same cases the dispersant additive also slightly decreases the cloud point of diesel fuel. Through the application of this additive it is possible to increase the effect of depressant additive and therefore as a rule they used to be applied together.

The effect of dispersant additive can be evaluated by several test methods. In our Research Institute for a long time the ARAL test according to the Exxon PTM-4.26 test method has been applying. The test models the properties of diesel fuel after the engine is switched off during the winter season. Within the duration of the test the fuel sample is cooled from the temperature of 27 °C down to -13 °C applying the gradient of -1 °C/10 minutes and is kept at this temperature for 16 hours (Fig. 5).

Figure 2: Efficiency of various MDFI on CFPP of diesel fuel class F

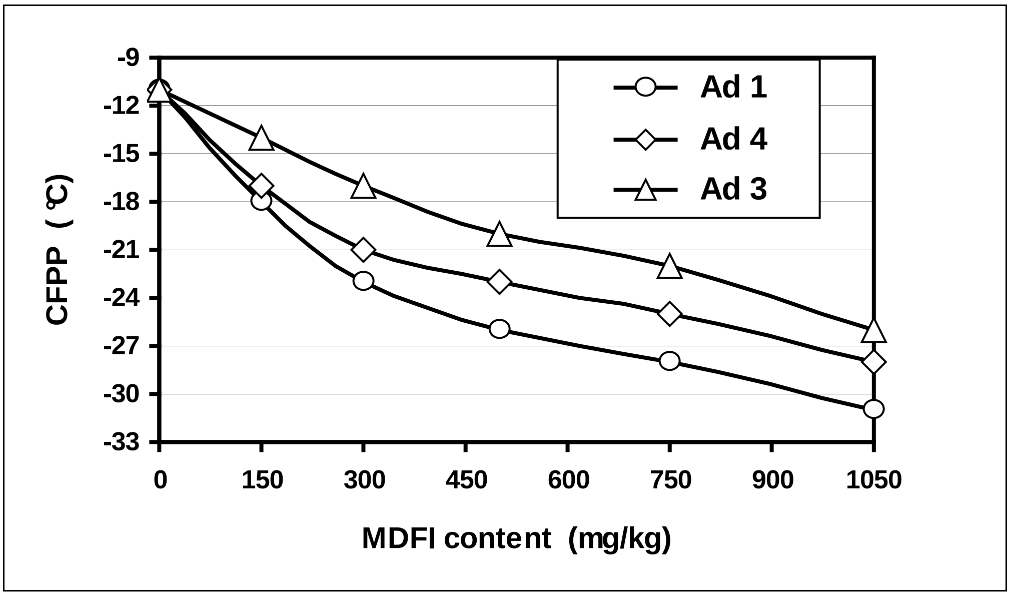


Figure 3: Efficiency of various MDFI on CFPP of arctic diesel fuel class 1

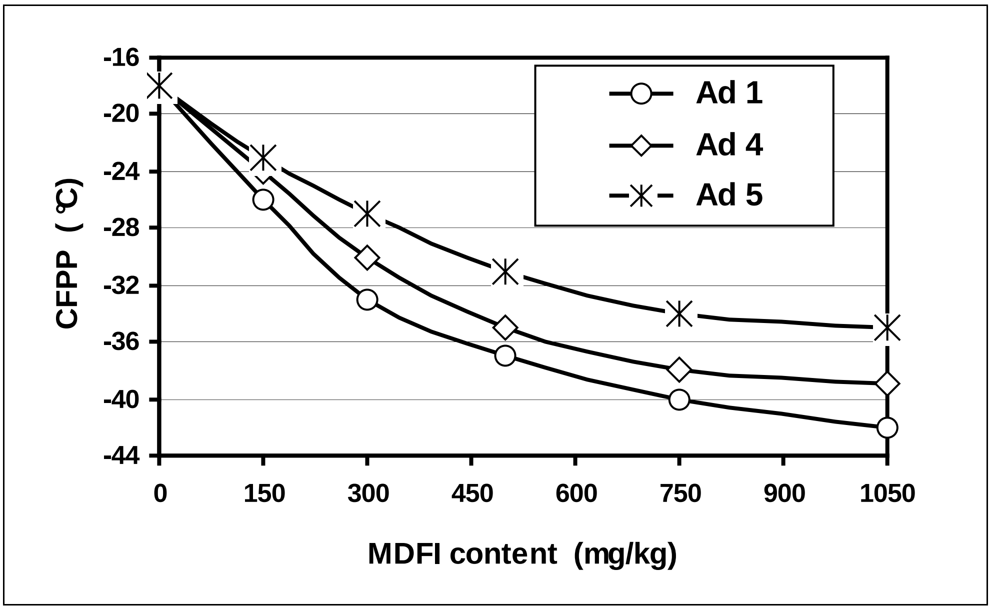


Figure 4: Efficiency of various MDFI on CFPP of arctic diesel fuel class 2

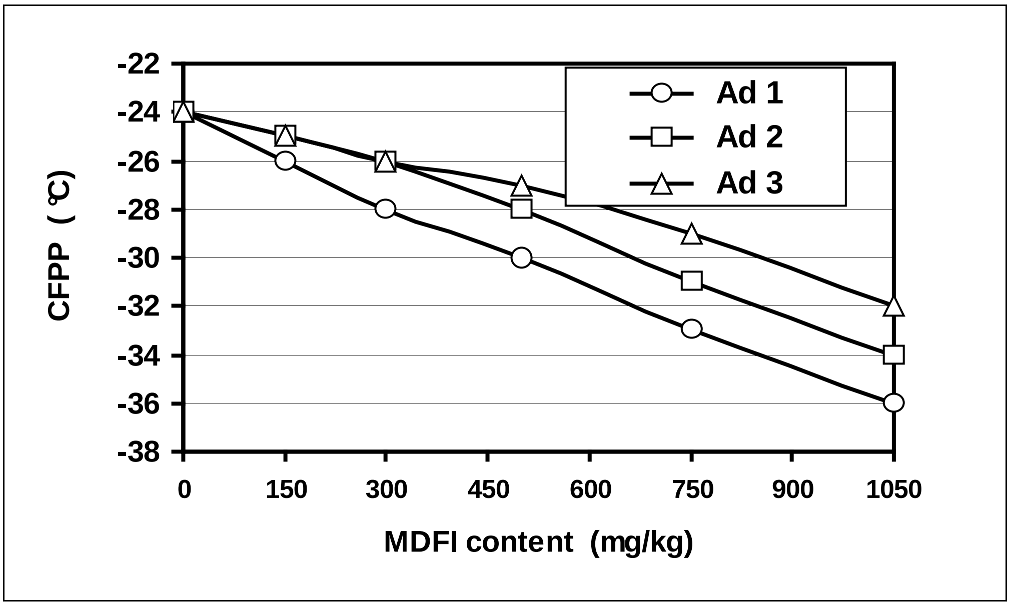
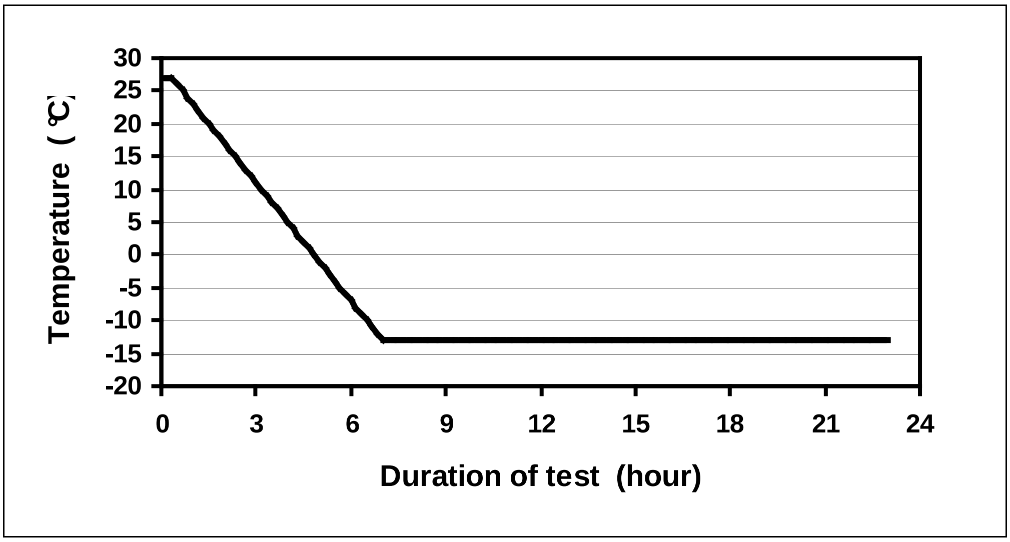


Figure 5: Temperature conditions of ARAL test



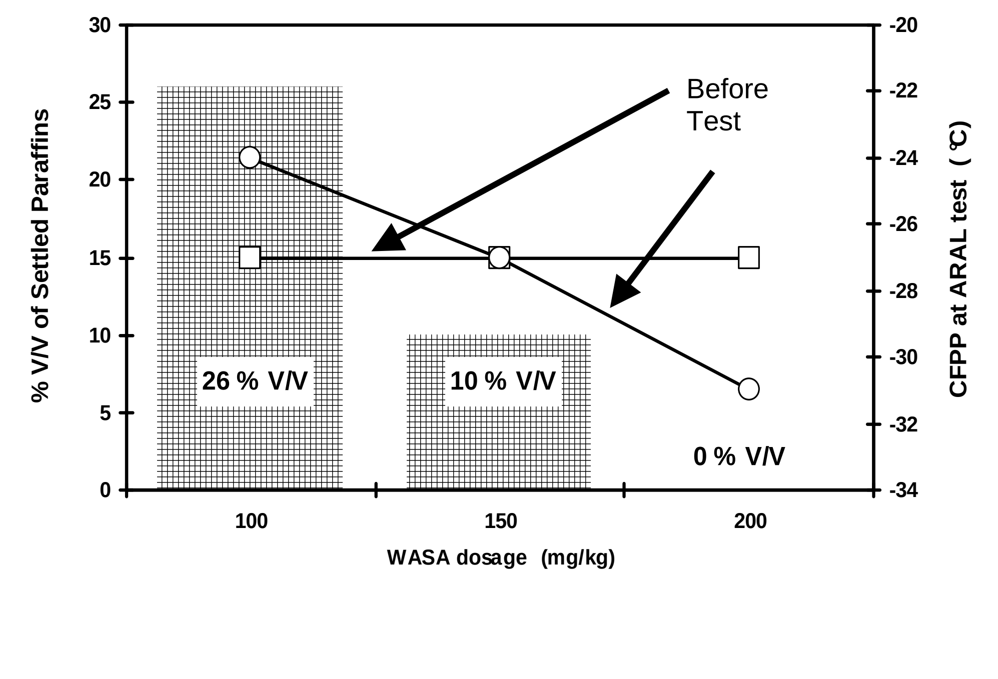
After the finishing of the test the transparency of the tested sample is rated visually and the volume of the settled paraffins is determined. After 80 % by volume from the upper part of the fuel sample is sucked off the rest of the sample (20 % by volume) is used for determination of its CFPP ($CFPP_{AT}$) and its cloud point (CP_{AT}).

From the values of CFPP before the ARAL test ($CFPP_{BT}$) and CP after the test (CP_{AT}) the value of low temperature operability (OP) of the tested fuel sample can be calculated using the formula as follows:

$$OP = 0.4 * CFPP_{BT} + 0.98 * CP_{AT} - 1.2$$

The efficiency of WASA treat rate as for the volume of settled paraffins during ARAL test and the value of $CFPP_{AT}$ is graphically illustrated in Figure 6.

Figure 6: Effect of WASA treat rate on ARAL test results



Injector detergent additive cleans or keeps clean injection nozzles. In the case that there is no detergent in diesel fuel the injection nozzles which are exposed in combustion chamber to the high temperatures and pressures are fouled by gummy deposits, which in relatively short time are transformed into carbon. The carbon deposits are formed in narrow channels of nozzles (approx. tenths of millimetre) as the product of diesel fuel cracking. The fouled nozzles do not spay the fuel properly what results in deterioration of exhaust gases composition, increasing of fuel consumption and problems at cold engine starting. Some detergent additives improve also the combustion process mainly from the exhaust gases generation and composition point of view.

In Europe the efficiency of detergent additives is evaluated by the engine test Peugeot XUD 9 according to the test method CEC PF – 023 TBA. For the characterisation of the individual additives efficiency instead of the throughput capacity decrease of the nozzles the one-dimensional fouling index is used.

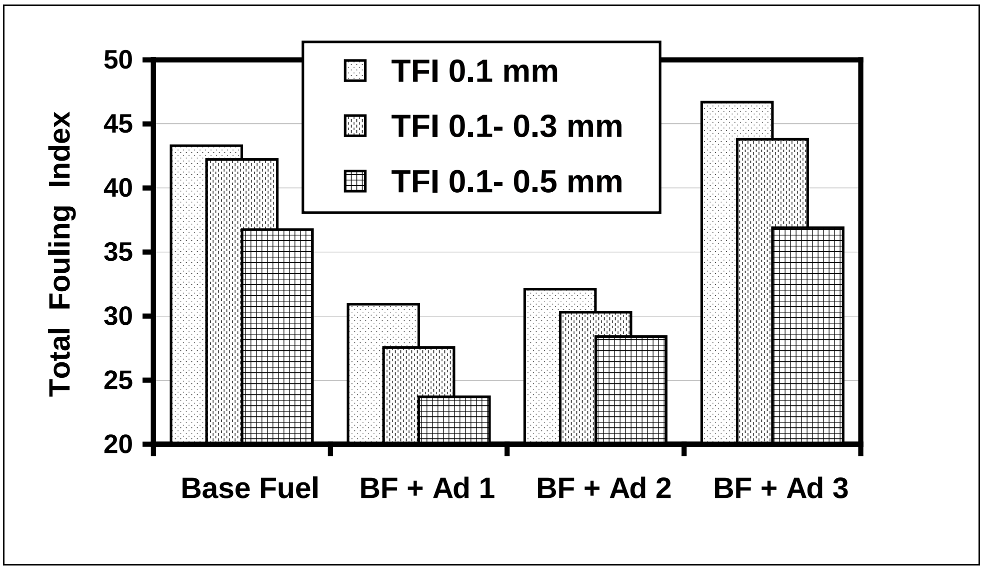
Fouling index (FI) of Peugeot XUD 9 engine nozzles is calculated according to the following equation:

$$FI = \frac{V_{BT} - V_{AT}}{V_{BT}} \times 100 \quad (\%)$$

V_{BT} = air flow through the nozzle before test (litre / minute)
V_{AT} = air flow through the nozzle after test (litre / minute)

Total fouling index at the needle lift is calculated as the arithmetical diameter of all 4 nozzles at needle lift 0.1 mm, average value for needle lifts 0.1 – 0.3 mm (TFI 0.1 – 0.3 mm) and average value for needle lifts 0.1 – 0.5 mm (TFI 0.1 – 0.5 mm).

Figure 7: Effect of selected additives on detergent properties of diesel fuel



The possibility of the improvement as for diesel fuel detergent properties by the detergent additives is presented in Fig. 7. As you can see the additive marked as Ad 3 does not improve the diesel fuel detergency. The results measured by the application of Ad 3 are presented only with the purpose to document the fact that not all the additives declared as detergents are effective in each sort of diesel fuel.

Lubricity additive improves lubricating properties of diesel fuel. Its application is caused by the fact that injection pump and injectors are lubricated only by diesel fuel itself. Even at diesel fuels with sulphur content of 500 mg/kg without lubricity additive in fuel the process of injection pump rotating parts is very rapid and it results in break-down of these parts. With the introduction of diesel fuels with sulphur content of 50 mg/kg or even sulphur-free diesel fuels (max. 10 mg/kg) will the importance and also consumption of lubricity additives significantly higher. (Fig. 8, 9 and 10).

In the case that diesel fuel contains in accordance with EN 590: 2004 up to 5% vol. of methyl esters of fatty acids (FAME), the application of lubricity additives is not necessary due to the excellent lubricating properties of FAME (Fig. 11). The addition of FAME however influences several properties of diesel fuel. The increase of density and kinetic viscosity can be in same cases the limiting factor for FAME application (Fig. 12).

Figure 8: Effect of selected additives treat rates on lubricity properties of diesel fuel class F

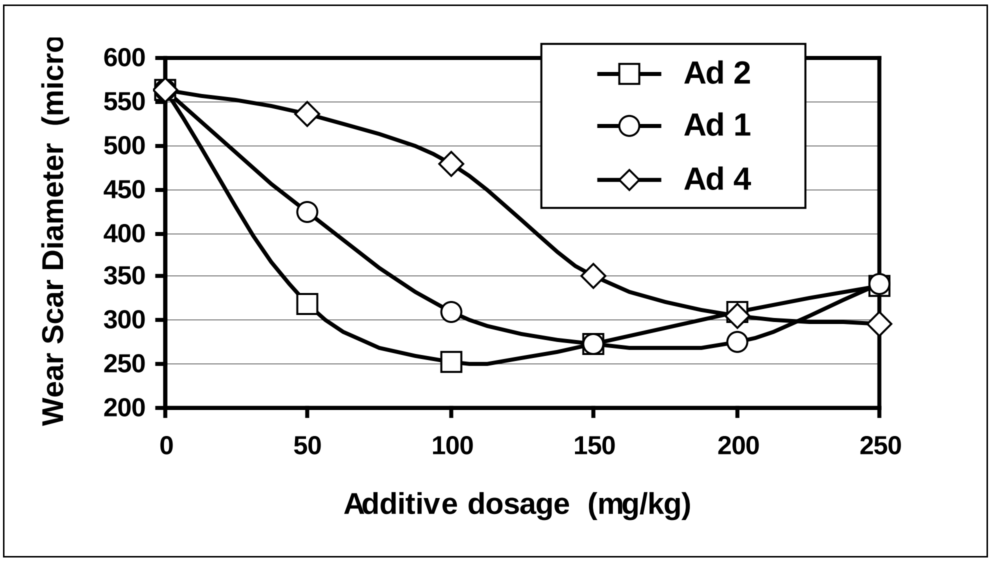


Figure 9: Effect of selected additives treat rates on lubricity properties of arctic diesel fuel class 1

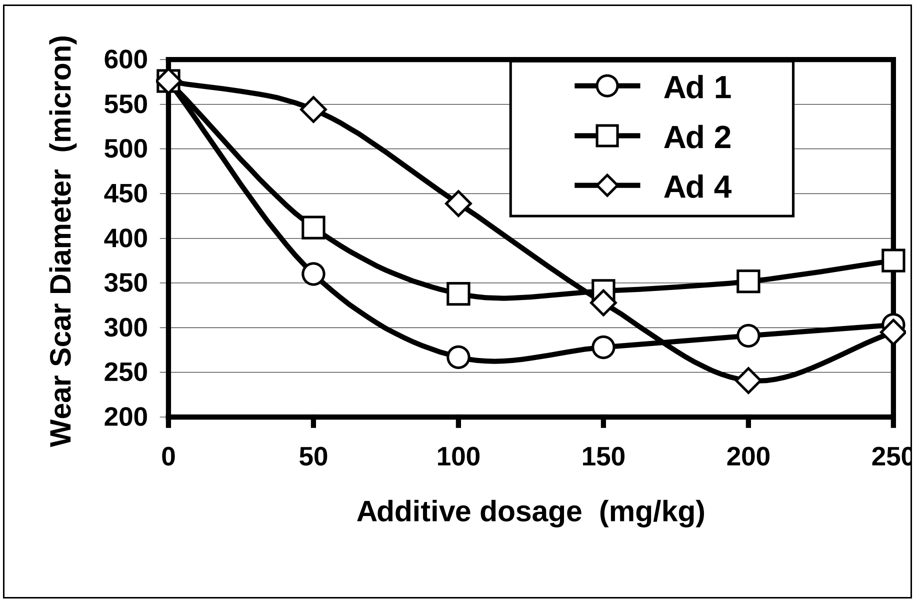


Figure 10: Effect of selected additives treat rates on lubricity properties of arctic diesel fuel class 2

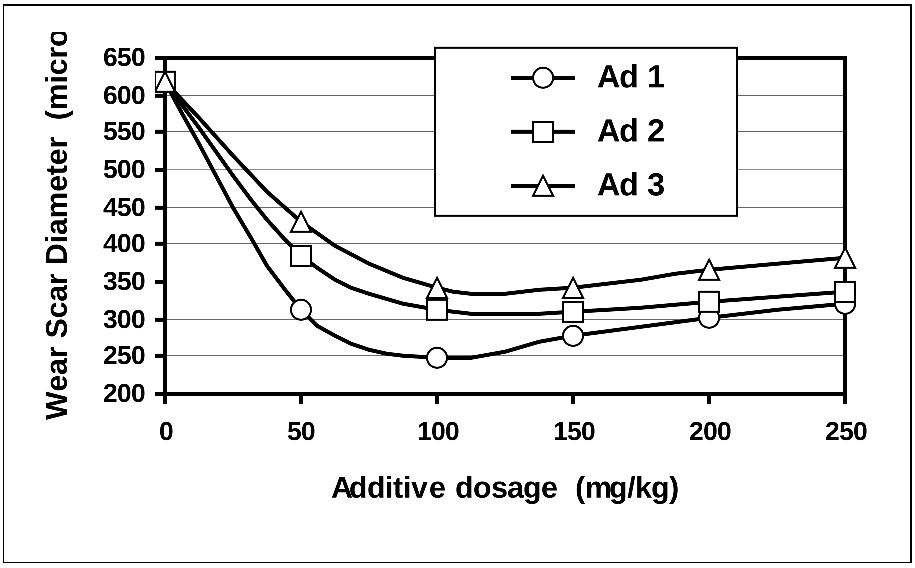


Figure 11: Effect of FAME dosage on lubricity properties of diesel fuel

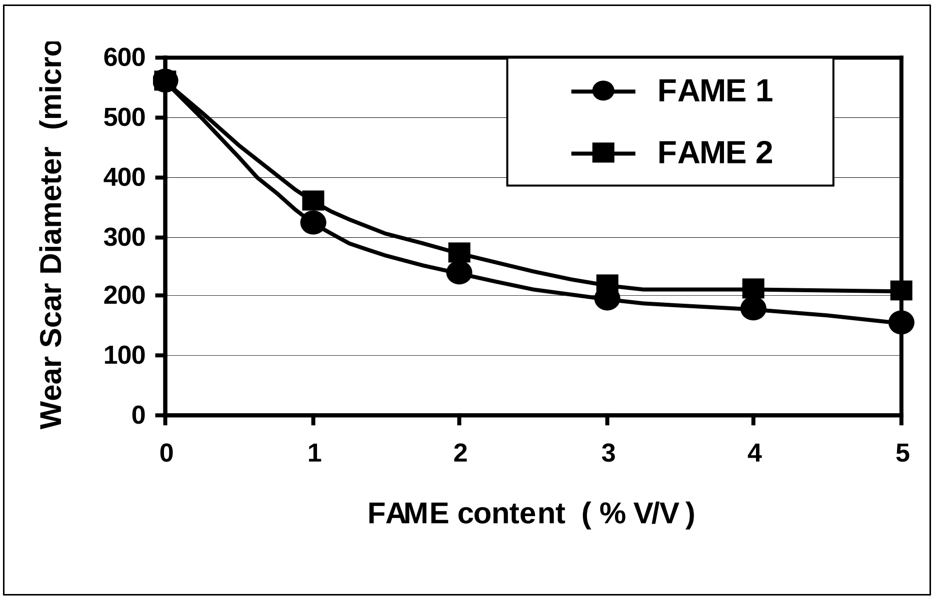


Figure 12. Effect of FAME dosage on density and viscosity of diesel fuel

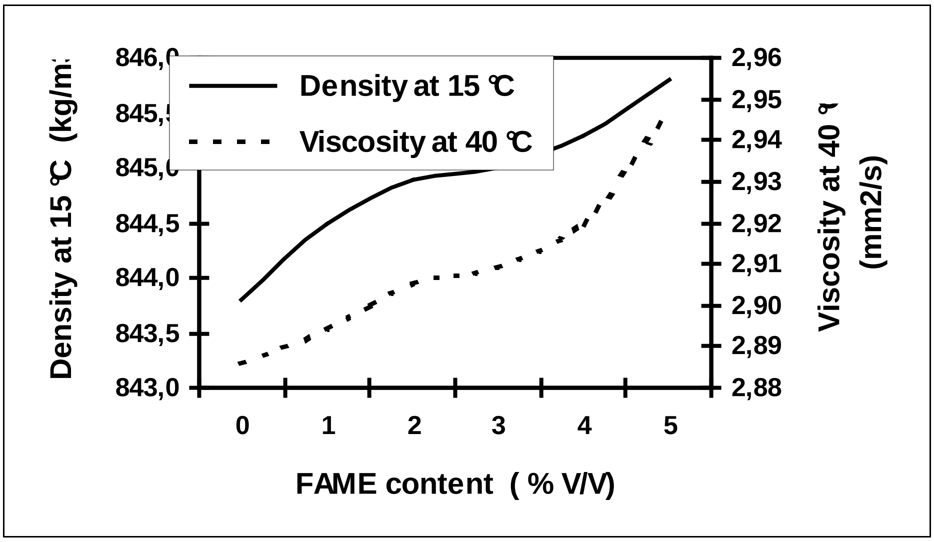
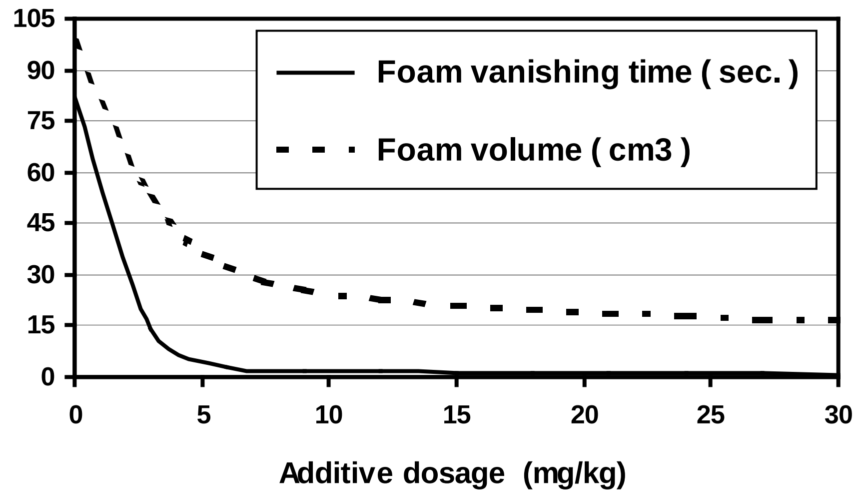


Figure 13: Effect of additive treat rate on foam properties of diesel fuel



Antifoaming additive decreases foaming of diesel fuel especially at the tanking using filling stands with high rate of flow. The foam creation prolonged the time of car tanking and causes danger of environment contamination and even fire arising at filling stations. The foam tendency is evaluated according to French standard NF M 07-075 as volume of created foam and its collapse time. The effect of antifoaming additive treatment on reduction of diesel fuel foam tendency is presented on Fig. 13.

Through the application of antistatic additives the conductivity properties of diesel fuel are improved with additional reduced danger of the static electricity inception and thereof the probability of explosion at diesel fuel pumping from tanker to storage tanks of filling stations and of course also at car tanking. It can be not excluded that in the near future the application of antistatic additive will become obligatory.

NOx reducing agent AUS 32 obviously marked as “AdBlue” although being not added into diesel fuel directly, there is no doubt that it is an indispensable means for proper function of the Selective Catalytic Reduction (SCR) system, which is since 2005 in increasing measure applied by European truck producers. As for the chemical structure this additive is a 32.5 % urea solution in water. For the testing of its quality the analytical methods according to the VDA 2025 standard are applied. As from the name results, NO_X reducing agent expressively reduces the NO_X content in exhaust gases and it is expected that also the fuel consumption by application of SCR system will be reduced by 5 – 7 %. AdBlue is at filling stations available in canisters or it is possible to pump it into the separated truck tank by special dispensers.

4. Conclusions

The application of different types of additives became a part of modern diesel fuels production. From point of view of their effects the additives assist to ensure the qualitative requirements of the European standard EN 590 (lubricity, oxidation stability, low-temperature properties, cetane number), then to fulfil expectations of engine manufacturers presented in World-Wide Fuel Charter, but also of the car users. In several cases the additives have also positive environmental impacts.

The further development of additives, their complex testing and selection of most suitable types and sorts requires enormous financial expenses and though their application is obviously capitalised as a part of marketing tools to obtain the maximal possible segment of market in specific region.

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Literatura / References:

[1] Owen, K., Coley, T.: Automotive Fuels Handbook. Society of Automotive Engineers, Inc. Warrendale, 1990.

[2] Firm literature of companies: Afton Chemicals, BASF, Chevron Chemical, Clariant, Infineum, Lubrizol.

[3] Bratsky, D., Stacho, D.: Possible Applications of Bio-ethanol, RME & RFO-ME in Diesel Fuel. 15th International Symposia on Alcohol Fuels, San Diego, 2005, CD Proceedings pp. 114-126.

[4] Bratsky, D., Stacho, D.: Components from Renewable Sources Suitable for Diesel Fuels. 42nd International Petroleum Conference, Bratislava, 2005. CD Proceedings 9 p. ISBN 80-969371-2-X.

[5] Mikulec, J., Stacho, D., Bratsky, D., Kocsisova, T., Paligova, J., Cvengros, J.: Tribological Parameters of Fatty Acid Alkyl Esters. 42nd International Petroleum Conference, Bratislava, 2005. CD Proceedings 6 p. ISBN 80-969371-2-X.

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665.753.4.038	dizelsko gorivo, aditivi i poboljšavanje	diesel fuel, additives and improvement
665.753.4.035	dizelsko gorivo, svojstva	diesel fuel, properties
.004.122	gledište prednosti	advantages viewpoint

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