Paliwa alkoholowe dla transportu – uwarunkowania, badania i rozwój

Alcohol fuels for transport – background, research and development

Praca zbiorowa pod redakcją Stanisława Oleksiaka

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Instytut Nafty i Gazu – Państwowy Instytut Badawczy

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Wstęp

Historia paliw alkoholowych jest tak długa jak historia silnika spalinowego. Już w latach 1824–1826 amerykański wynalazca Samuel Morey skonstruował pierwszy na świecie silnik spalinowy, pracujący na etanolu i terpentynie. Znany jako twórca pierwszego silnika czterosuwowego Nikolaus Otto w 1860 roku stosował etanol do napędu jednego ze swoich silników. W 1896 roku Henry Ford zbudował pierwszy samochód (the Quadricycle), którego dwucylindrowy silnik został zaprojektowany do zasilania go czystym etanolem. Był to znaczący krok w rozwoju paliw etanolowych dla przemysłu samochodowego.

W 1908 roku wyjechał z fabryki pierwszy, produkowany przez prawie 20 lat, samochód Forda – Model T. Silnik tego pojazdu mógł być zasilany etanolem, benzyną lub naftą. W latach 20. ubiegłego wieku firma Standard Oil zaczęła dodawać etanol do benzyny w celu podwyższenia liczby oktanowej paliwa. W latach 30. gazohol stał się popularnym paliwem w USA, w których ponad 2000 stacji sprzedawało benzynę z zawartością 6–12% etanolu. Zastosowanie tetraetylku ołowiu jako dodatku poprawiającego liczbę oktanową zmniejszyło w tym czasie atrakcyjność etanolu.

Kryzys w zaopatrzeniu w ropę naftową w krajach Ameryki Północnej i Południowej, który nastąpił w latach 70. ubiegłego wieku, dał impuls do powtórnego zainteresowania się etanolem jako potencjalnym komponentem paliw. W kolejnych latach rosnące zużycie paliw silnikowych na świecie i idące za tym stopniowe ograniczanie emisji spowodowały, że etanol pochodzący z biomasy stał się jedną z dróg redukcji emisji gazów cieplarnianych z sektora transportu samochodowego. Wykorzystanie etanolu w formule benzyny silnikowej w różnych krajach świata jest zróżnicowane pod względem ilości tego komponentu w składzie paliwa. W 2011 roku w niektórych krajach Unii Europejskiej pojawiła się benzyna silnikowa zawierająca do 10% etanolu (paliwo E10), ale nadal dostępna jest benzyna o zawartości do 5% etanolu do samochodów nieprzystosowanych do paliwa E10 (dyrektywa 2009/30/WE).

Wykorzystanie mieszanin o niższej zawartości etanolu w niezmodyfikowanych pojazdach było tematem intensywnych prac badawczych w ciągu ostatnich kilkunastu lat. Prowadzono również badania dotyczące zastosowania jako paliwa innych alkoholi, m.in. izomerów alkoholu butylowego, produkowanych z biomasy przy kosztach i nakładach energii porównywalnych z etanolem. W stosunku do etanolu alkohol butylowy posiada wyższą gęstość energii, niższą higroskopijność, większą lepkość, niższe ciśnienie pary i jest mniej agresywny wobec wielu materiałów stosowanych w układach zasilania samochodów.

Paliwem rynkowym o najwyższej zawartości etanolu jest paliwo alkoholowe E85, stanowiące mieszaninę alkoholu i benzyny zawierającą od 50% do 85% etanolu (CEN/TS 15293:2011), które może być używane jedynie w pojazdach specjalnie przystosowanych. Paliwo E85 jest wciąż nowością na rynku europejskim, słabo rozpowszechnionym gatunkiem i wymaga dalszego rozwoju poprzez prowadzenie prac badawczych. Uzyskanie wymaganych właściwości użytkowo-eksploatacyjnych mieszanek etanolu z benzyną i pełne wykorzystanie ich walorów jako paliwa proekologicznego stanowią duże wyzwanie i wymagają pokonania wielu problemów, zwłaszcza w zakresie opracowania składu i sposobu uszlachetniania takich paliw.

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Streszczenie

Niniejsza praca zawiera zbiór artykułów naukowych dotyczących szeroko pojętych zagadnień związanych z możliwością wykorzystania paliw alkoholowych w transporcie samochodowym. Przedstawia trendy rozwojowe paliw alkoholowych w Europie i na świecie oraz omawia problemy związane z wykorzystaniem alkoholi jako paliwa lub komponentu paliw do zasilania silników pojazdów samochodowych. Porusza ponadto sprawy toksyczności paliw alkoholowych i ich wpływu na środowisko naturalne w powiązaniu z zagadnieniami normalizacyjnymi.

Abstract

The study contains a set of scientific papers, concerning the widely comprehended issues associated with the possibility of using alcohol fuels in motor transport. It presents developmental trends of alcohol fuels in Europe and around the world as well as discusses problems associated with using alcohol as fuel or a component of fuels for powering engines of motor vehicles. Moreover it raises matters of the toxicity of alcohol fuels and their impact on the environment as well as in connection with standardizing issues.

Kierunki rozwoju paliw etanolowych

Development trends of ethanol fuels

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Abstract

The article presents an overview of the world activity in the use of ethanol for fuels used in spark-ignition engines, as well as a review of research on the impact of new fuel quality parameters on the performance of vehicles. The paper also presents the results of own research on the tendency of E10 and E85 to pollute the combustion chamber test engine, and the results of the study on improving these tendencies by using the appropriate additive packages.

Keywords: ethanol, fuel, combustion chamber, additives

Streszczenie

W artykule przedstawiono przegląd podejmowanych na świecie działań w zakresie wykorzystania etanolu w paliwach stosowanych w silnikach o zapłonie iskrowym, a także przegląd badań wpływu parametrów jakościowych nowych paliw na właściwości eksploatacyjne pojazdów. Zaprezentowano wyniki własnych badań w zakresie oceny skłonności paliwa E10 i E85 do zanieczyszczania komór spalania silnika testowego, a także wyniki badania dotyczącego poprawy tych skłonności poprzez zastosowanie odpowiednich pakietów dodatków uszlachetniających.

Słowa kluczowe: etanol, paliwo, komora spalania, dodatki

Wstęp

Kryzys w zaopatrzeniu w ropę naftową w krajach Ameryki Północnej i Południowej, do którego doszło w latach siedemdziesiątych ubiegłego wieku, dał impuls do powtórnego zainteresowania się etanolem pochodzącym z biomasy jako potencjalnym komponentem paliw. W kolejnych latach rosnące zużycie paliw transportowych na świecie – a w związku z tym rosnące zanieczyszczenie powietrza atmosferycznego – spowodowało, że etanol pochodzący z biomasy staje się jedną z dróg redukcji emisji gazów cieplarnianych z sektora transportu drogowego. Światowa polityka budowana wokół problemów emisji szkodliwych składników spalin do powietrza atmosferycznego narzuca kierunek działań w obszarze harmonizacji jakości zarówno biokomponentów, jak i paliw. Zastosowanie etanolu w formule benzyny silnikowej w różnych krajach świata jest zróżnicowane pod względem jego ilości w składzie paliwa. Jest to uwarunkowane dostępnością i ceną surowca, a także polityką poszczególnych państw, która określa cele podporządkowane wymaganiom ochrony zdrowia człowieka i środowiska naturalnego, w tym powietrza atmosferycznego.

Stanowisko producentów samochodów w sprawie nowych paliw etanolowych

Producenci samochodów, udzielając gwarancji na swój produkt, zastrzegają, że paliwo stosowane do zasilania produkowanych przez nich pojazdów samochodowych musi spełniać wymagania odpowiednich norm produktowych. Ustalone w tych normach limity stanowią optymalny konsensus wiedzy technicznej z obszaru technologii wytwarzania, magazynowania i dystrybucji paliw, biopaliw i biokomponentów oraz z obszaru technologii i eksploatacji silników, w tym układów zasilania i układów oczyszczania spalin. Paliwo, aby mogło zostać zastosowane do napędu silników o zapłonie iskrowym, musi spełnić opracowane w stosunku do niego wymagania normy jakościowej. Producenci samochodów i silników samochodowych zrzeszeni w organizacjach ACEA, Alliance, EMA, JAMA, wychodząc naprzeciw globalnej harmonizacji wymagań jakościowych dla biopaliw i biokomponentów, opracowali wymagania dla bioetanolu wykorzystywanego jako komponent paliw etanolowych. Wymagania te zawarto w pierwszym wydaniu *Ethanol Guidelines* z marca 2009 r. [1]. Specyfikacja została opracowana na podstawie doświadczeń producentów silników i pojazdów samochodowych w stosowaniu paliw etanolowych na obszarze całego świata.

Według Röja [2] paliwo jest istotnym elementem procesu inżynierii samochodowej, na który to proces składa się wybór materiałów konstrukcyjnych, takich jak metale, polimery, oleje smarowe do samochodu i silnika samochodowego, ale także dla systemów dystrybucji i magazynowania paliwa. Właściwości paliwa determinują limity dla regulacji silnika i optymalizacji emisji szkodliwych składników spalin, optymalizacji osiągów oraz właściwości jezdnych. Autor zwraca też uwagę na wagę problemu jakości paliwa, która jest częścią systemu zapewnienia jakości dla klienta. Właściwe paliwo gwarantuje techniczną funkcjonalność i odpowiednie właściwości użytkowo-eksploatacyjne pojazdu, utrzymanie właściwych normatywnych norm emisji w cyklu życia silnika oraz zapewnia ważność gwarancji, a każda zmiana paliw na rynku musi być dostosowana do istniejącego parku pojazdów samochodowych. Dotyczy to także zawartości etanolu w benzynie silnikowej. ACEA odniosła się pozytywnie do zwiększenia zawartości biokomponentów w paliwach [2], jednak z pewnymi zastrzeżeniami, to jest:

- dla nowych paliw innych niż benzyna silnikowa i olej napędowy potrzebne są odrębne normy jakościowe, jednak bez pogarszania istotnych parametrów jakościowych paliwa;
- starsze pojazdy na rynku powinny być objęte przejściową ochroną, co wiąże się z pozostawieniem w dystrybucji odrębnych gatunków paliw;
- niezbędne jest wsparcie dla nowych paliw ze strony dostawców podzespołów silnika (np. producentów układów wtrysku).

Paliwa o jakości innej niż określona normami EN 228 i EN 590 powinny być przeznaczone do silników i pojazdów do nich dostosowanych, a ich jakość powinna być określona odpowiednimi normami. Jak zaznaczono powyżej, pojazdy wykorzystujące paliwa inne niż wyznaczone normami EN 228 i EN 590 są opracowywane z uwzględnieniem wszystkich szczegółowych wymagań technicznych i prawnych we właściwy sposób.

Przykładami są:

- silniki o zapłonie samoczynnym dla etanolu przystosowane do paliwa E_d95;
- pojazdy zasilane CNG/biogazem (metan);
- pojazdy FFV (*Flexible-Fuel Vehicle*) napędzane paliwem etanolowym E85.

Paliwa etanolowe w krajach Ameryki Północnej i Południowej

USA

Redukcja zanieczyszczenia powietrza atmosferycznego jako główny cel polityki światowej jest kołem napędowym działań uruchamiających programy badawcze w obszarze motoryzacji. Takimi programami były amerykańskie: AQIRP (Auto-Oil Air Quality Improvement Research Program) oraz Auto/Oil Air Improvement Research Program (1997). Badania te miały na celu określenie wpływu składu chemicznego paliw na emisję szkodliwych składników spalin wydalanych z samochodów osobowych i były podstawą do sformułowania wymagań norm Tier dla szkodliwych składników emisji spalin w USA. Mając na uwadze cele ochrony środowiska naturalnego, w tym również zdrowia człowieka, specyfikacje techniczne tak paliw, jak i biokomponentów ewoluują w kierunku spełnienia oczekiwań konsumentów i uregulowań prawnych dotyczących jakości powietrza atmosferycznego.

Etanol jako komponent paliw w USA ma długą historię. W czasach kryzysu energetycznego dokument *Energy Tax Act* z 1978 r. zdefiniował gazohol jako mieszaninę benzyny silnikowej z 10-proc. zawartością etanolu i umożliwił zwolnienie takich mieszanin z części podatku autostradowego oraz zastosowanie ich do określonych pojazdów dokumentem *Clean Air Act* z 1978 r. W USA etanol jest dodawany do benzyny silnikowej od lat 70. XX wieku. Początkowo jego zawartość w benzynie wynosiła 7,7% (*V/V*), a następnie wzrosła do 10% (*V/V*). Jakość tego gatunku paliwa została wyspecyfikowana w normie ASTM D 4814. Udział etanolu w benzynie silnikowej wynika z postanowień dokumentu *Clean Air Act Amendments* z 1990 r. z późniejszymi zmianami i jest konsekwencją programów amerykańskiej Agencji Ochrony Środowiska (EPA) dotyczących ograniczania zanieczyszczenia powietrza. Obecnie 95% benzyny silnikowej zużywanej w USA zawiera 10% etanolu [3].

W 2011 r. EPA zatwierdziła możliwość stosowania benzyny silnikowej E15 w konwencjonalnych samochodach osobowych, lekkich dostawczych i ciężarowych w modelach z 2001 r. oraz nowszych [5], biorąc pod uwagę wyniki przeprowadzonych testów i badań [3, 4]. EPA zdefiniowała paliwo E15 jako mieszaninę benzyny silnikowej i etanolu, którego zawartość mieści się w granicach powyżej 10% (*V/V*) i poniżej 15% (*V/V*) [6]. Według danych z raportu amerykańskiego Narodowego Laboratorium Energii Odnawialnej (NREL) na koniec 2014 r. 65% zarejestrowanych pojazdów benzynowych stanowiły modele z 2001 r.

i nowsze [6]. Paliwo E15 nie jest jeszcze powszechnie dostępne, w dużej mierze z powodu dezinformacji i obaw sprzedawców. Ponieważ w USA prowadzone są także badania benzyny silnikowej z wyższymi udziałami etanolu, jak E20 czy E30, należy się spodziewać, że w przyszłości gatunki o średnim poziomie zawartości etanolu będą wprowadzane na rynek [7].

Kolejnym paliwem dostępnym obecnie na rynku amerykańskim jest E85, o jakości określonej normą ASTM D 5798. Paliwo to zostało wprowadzone na rynek jako alternatywne paliwo silnikowe zgodnie z *Energy Policy Act of 1992, Section 301(2)* [8]. Zawiera ono od 51% (*V/V*) do 83% (*V/V*) etanolu, w zależności od okresu klimatycznego i położenia geograficznego danego stanu. Ze względu na dużą zawartość etanolu paliwo to jest przeznaczone jedynie do samochodów o silnikach z zapłonem iskrowym specjalnie dostosowanych do spalania takiego paliwa. Jako że pojazdy te mogą być zasilane zarówno biopaliwem E85, jak i konwencjonalną benzyną silnikową, nazywane są *flexsible-fuel vehicles* (FFV). Obecnie paliwo E85 jest stosowane do napędu więcej niż 17,4 miliona samochodów FFV [9].

Wg [10], w 2013 r. około 345 stacji paliwowych w USA (głównie w środkowo- zachodnich stanach) oferowało właścicielom samochodów FFV benzyny silnikowe o średnim poziomie zawartości etanolu, tj. E20 (20% etanolu i 80% benzyny) oraz E30 (30% etanolu i 70% benzyny).

Dla paliw, jak również dla ich komponentów opracowano normy jakościowe, takie jak:

- *ASTM D7794-14 Standard Practice for Blending Mid-Level Ethanol Fuel Blends for Flexible-Fuel Vehicles with Automotive Spark-Ignition Engines*;
- *ASTM Standard D5798-14 Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark Ignition Engines*;
- *ASTM Standard D4814-15a Standard Specification for Automotive Spark-Ignition Engine Fuel*;
- *ASTM Standard D4806-15 Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark- Ignition Fuel.*

Brazylia

W Brazylii podobnie jak w USA kryzys naftowy w 1973 r. był podstawą do zapoczątkowania promocji etanolu. Rządowy program Pró-Álcool umożliwił zastępowanie części paliw kopalnych paliwami zawierającymi komponent bioodnawialny, jakim jest etanol produkowany z trzciny cukrowej. W latach 1976–1992 rząd brazylijski wprowadził obowiązek dodawania etanolu do benzyny silnikowej w ilości pomiędzy 10% a 22% (*V/V*).

Od lipca 2007 r. obowiązkowa zawartość etanolu w benzynie silnikowej zwiększyła się do 25% (*V/V*) alkoholu bezwodnego. W Brazylii dystrybuowane były dotychczas dwa rodzaje paliw: E25 i E100. Większość pojazdów sprzedawanych w Brazylii to pojazdy FFV, które mogą być zasilane jednym albo drugim paliwem. W marcu 2015 r. rząd zwiększył do 27% (*V/V*) udział etanolu w benzynie silnikowej [11], która może być obecnie stosowana w samochodach FFV. Wobec zdecydowanego stanowiska brazylijskiego stowarzyszenia producentów samochodów ANFAVEA maksymalna zawartość etanolu w benzynie premium pozostała na poziomie 25% (*V/V*) [11]. Rząd przyjął wyższą zawartość etanolu w benzynie silnikowej jako zachętę ekonomiczną dla producentów etanolu, ze względu na istniejący nadmiar jego zapasów. Oczekuje się, że wprowadzenie E27 na rynek umożliwi konsumpcję nadmiaru zapasów do końca 2015 r. [11].

Europa

Zalecenia dyrektywy FQD w sprawie wspierania użycia w transporcie biopaliw lub innych paliw odnawialnych zaowocowały wprowadzeniem na rynki europejskie zarówno benzyny silnikowej zawierającej 10% (*V/V*) etanolu (E10), jak i paliwa o zawartości nominalnej do 85% (*V/V*) etanolu i 15% (*V/V*) benzyny. Ten rodzaj wysokoetanolowego paliwa jest przeznaczony do zasilania samochodów FFV, wyposażonych w zmodyfikowane silniki. Silniki te mogą być eksploatowane na każdym rodzaju mieszaniny benzyny silnikowej z etanolem w zakresie 0–85% (*V/V*) etanolu. Wybór parametrów jakościowych paliwa E85 [12] został oparty na badaniach i doświadczeniach rynku, a jakość określona w specyfikacji CEN/TS 15293:2011. Krajem europejskim o największej liczbie użytkowników samochodów FFV i paliwa E85 jest Szwecja. W 2008 r. sprzedaż samochodów FFV w Szwecji wyniosła 59 066 samochodów [24], a paliwo dostępne było na 1 440 stacjach paliwowych [24]. Rynek oferował ponad 40 modeli samochodów FFV. Inne kraje europejskie, w których dostępne jest paliwo E85, to Niemcy (10 000 samochodów i 255 stacji paliw), Francja (7000 samochodów i 305 stacji), Irlandia (7000 samochodów i 31 stacji), Holandia (6000 samochodów i 29 stacji) [13]. Paliwo to dostępne jest także w Austrii, na Węgrzech i w Estonii. Według wyników badań możliwy udział pojazdów FFV zasilanych paliwem E85 na rynku wzrośnie z 1% w 2012 r. do 10% w 2020 r. [13].

Rynek takich paliw w Europie, pomimo rozwoju, jest jeszcze niewielki, głównie z powodu ograniczonej infrastruktury dystrybucyjnej, wysokiej ceny etanolu i małej dostępności modeli samochodów FFV [13]. Przegląd możliwości i scenariuszy rozwoju biopaliw na rynku europejskim [13] wykonany na zlecenie Komisji Europejskiej w konkluzjach wyraźnie wskazuje na:

- wdrożenie w okresie długoterminowym wyższych limitów zawartości bioetanolu w benzynie silnikowej E20 lub E30;

- konieczność wsparcia realizacji tych zamierzeń w zakresie specyfikacji paliw (CEN) oraz standardów emisji zanieczyszczeń.

Badania paliw etanolowych

Wprowadzenie etanolu do formuły benzyny silnikowej skutkuje określonym wpływem na właściwości fizykochemiczne i użytkowe takich paliw [14–16]. Wśród wielu pozycji literaturowych przytaczających wyniki badań paliw etanolowych o zawartościach etanolu w zakresie 10–85% (*V/V*) znaczące miejsce stale zajmują te, które skupiają się na pojawiających się okresowo problemach eksploatacyjnych. Pakiety dodatków uszlachetniających dozowane do benzyny silnikowej z jednej strony poprawiają czystość zaworów dolotowych, z drugiej strony powodują zwiększanie się osadów w komorach spalania. Stąd niezwykle istotny pozostaje dobór właściwych dodatków i optymalizacja ich dozowania tak, aby minimalizować skłonność finalnego paliwa do zanieczyszczania elementów silnika. Metody oceny skłonności paliw do formowania osadów podaje Światowa Karta Paliw [17]. Jęczmionek i wsp. [18] podjęli próbę oceny korelacji wyników otrzymanych dwiema różnymi metodami w odniesieniu do rezultatów badań benzyny konwencjonalnej.

W badaniach DuMonta i wsp. [19] prowadzonych na benzynie tradycyjnej i paliwie etanolowym E85 wykazano tendencję do formowania osadów na zaworach dolotowych IVD (*Intake Valve Deposit*) wyższą w przypadku paliwa E85. W badaniach tych wykorzystywano etanol z dwóch różnych źródeł. Różniły się one zawartością skażalników, inhibitorów korozji oraz siarczanów. Badania te wykazały, że zastosowanie odpowiednich dodatków detergentowych do paliwa E85 minimalizowało efekt powstawania osadów.

Chapman i wsp. [20] zwrócili uwagę na problem inhibitorów korozji obecnych w benzynie silnikowej i etanolu. Otóż ze względu na odrębne systemy dystrybucji i blendingu etanolu jest możliwe, że inhibitory korozji dodawane są osobno do benzyny silnikowej przed transportem jej rurociągiem i osobno do etanolu przez jego producentów. Skumulowana dawka inhibitorów może wpływać na wzrost osadów na zaworach. Autorzy ci badali również wpływ różniących się składami chemicznymi inhibitorów korozji na tworzenie się osadów na zaworach dolotowych silnika testowego GM's. LE9 (2.4L).

Z kolei Galante-Fox i wsp. [21] przeprowadzili badania wpływu właściwości handlowego paliwa E85 na efektywność pracy wtryskiwaczy PFI (*Port Fuel Injector*). Stwierdzono, że tworzone w nich osady, korozyjność i brak smarności paliwa E85 odpowiadają za pogorszenie pracy tych elementów silnika. Przedmiotem badań było także określenie wpływu zaobserwowanej wysokiej zawartości wody, chlorków, kwasów organicznych w handlowych próbkach E85.

W nurt badań nad paliwami etanolowymi wpisują się także badania Instytutu Nafty i Gazu –PIB. Stępień [22] przedstawił wyniki badań tendencji do tworzenia szkodliwych osadów na elementach układu dolotowego silnika *flex-fuel* w zależności od składu paliwa, jego uszlachetniania, konstrukcji silnika i warunków jego eksploatacji. W artykule tym wykazano także duże znaczenie nowoczesnych pakietów dodatków detergentowych specjalnie opracowanych i przeznaczonych do paliw o wysokiej zawartości etanolu w kontroli i przeciwdziałaniu tworzeniu się osadów w silniku.

Z kolei autorka niniejszego artykułu i wsp. [23] przedstawili tendencje rozwojowe wprowadzania na rynki paliw o podwyższonej zawartości etanolu oraz modeli samochodów FFV. Omówiono trendy w prawodawstwie europejskim w odniesieniu do norm emisji szkodliwych składników spalin z silników o zapłonie iskrowym. Przedstawiono wyniki badań skłonności benzyny bezołowiowej E10 do zanieczyszczania zaworów dolotowych w teście silnikowym CEC F-20-98. Pokazano także wyniki badania skłonności paliwa etanolowego E85 do tworzenia osadów na elementach układu zasilania silnika, gdy zawierało ono nieodpowiedni pakiet dodatków detergentowych.

Badania paliw etanolowych w ramach projektu BIOTRETH

Skłonność do tworzenia osadów w komorach spalania silnika benzynowego występuje niezależnie od rodzaju paliwa przeznaczonego do tego silnika. Światowa Karta Paliw [17] podaje metody oceny tego parametru w paliwie do silników o zapłonie iskrowym. W badaniach prowadzonych w trakcie realizacji projektu, finansowanego ze środków funduszy norweskich w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju, do oceny skłonności paliwa do zanieczyszczania komór spalania zastosowano:

- metodę oznaczania zawartości żywic nieprzemywanych zgodnie z PN-EN ISO 6246;
- metodę termicznego rozkładu żywic według metodyki TGA BZ 154-01 oraz
- metodę spalania paliwa w silniku stanowiskowym Mercedes Benz M111 według CEC F-20-A-98.

Przedmiotem badania w pierwszej części projektu było paliwo etanolowe E10 (benzyna silnikowa bezołowiowa zawierająca 10% etanolu). Do paliwa tego dozowano eksperymentalne pakiety dodatków detergentowych w celu poprawy jego właściwości eksploatacyjnych. W ramach badań laboratoryjnych podjęto próbę znalezienia korelacji wyników współczynnika A uzyskanych z analizy termograwimetrycznej próbek benzyny E10 uszlachetnianej różnymi pakietami dodatków detergentowych przy tym samym dozowaniu z wynikami testów silnikowych M111 wykonanych dla tych próbek. W tabeli 1 przedstawiono właściwości benzyny E10, a w tabeli 2 – wyniki współczynników rozkładu żywic A i odpowiadające im wyniki masy osadów uzyskane w teście silnika M111.

Tabela 1. Wyniki badania właściwości benzyny E10

Parametr		Benzyna E10	Wymagania według PN-EN 228:2013-04	Metoda badania według:
1	Liczba oktanowa (LOB)	102,1	min. 95,0	PN-EN ISO 5164
2	Liczba oktanowa (LOM)	90,2	min. 85,0	PN-EN ISO 5163
3	Zawartość ołowiu [mg/l]	–	maks. 5	PN-EN 237
4	Gęstość w 15°C [kg/m^3]	732,2	720–775	PN-EN ISO 12185
5	Zawartość siarki [mg/kg]	<5,0 (2,4)	maks. 10,0	PN-EN 20846
6	Okres indukcyjny [min]	>480	min. 360	PN-ISO 7536
7	**Zawartość żywic [mg/100 ml]:**			
	– nieprzemywane	0,9	–	PN-EN ISO 6246
	– obecne	0,1	maks. 5	

	Parametr	Benzyna E10	Wymagania według PN-EN 228:2013-04	Metoda badania według:
8	Badanie działania korodującego na płytce z miedzi [stopień]	–	klasa 1	PN-EN ISO 2160
9	Wygląd	jasny i przezroczysty		wizualnie
10	**Skład grupowy według FIA [% (*V/V*)]:**			
	– parafino-nafteny	68,7	–	PN-EN 15553
	– olefiny	4,5	maks. 18,0	
	– aromaty	16,8	maks. 35,0	
11	Zawartość benzenu [% (*V/V*)]	–	maks. 1,00	PN-EN 238
12	Zawartość tlenu [% (*m/m*)]	3,5	maks. 3,7	PN-EN 1601
13	Zawartość etanolu [% (*V/V*)]	10,0	maks. 10,0	PN-EN 1601
14	Prężność par (DVPE) [kPa]	62,5	45–60 lato	PN-EN 13016-1
15	Skład frakcyjny: IBP			PN-EN ISO 3405
	– do 70°C odparowuje [% (*V/V*)]	42,1	22,0–50,0	
	– do 100°C odparowuje [% (*V/V*)]	56,9	46,0–72,0	
	– do 150°C odparowuje [% (*V/V*)]	93,8	min. 75,0	
	– koniec destylacji [°C]	182,0	maks. 210	
	– pozostałość [% (*V/V*)]	1,0	maks. 2	

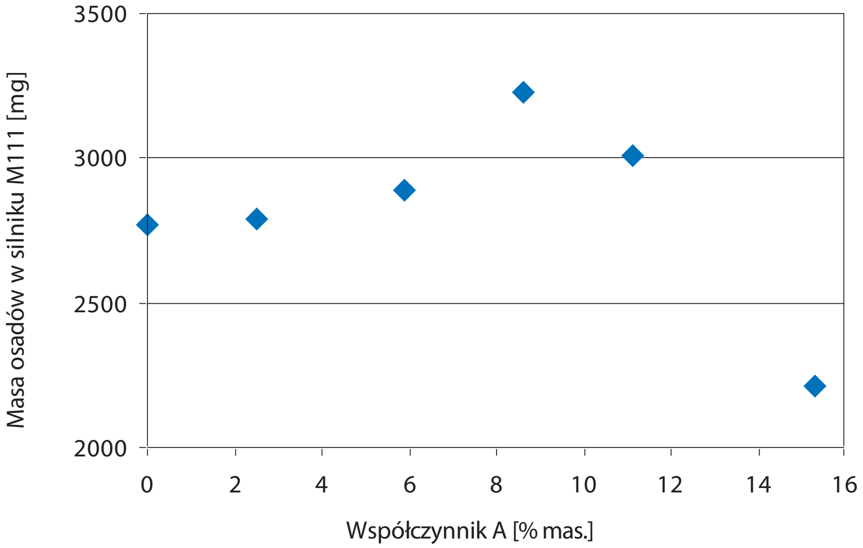
Tabela 2. Wyniki zawartości żywic nieprzemywanych, współczynników A i masy osadów utworzonych w komorach spalania silnika M111

Badane paliwo E10	Zawartość żywic nieprzemywanych [mg/100 ml] limit maks. 30	Współczynnik A [% mas. @450°C] limit maks. 20	Masa osadów w komorach silnika M111 (TCCD) [mg] Kategoria 3–5 limit maks. 2500
Benzyna E10 (10% EtOH) bez dodatku	–	–	2771
Benzyna E10 (10% EtOH) + 540 mg/kg NOR5	17,8	2,5	2787
Benzyna E10 (10% EtOH) + 540 mg/kg NOR3	13,7	5,9	2891
Benzyna E10 (10% EtOH) + 540 mg/kg NOR2	16,1	8,6	3231
Benzyna E10 (10% EtOH) + 540 mg/kg NOR1	17,1	11,1	3012
Benzyna E10 (10% EtOH) + 540 mg/kg NOR4	13,5	15,3	2212

Analiza uzyskanych wyników zawartości żywic nieprzemywanych pozwala stwierdzić, że przy tym samym dozowaniu pakietu dodatków 540 mg/kg zawartość ta pozostawała na podobnym poziomie w przypadku każdej z zastosowanych formuł dodatków, nie przekraczając limitu 30 mg/100 ml. Z kolei rozkład termograwimetryczny tych żywic, następujący w temperaturze 450°C, przebiegał różnie. Najniższy współczynnik A uzyskano dla pakietu dodatków NOR5. Żaden z wyznaczonych współczynników A nie przekroczył limitu 20%. Z kolei masy osadów w komorach spalania w większości przekraczały limit 2500 mg (TCCD). Jeden wynik uplasował się poniżej 2500 mg, przy pozostałych wskaźnikach uzyskujących wartości także poniżej limitów maksimum.

Analiza porównawcza otrzymanych wyników współczynników A i masy osadów pozwala stwierdzić, że przy tym samym dozowaniu (540 mg/kg) pakietu dodatków o różnej formule ilość osadów generowanych w komorach spalania silnika M111 wykazywała tendencję rosnącą, odpowiadającą wzrostowi współczynnika rozkładu żywic A. Wyjątek stanowiła próbka z dodatkiem NOR4, w przypadku której uzyskano równocześnie najniższe osady w komorach spalania M111 i najwyższy współczynnik rozkładu żywic A. Formuła chemiczna zastosowanych składników pakietu dodatków w badanej próbce paliwa zawierającego dodatek NOR4 różniła się od innych badanych formuł dodatków, co mogło być przyczyną uzyskania powyższych wyników.

Na rysunku 1 przedstawiono wyniki uzyskanych mas osadów w komorach silnika M111 i odpowiadających im. współczynników rozkładu żywic nieprzemywanych A.



Rys. 1. Wyniki masy osadów w silniku M111 i odpowiadających jej współczynników A

Przedmiotem badań w drugiej części projektu BIOTRETH było paliwo etanolowe E85. Paliwo składało się z 85% (*V/V*) bioetanolu I generacji pochodzącego z przetwórstwa melasy buraczanej i 15% (*V/V*) węglowodorowej benzyny bezołowiowej 95 (E0). Wyniki oznaczeń właściwości paliwa E85/EtOH IG podano w tabeli 3.

Tabela 3. Właściwości paliwa etanolowego E85

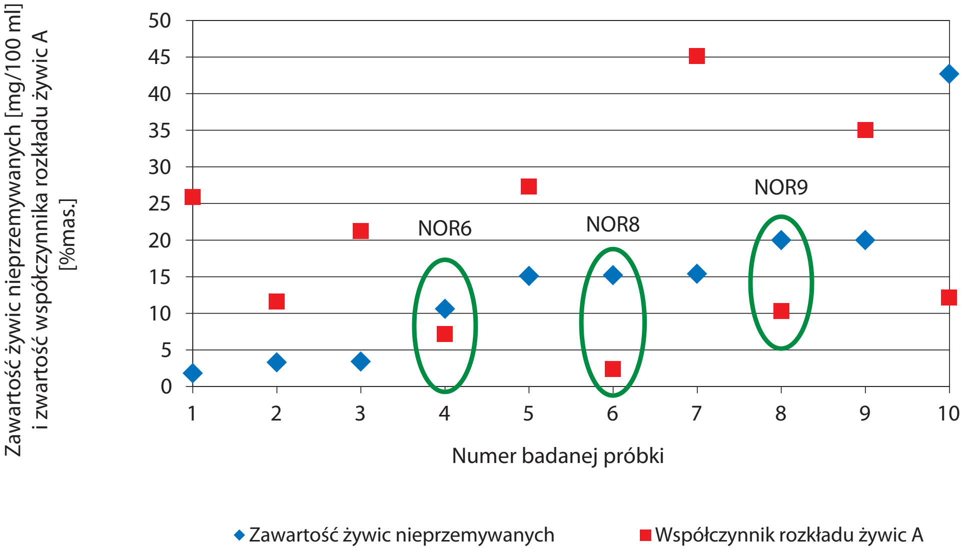
Wymagania	E85/EtOH IG	Wymagania według PKN-CEN/TS 15293	Metoda badania według:
1. Gęstość (w 15°C) [kg/m^3]	784	760,0–800,0	EN ISO 12185
2. Okres indukcyjny [minuty]	>360	min. 360	EN ISO 7536
3. Zawartość żywic obecnych [mg/100 ml]	<1	maks. 5	EN ISO 6246
4. Badanie działania korodującego na płytce miedzianej (3 h w 50°C) [klasa]	1A	klasa 1	EN ISO 2160
5. Całkowita kwasowość (w przeliczeniu na kwas octowy) [% (*m/m*)]	<0,003	maks. 0,005	EN ISO 15491
6. Przewodność elektryczna [μS/cm]	1,0	maks. 1,5	EN 15938
7. Zawartość metanolu [% (*V/V*)]	<0,17	maks. 1,0	EN 1601
8. Zawartość wyższych nasyconych alkoholi jednowodorotlenowych (C3-C5) [% (*V/V*)]	2,5	maks. 6,0	EN 1601
9. Zawartość eterów (z pięcioma lub więcej atomami węgla) [% (*V/V*)]	<0,17	maks. 11,0	EN 1601
10. Zawartość wody [% (*m/m*)]	0,118	maks. 0,400	EN 15489
11. Zawartość chlorków nieorganicznych [mg/kg]	<1,0	maks. 1,2	EN 15492
12. Zawartość miedzi [mg/kg]	<0,05	maks. 0,10	EN 15837
13. Zawartość fosforu [mg/l]	<0,15	maks. 0,15	EN 15487
14. Zawartość siarki [mg/kg]	<5,0	maks. 10,0	EN 15486
15. Zawartość siarczanów [mg/kg]	2,7	maks. 4,0	EN 15492
16. Prężność par [kPa]	45,2	35,0–60,0 klasa a	EN 13016-1

W celu doboru odpowiedniego pakietu dodatków detergentowych paliwo etanolowe E85 było uszlachetniane różnymi pakietami tych dodatków przy tym samym poziomie dozowania. Analogicznie jak w przypadku paliwa E10 dla każdej próbki paliwa E85 wykonano analizę zawartości żywic nieprzemywanych oraz analizę ich rozkładu metodą termograwimetryczną. W tabeli 4 zamieszczono wyniki zawartości żywic nieprzemywanych oraz odpowiadające im. współczynniki rozkładu A.

Tabela 4. Wyniki zawartości żywic nieprzemywanych i współczynników A

Badane paliwo E85	Zawartość żywic nieprzemywanych [mg/100 ml] limit maks. 30	Współczynnik A [% mas. @450°C] limit maks. 20
E85 (85% EtOH + 15% BB95) bez pakietu dodatków	1,5	–
1. E85 (15% paliwa handlowego A z typową dawką pakietu dodatków)	1,8	25,9
2. E85 (15% paliwa handlowego B z typową dawką pakietu dodatków)	3,3	11,6
3. E85 (15% paliwa handlowego C z typową dawką pakietu dodatków)	3,4	21,2
4. E85 + 600 mg/kg NOR8	10,6	7,2
5. E85 + 600 mg/kg NOR12	15,1	27,3
6. E85 + 600 mg/kg NOR6	15,2	2,4
7. E85 + 600 mg/kg NOR11	15,4	45,1
8. E85 + 600 mg/kg NOR9	20,0	10,3
9. E85 + 600 mg/kg NOR10	20,0	35,0
10. E85 + 600 mg/kg NOR13	42,7	12,1

Analiza uzyskanych wyników zawartości żywic nieprzemywanych wskazuje, że paliwo etanolowe E85 niezawierające pakietu dodatków wygenerowało najmniejszą zawartość żywic nieprzemywanych, tj. 1,5 mg/100 ml. Paliwa E85 otrzymane ze zmieszania 85% etanolu z 15% benzyny handlowej różnych dostawców (A, B, C) zawierającej typowe ilości pakietów dodatków detergentowych wykazały niewielkie ilości żywic nieprzemywanych, jednak wartości współczynnika rozkładu żywic A były wysokie i w dwóch przypadkach przekraczały jego limit, tj. 20%. Warty odnotowania jest fakt, że ilość pakietu dodatków w tych próbkach paliwa była wielokrotnie mniejsza niż w kolejnych badanych próbkach, gdzie stosowano pakiety eksperymentalne. Wśród wyników uzyskanych dla próbek E85 zawierających doświadczalne formuły pakietów dodatków najniższe wartości zarówno dla żywic nieprzemywanych, jak i współczynnika ich rozkładu otrzymano w przypadku formuł pakietów NOR6, NOR8, NOR9. Uzyskane wyniki przedstawiono w formie graficznej na rysunku 2.



Rys. 2. Wyniki zawartości żywic nieprzemywanych i współczynnika A w paliwie etanolowym E85

W tabeli 5 zamieszczono wyniki całkowitej masy osadów w komorach spalania silnika Ford FlexFuel uzyskane w opracowanym teście silnikowym.

Tabela 5. Wyniki oznaczeń współczynników A i masy osadów utworzonych w komorach spalania silnika Ford FlexFuel

Badane paliwo E85	Współczynnik A [% mas. @450°C] limit maks. 20	Masa osadów w komorach silnika Ford FlexFuel (TCCD) [mg] Kategoria 3–5 limit maks. 2500
E85 (85% EtOH + 15% BB95) bez pakietu dodatków	–	426
E85 + 600 mg/kg NOR9	10,3	1840
E85 + 600 mg/kg NOR14	5,0	335
E85 + 600 mg/kg NOR15	19,4	1098

Badane paliwo E85	Współczynnik A [% mas. @450°C] limit maks. 20	Masa osadów w komorach silnika Ford FlexFuel (TCCD) [mg] Kategoria 3–5 limit maks. 2500
E85 + 600 mg/kg NOR16	16,5	1223
E85 + 600 mg/kg NOR17	28,4	792
E85 + 600 mg/kg NOR18	29,7	822
E85 + 600 mg/kg NOR19	13,6	906

Analiza wyników współczynnika rozkładu żywic A wskazała, że większość wartości współczynnika A plasowała się poniżej limitu 20%. Podobnie wartości TCCD układały się poniżej 2500 mg/silnik. Nie zaobserwowano jednak korelacji pomiędzy wynikami otrzymanymi różnymi metodami. Różnice w formułach chemicznych pakietów eksperymentalnych są jednak widoczne. Przy tym samym dozowaniu pakiet NOR14 dał korzystnie najniższe wyniki w obu metodach. Z kolei pakiet NOR9 przy względnie niskim wyniku współczynnika rozkładu żywic A dał najwyższy wynik TCCD. Przyczyny należy w tym przypadku upatrywać w formule chemicznej pakietu dodatku NOR9.

Podsumowanie i wyniki

Jak wspomniano we wstępie, wzrost zawartości etanolu w formule paliwa do silników o zapłonie iskrowym jest wynikiem wielu aspektów globalnej polityki. Mając na uwadze sytuacje w obu Amerykach i plany Unii Europejskiej, zwiększenie udziału etanolu w podstawowym wolumenie paliw transportowych jest w przyszłości nieuniknione.

Wprowadzanie takich paliw na rynek jest jednak uwarunkowane aprobatą producentów silników i samochodów, dających gwarancję na swój produkt, który musi być kompatybilny z wszystkimi płynami eksploatacyjnymi, w tym z paliwem, oraz musi spełniać wymagania norm emisji spalin. Jak zasygnalizowano powyżej, wpływ nowych paliw na stan techniczny elementów silnika i ich osiągi jest monitorowany przez rynek motoryzacyjny, w celu ewentualnej poprawy ustalonych w specyfikacji parametrów jakościowych lub wprowadzenia nowych.

Przytoczone wyniki badań INiG związanych z paliwem E85 mają przyczynić się do opracowania formuły pakietu dodatku poprawiającego właściwości eksploatacyjne. Z badań przeprowadzonych w trakcie realizacji projektu, finansowanego ze środków funduszy norweskich w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju, wynika, że:

- nieuszlachetnione paliwo o niskiej zawartości etanolu (E10) wykazało dużo większą skłonność do tworzenia osadów w komorach spalania niż paliwo o wysokiej zawartości etanolu (E85);
- uszlachetnianie paliwa E10 i E85 eksperymentalnymi pakietami dodatków w większości powodowało wzrost masy osadów w komorach spalania silnika;
- wynikom minimalnych wartości mas osadów w silnikach odpowiadały niższe od granicznych wartości współczynników rozkładu żywic oraz zawartości żywic nieprzemywanych.

Artykuł powstał na podstawie wyników badań uzyskanych w projekcie prowadzonym w INiG – PIB i finansowanym ze środków funduszy norweskich w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju.

Literatura

[1] *Ethanol Guidelines*. March 2009. Worldwide Fuel Charter, http://www.acea.be, dostęp: sierpień 2015.

[2] Röj A.: *An Automotive Industry Perspective on Biofuels*. Volvo Technology Corporation. International Conference on Biofuels Standards, Brussels, 27–28 February 2007.

[3] McCormick R. L., Yanowitz J., Ratcliff M., Zigler B. T.: *Review and Evaluation of Studies on the Use of E15 in Light-Duty Vehicles*. Prepared for the Renewable Fuels Association Under Technical Services Agreement No. 13-505. National Renewable Energy Laboratory. Golden, CO. October 2013, http://ethanolrfa.org/page/-/rfa-as-

sociation-site/studies/RFA%20NREL%20Review%20and%20Evaluation%20of%20E15%20Studies.pdf?nocdn=1-, dostęp: sierpień 2015.

[4] Yanowitz J., Ratcliff M., Zigler B. T., McCormick R. L.: *Appendix: Studies on the Use of E15 and E20 in Light-Duty Vehicles*. http://ethanolrfa.org/page/-/rfa-association-site/studies/RFA%20NREL%20Review%20and%20Evaluation%20E15%20Appendix.pdf?nocdn=1 – dostęp sierpień 2015

[5] EPA: *E15: Notices & Regulations*. http://www3.epa.gov/otaq/regs/fuels/additive/e15/e15-regs.htm – dostęp wrzesień 2015

[6] Moriarty K., Yanowitz J.: *E15 and Infrastructure*. Strategic Partnership Project Report NREL/TP-5400-64156, May 2015; http://www.afdc.energy.gov/uploads/publication/e15_infrastructure.pdf – dostęp październik 2015

[7] *Acelerating Industry Innovation – 2012 Ethanol Industry Outlook*. http://www.ethanolrfa.org/wp-content/uploads/2015/09/2012-Ethanol-Industry-Outlook.pdf – dostęp październik 2015

[8] *Energy Policy Act of 1992, Section 301(2)*. http://www1.eere.energy.gov/vehiclesandfuels/epact/alt_fuel_petitions.html – dostęp wrzesień 2015

[9] *Ethanol*. http://www.afdc.energy.gov/fuels/ethanol.html – dostęp wrzesień 2015

[10] *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends*; DOE/GO-102013-3861, September 2013; http://www.afdc.energy.gov/uploads/publication/ethanol_handbook.pdf – dostęp październik 2015

[11] *Aumento do etanol na gasolina foi precedido por estudo*. http://www.brasil.gov.br/economia-e-emprego/2015/03/aumento-do-etanol-na-gasolina-foi-precedido-por-um-estudo-entenda – dostęp wrzesień 2015

[12] Pałuchowska M., Jakóbiec J.: *Wybór parametrów jakościowych do specyfikacji technicznej paliwa Etanol (E85) stosowanego do zasilania silników samochodów FFV*. Zeszyty Naukowe Instytutu Pojazdów /Politechnika Warszawska 2012, z. 1, s. 39–47.

[13] Kampman B., Verbeek R., van Grinsven A., van Mensch P., Croezen H., Patuleia A.: *Bringing biofuels on the market. Options to increase EU biofuels volumes beyond the current blending limits.* Report, Delft, July 2013; Commissioned by: The European Commission, DG Energy. https://ec.europa.eu/energy/sites/ener/files/documents/2013_11_bringing_biofuels_on_the_market.pdf – dostęp: sierpień 2015.

[14] Pałuchowska M., Jakóbiec J.: *Badania właściwości użytkowych benzyny silnikowej E10*. Nafta-Gaz 2011, nr 12, s. 929–932.

[15] Pałuchowska M., Jakóbiec J.: *Wpływ składu chemicznego benzyny i zawartości etanolu w kształtowaniu właściwości eksploatacyjnych*. Autobusy – Technika, Eksploatacja, Systemy Transportowe 2012, nr 7–8, s. 56–60.

[16] Danek B., Rogowska D.: *Destylacja benzyny silnikowej z zawartością do 10% (GV/V) etanolu – obliczanie jej parametrów metodą addytywnych wskaźników mieszania*. Nafta-Gaz 2014, nr 3, s. 192–196.

[17] *Worldwide Fuel Charter.* Fifth Edition, September 2013. http://www. acea.be – dostęp: wrzesień 2015.

[18] Jęczmionek Ł., Krasodomski W., Pałuchowska M., Porzycka-Semczuk K.: *Problems of assessment of the petrol propensity to combustion chamber deposits forming according to methods specified in Worldwide Fuel Charter: M 111 test and BZ-154-01*. Nafta-Gaz 2014, nr 3, s. 176–184.

[19] DuMont R., Cunningham L., Oliver M., Studzinski M., Galante-Fox J. M.: *Controlling Induction System Deposits in Flexible Fuel Vehicles Operating on E85*. doi:10.4271/2007-01-4071.

[20] Chapman E., Cummings J., Conran D.: *Effects of Gasoline and Ethanol Fuel Corrosion Inhibitors on Powertrain Intake Valve Deposits*. doi:10.4271/2013-01-0893.

[21] Galante-Fox J., Von Bacho P., Notaro C., Zizelman J.: *E-85 Fuel Corrosivity: Effects on Port Fuel Injector Durability Performance*. SAE Technical Paper 2007-01-4072, 2007, doi:10.4271/2007-01-4072.

[22] Stępień Z.: *Wielokierunkowe badania wpływu paliw wysoko-etanolowych na tworzenie osadów w silnikach z zapłonem iskrowym*. VI International Congress on Combustion Engines, Olsztyn, 22–24 June 2015, PTNSS–2015–3418.

[23] Pałuchowska M., Stępień Z., Żak G.: *Perspektywy wykorzystywania etanolu jako składnika paliwa i jego potencjał w redukcji emisji szkodliwych składników spalin.* Combustion Engines 2014, R. 158, nr 3, s. 80–92.

[24] *BioEthanol for Sustainable Transport. Results and recommendations from the European BEST project.* http://www.sekab.com/wp-content/uploads/2011/04/BEST- Bio-Ethanol-for-Sustainable-Transport.pdf – dostęp wrzesień 2015

An Overview of the Usage of Ethanol as a Fuel for Spark Ignition Engines

Przegląd zastosowania etanolu jako paliwa do silników o zapłonie iskrowym

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Abstract

The idea of using ethanol in spark ignition engines (SI) is not new, but has returned to the technical agenda in recent years. Usage of ethanol as a transport fuel is growing and interest in using ethanol-gasoline blends is high. Various characteristics of ethanol make it suitable for usage as an automotive fuel, although there are some challenges. These issues are briefly described in this paper. Moreover, this paper reviews some of the most important points and comments on the past, present and future of ethanol as a fuel for spark ignition engines. In the context of the past this paper briefly describes the history of usage of ethanol in the automotive industry. In the present context, an ethanol SWOT matrix reveals its current and potential position on the fuel market. The possible future vision of ethanol as an engine fuel is considered in the context of opportunities for and threats to ethanol, together with the possible short and long-term tendencies.

INTRODUCTION

Ethanol, a familiar organic compound, is employed in a wide variety of applications in many branches of human activity. The significance of usage of ethanol has become particularly important in the automotive industry. There are many reasons for this growing interest, but the most important amongst them are the following:

- ethanol as a key element in establishing a domestic or regional fuel independence strategy from supplies of fossil-based fuels,
- ecological lobbying and a global tendency for switching to more eco-friendly fuels,
- biodegradability, renewability and the relative easiness of ethanol's. implementation in combustion engines, especially by means of various blends with gasoline,
- advantageous physicochemical properties in terms of engine applications.

The issue of exploitation of ethanol in the automotive sector, especially in a context of ethanol-gasoline blends with varying levels of ethanol, reveals highly complex specifics. However, the potential for an improvement in air quality, engine performance, fuel supply security and sustainability makes work on the production and usage of ethanol and its blends a multidisciplinary research priority.

Ethanol and bioethanol as automotive fuels

Ethanol is the most widely-used biofuel, although geographically its usage is somewhat restricted. Ethanol can be produced using crude oil as a feedstock, but is more commonly sourced from conversion of biomass ('bioethanol'). Since it is derived from biomass (and not fossil hydrocarbon deposits), bioethanol has been identified a fuel of great potential in efforts to make energy consumption in the transportation sector sustainable [18, 25, 45]. In this context ethanol has been perceived as a partial replacement for gasoline in SI engines for some time and this trend seems to be continued over the coming years [52, 61]. The applications of ethanol itself and its blends with gasoline in the transportation sector are the most widespread in Brazil (E5-E85, E100), USA and Germany (E15-E85), Sweden (E85) and Thailand (E75) [12, 17].

Bioethanol can potentially deliver greenhouse gas savings of up to 87% over conventional fossil fuels, although this value can be much lower, as it depends strongly on the feedstock and means of processing and production [20]. Environmentally friendly character of ethanol, especially in terms of its renewability and effective biodegradability has been visualized as an *ethanol lifecycle,* depicted in Figure 1 [44]. First generation bioethanol is produced from the fermentation of sugar-rich edible crops, while second generation bioethanol uses inedible cellulosic material as a production feedstock. In the technical literature it can be identified an 'intermediate generation' of bioethanol but only when technological process of production reveals characteristics common to both generations [44, 36]. However, as with other biofuels, doubts over the sustainability and ethics of using edible crops as fuel mean that second-generation bioethanol is of great interest [11].

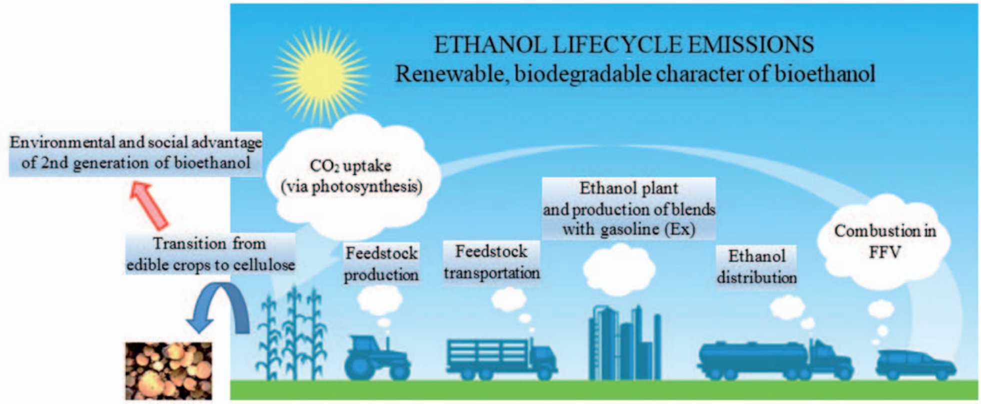

Figure 1. Bioethanol in the context of environmental issues [44]

Currently, almost all ethanol is produced from the fermentation of edible crops, most notably corn (in the USA) and sugar-cane (in Brazil). It should be noted that those two countries constitute the biggest producers of ethanol worldwide. Specialists analysing the performance and potential of ethanol as a transport fuel almost invariably assume ethanol to be of plant origin, rather than from fossil hydrocarbon sources [11]. The goal of this great interest is to expand production of 2nd generation of bioethanol as well as reducing water usage in ethanol production [36].

History of ethanol as an automotive fuel

Knowledge of potential usage of ethanol as a vehicular fuel dates to the conception of the automobile. The first known usage of ethanol in engine application was recorded at the beginning of the 20th century. Engine designers noticed the favourable properties of ethanol as a fuel and a potentially promising substitute for gasoline. The main points of interest were then issues such as the impact of adding alcohol to gasoline on the thermal efficiency of the engine and its operational stability [48, 12].

The production of ethanol in a large scale began in the 1920s, mainly in the US and Europe. Automotive industry pioneer Henry Ford published a paper in The New York Times in 1925 where he stated that the fuels of the future would be produced from plant waste and even from fermented fruits [48]. The production of ethanol-gasoline blends in Poland started in 1928 mainly in the proportions of 70% gasoline and 30% ethanol. After the Second World War, ethanol was driven out of the market by crude oil, due to the relatively higher costs of production. As a result, the market significance of ethanol as a fuel was diminished substantially. The concept of using ethanol in the transport sector was re-evaluated and implemented at the beginning of the 1970s, which was connected with the arisen energy crisis and subsequent high oil prices. It is estimated that in 1979 the US produced about 190 million liters of ethanol from corn [13].

More stringent emission standards and strong ecological lobbying in the 1990s meant that ethanol has become the subject of numerous scientific studies. The subject of research was related mainly to possibilities of usage of ethanol in spark-ignition engines (SI), determination of the emission levels of exhaust compounds, fuel consumption and engine component wear and corrosion occurrences. At that time, research centres related to the Polish fuel industry performed many investigations on the introduction of ethanol as an alternative fuel for spark ignition engines (SI), particularly in the variants of an additive to gasoline. Recent scientific studies have looked at the issue of the necessary modifications to SI engines and its fixtures depending on the content of ethanol mixed with gasoline [11, 12].

Nowadays, the share of ethanol in a global fuel supply in the market is increasing. Global production of ethanol in 2014 amounted to approximately more than 10^2 [billion liters] (US: 55 [billion liters], Brazil 27 [billion liters] EU: 5 [billion liters], other countries: 13 [billion liters]) [13]. At present the estimated ethanol production capacity in Poland is about 0.75 [billion liters] [40]. A currently noticeable trend reveals an increase of the production of second-generation bioethanol, mainly due to the pressure exerted from environmental protection agencies [36]. Interestingly, consumption of ethanol in transport applications is also growing from year to year, however the growth rate is decreasing, which may indicate partial market saturation [55]. It is important to notice that in many circumstances bioethanol production is substantially supported by government support (e.g. in the US, Germany), particularly by means of providing financial grants and supportive investment initiatives related to the restructuration of automotive industry and transport facilities.

Nowadays the implementation of ethanol and ethanol-gasoline blends on a large scale reveals interdisciplinary specifics, involving political, legislative, economic, logistical and environmental issues [52, 44, 12]. In political and economic terms, ethanol is considered as a crucial element of the strategy of energy security and independence from crude oils. In technical terms, ethanol is becoming widely used in SI engines with both port fuel and direct fuel injection [50]. Moreover, ethanol is taken into consideration as a promising fuel for innovative downsized engines with high compression ratios. In environmental aspects, ethanol is perceived as a sustainable energy source and effective tool for reducing many of exhaust compounds as well as particulates [12, 57].

Physicochemical properties of ethanol

Ethanol (C_2H_5OH), a primary alcohol, is the second simplest alcohol. Humanity has great experience in its methods of production. Ethanol is fully biodegradable and renewable when produced from biomass [18, 24]. Ethanol's properties such as density and octane number make it suitable for combustion in spark-ignition engines. However, it is much more commonly splash blended with gasoline than used neat. Ethanol can also be mixed with Diesel to form blends for use in compression-ignition engines, although this application has received less attention in the literature and indeed in practical applications [9, 11].

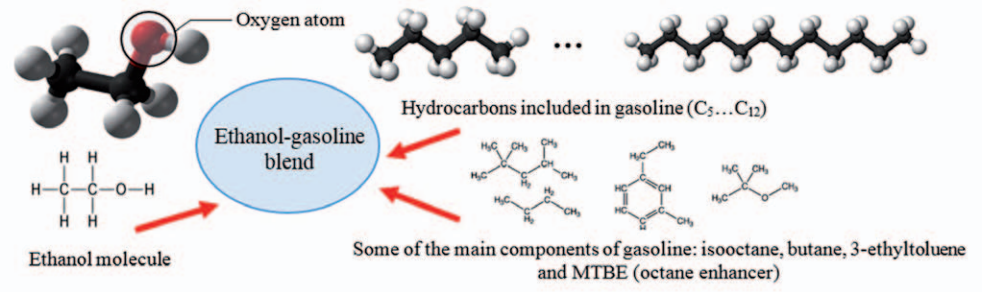

Figure 2. A comparison of the ethanol molecule and compounds contained in standard gasoline

Ethanol can be splash blended with gasoline to form ethanol-gasoline blends (see Figure 2), identified by an 'E' followed by the volumetric percentage of ethanol in the blend. The most common blends differ geographically, but mainly include E5, E10 and E85 [8]. Blends up to E10 are permitted for sale in the European Union [20]. In 2007, nearly 40% of all gasoline sold in the USA contained added ethanol and this tendency appears to be growing constantly [56, 11, 52]. Usage of high ethanol content blends (E85) is becoming more and more intensive in many countries like the USA, Germany, Sweden and particularly Brazil, which is reflected in the growing market share of flex-fuel-vehicles (FFV) [15, 52].

The physicochemical properties of neat ethanol and its blends with gasoline reveal quite appreciable features which are quantified in Tables 1–2. Ethanol is also fully water-miscible and readily absorbs water, so any blend containing ethanol will likely also contain a small but significant proportion of water [18]. Ethanol and its blends with gasoline occur as liquids, and therefore have energy densities superior to gaseous fuels. Moreover, ethanol has a higher density and viscosity than gasoline [24, 37, 43] and is generally more penetrative through physical barriers [4]; however it reveals substantially lower lubricity [28, 9]. Ethanol can be perceived as an oxygenated fuel in comparison to gasoline, diesel and LPG, which do not contain appreciable quantities of oxygen. The presence of an oxygen atom means that ethanol can be thought as a partially oxidized fuel [7, 5]. This feature shapes its appreciable octane rating and as a result of this ethanol fuels are substantially more resistant to knock combustion which can be successfully exploited in a few upcoming innovative engine technologies (see Table 4) [24].

Table 1. The physicochemical properties of ethanol and gasoline [12]

Parameter	Unit	Gasoline	Ethanol (E100)
Chemical formula	-	Mainly hydrocarbons: C_5-C_{12}	C_2H_5OH
Molecular mass	[kg kmol^{-1}]	114.15	46.07
Specific gravity	[kg m^{-3}]	0.7-0.78	0.794
Density at 15°C	[kg/m^3]	750-765	785-810

Parameter	Unit	Gasoline	Ethanol (E100)
Kinematic viscosity	[mm²/s]	0.494	1.221
Heating value	[MJ/kg]	42.7	26.8
Latent heat of vaporization	[kJ/kg]	380–400	900–920
Volatility index	–	> 840	< 234
Lubricity * (PN-ISO 12156-1)	[μm] *	≈ 760	< 600
Vapor pressure (at 37,815°C)	kPa	53–60	17
Research Octane Number (RON)	–	95.0	108.6–110
Auto-ignition temperature	[°C]	257	425
AFR ratio	–	14.2–15.1	8.97
C:H ratio	–	0.53	0.33
Carbon content	[% mass]	87.4	52.2
Oxygen content	[% mass]	Negligible	34.7
Hydrogen content	[% mass]	12.6	13.0
Water content	[% mass]	Negligible	0.5–5 (depending on quality and storage conditions)
Solubility in water	[%]	0	100

Table 2. The physicochemical properties of selected ethanol-gasoline blends [12]

Parameter	Unit	E10	E50	E85
Volumetric percentage of each compound	[v/v]	10% ethanol 90% gasoline	50% ethanol 50% gasoline	85% ethanol 15% gasoline
Density at 15°C	[kg/m^3]	756.0	772.4	788.9
Vapor pressure (at 37,815°C)	kPa	57.8	51.4	32.5
Heating value	MJ/kg	41.24	33.72	30.38
Volatility index	–	903	714	234
Lubricity * (PN-ISO 12156-1)	μm*	823	724	636
Research Octane Number (RON)	–	96.6	103.2	106.8
C:H ratio	–	0.51	0.44	0.36
Hydrocarbons content:	% (v/v)	40.8	25.2	8.5
- olefin hydrocarbons		10.5	5.7	1.6
- aromatic hydrocarbon		30.3	19.5	6.9
Benzene content	% (v/v)	0.67	0.38	0.13
Compounds contain oxygen	% (v/v)	13.31	51.16	85.74

Furthermore, it is worth considering that the relatively low carbon to hydrogen ratio of ethanol (0.33) means that ethanol blends are a noteworthy option for reducing vehicular CO_2 emissions. Complete combustion of pure hydrocarbons would produce only two products – carbon dioxide (CO_2) and water (H_2O). The ratio in which molecules of these two species are produced by a combustion reaction is controlled by the carbon to hydrogen ratio of the fuel [11, 8]. That is why fuels with lower carbon to hydrogen ratios are an attractive option for reducing CO_2 emissions [11]. Therefore, the addition of even relatively small proportions of ethanol to standard gasoline lowers the overall C:H ratio of the fuel and can make the resulting blend more attractive in terms of CO_2, CO and particulate emissions [11, 8, 9, 29, 57]. However, the reduced content of H_2 in ethanol's. molecule causes a reduced calorific value which has a negative impact on fuel consumption and can increase CO_2 emissions [24, 37, 6, 22]. It is noteworthy that the overall life-cycle of CO_2 is highly dependent on the method of ethanol production [19, 39, 8].

On the other hand, the usage of ethanol blends is strongly associated with certain unfavorable issues, which derive from the acid-like and solvent-like character of ethanol. Some adverse issues include: corrosion and accelerated wear of various parts of the fuel storage and delivery systems [23, 3, 49, 47], possible interactions with engine lubricants due to water content and impurities, possible slight increases in emissions of NO_x [39, 22, 27] and emissions of some unregulated organic compounds (benzene, aldehydes, ethanol) [39, 35, 26, 8]. Additionally, conventional aftertreatment systems may not always be compatible with usage of high content ethanol blends, causing reduced conversion efficiency [8, 34].

In conclusion, there are no doubts that some ethanol properties are definitely favorable, creating a comparative advantage for ethanol relative to other alternative fuels. However, some properties imply problematic issues that need to be solved in order to maintain ethanol's. advantages and its favorable position on the fuel market. In such a configuration the physicochemical properties of ethanol have been balanced in Table 4.

Ethanol's combustion characteristics

The chemistry of the ethanol as well as its combustion specifics and efficiency affect many significant engine issues such as exhaust emissions and fuel consumption. It is noteworthy that the combustion characteristics of ethanol are specific and that the issue has been broadly considered in many technical descriptions [37, 62, 2]. In essence, the short length of the ethanol carbon chain, together with the presence of the oxygen atom, make the combustion of ethanol quite different than that of pure gasoline [31, 2]. Differences in molecule characteristics, in particular the presence of the oxygen atom within the molecule, cause many changes in the manner in which the ethanol molecules are broken down, subsequently oxidized and how efficiently and rapidly the entire process proceeds [2, 33].

In a brief review there are several issues worth to note. Firstly, the combustion process of the ethanol is characterized by lowered temperature relative to the combustion of gasoline [41, 54]. Secondly, the flame propagation of combustion of neat ethanol is approximately 30% faster than gasoline [37]. These two factors raise many implications over the overall pollutant emission profile, mainly in terms of oxides of nitrogen (NO_x). Due to the lowered temperature of combustion and its increased velocity, the total time of the combustion process is reduced and therefore may limit the time available for the formation of NO_x [62]. However, the flame propagation does not reveal a linear trend with increasing ethanol blend content [41]. Furthermore, greater absorption of heat in the cylinder due to ethanol's. higher latent heat of vaporization should inhibit NO_x formation [1]. However, the overall trends of NO_x emissions are not consistent [22, 27, 10, 8]. The effect of leaner mixtures when using ethanol ($\lambda>1$) may reduce NO_X conversion efficiency in a three-way catalyst (TWC), which may slightly outweigh the benefits gained from the increased combustion rate [11, 8].

Needless to say, partial oxidation of ethanol-gasoline blends determines that the quantity of oxygen required for complete combustion of a given mass is reduced, and thus the stoichiometric ratio is lower than for pure gasoline. For instance, the ratios for E10 and E85 blends are 3.8% and 32.8% lower (respectively) than for gasoline alone. In light of this, a greater rate of fuel injection is required in order to maintain a stoichiometric mixture [6, 11] and as a consequence fuel consumption is usually considered to grow in response to increasing fuel ethanol content [24, 56, 37, 6, 22, 19]. In this context the E85 blend is invariably considered to cause higher volumetric fuel consumption than pure gasoline [60, 58, 51, 46], but when the difference in energy density is factored out, E85 has been reported to outperform gasoline, due to improved thermodynamic efficiency [51, 11]. It is noteworthy that the lower stoichiometric ratio makes complete oxidation of the fuel relatively easier to achieve. Emissions of carbon dioxide are greater, primarily due to the lower energetic content of the fuel, but also due to improved oxidation of HC and CO to CO_2 [9, 8].

Finally, it is worth stating again that the oxygen content in the ethanol molecule raises its resistance to knocking. In this context the research octane number of ethanol is substantially higher than that of gasoline. Even small additions of ethanol to gasoline raise its ability to withstand knocking combustion, which is indisputably a noteworthy advantage when used in downsized engines with a high compression ratio or with high degree of turbocharging applied.

In conclusion, the specifics of ethanol combustion is deemed as a technically very complex issue dependent on many variables. In this context it implies consequences related with the regulated and unregulated emissions issues, which remain the subject of other studies [9, 10, 8, 2, 30, 33].

Compatibility with gasoline-fuelled vehicles

The application of the ethanol-gasoline blends in modern vehicles is associated with multiple modifications that need to be implemented according to the scheme shown in Table 3 [12, 14]. The type and range of changes required depends on the vehicle's. age and the blend to be employed. It is agreed that blends up to E15 can be used in modern PFI and DISI engines without problems, however beyond that point vehicles not designed for use with ethanol blends may suffer severe failures [59, 11]. In case of FFVs, the technical specification originally includes the modifications included in Table 3, therefore these vehicles are capable of running on high ethanol blends with a much smaller risk of failure [11]. The issue of the compatibility of modern vehicles with ethanol blends remains under investigation by entities such as the EPA [42].

Table 3. Modifications required for usage of ethanol blends in modern vehicles [12, 14]

Ethanol content in blend with gasoline		<5%	5 – 15%	15 – 25%	25 – 85%	>85%
Fuel injection parts (fuel lines, injectors)	improved corrosion resistance	–	–	+	+	+
Fuel pump		–	–	+	+	+
Fuel pressure device		–	–	+	+	+
Fuel filter		–	–	+	+	+
Ignition system (spark plugs)		–	–	+	+	+
Evaporative fuel vapor system		–	–	+	+	+
Fuel tank – reinforced and corrosion resistant		–	–	+	+	+
Catalytic converter capable of working in higher temperatures		–	–	+	+	+

Ethanol content in blend with gasoline	<5%	5 – 15%	15 – 25%	25 – 85%	>85%
Engine parts (pistons, piston rings, intake and exhaust valves) – replacing, re-coating, reinforcements	–	–	–	+	+
Engine lubricant + fuel additives preventing deposits formation	–	–	–	+	+
Intake manifold	–	–	–	+	+
Exhaust system	–	–	–	+	+
Engine cold-start support system	–	–	–	– (+ for >E50)	+
Engine control unit adjustments or complete recalibration	–	–	*	+	+
+ NECESSARY – UNNECESSARY * slight adjustments					

The direct causes of the necessity of these modifications derive mainly from the physicochemical properties of ethanol. The most common adverse phenomena associated with using ethanol blends are i.e.: corrosion issues, the penetrative character of ethanol due to impurities contained therein [16, 23], possible negative interactions with engine oil, deteriorations in lubrication quality and increased deposit formation [56, 3, 12]. However, corrosion is perceived as a major concern even greater than reduced ethanol blends lubricity [28]. In essence, the aforementioned adverse and problematic issues have been chosen as the most critical of ethanol's weaknesses and are listed in Table 4.

The global potential of ethanol – SWOT analysis

The global potential of ethanol as an automotive fuel can be presented as a SWOT matrix which is a structured planning method used to assess a product's strengths, weaknesses, opportunities and threats and recognize its placement in the market.

The strength characteristics define ethanol's features which give it a comparative advantage over other fuels. The weaknesses characteristics define ethanol's features that may create a comparative disadvantage relative to other fuels. The opportunities characteristics imply external circumstances or factors related to ethanol that could be exploited to gain its advantage in the market applications in a long-term perspective. The threats characteristics imply external circumstances or factors related to the ethanol that may diminish its significance in the market and are likely to lead to the ultimate collapse of ethanol's concept in a long-term perspective. In such a configuration ethanol's SWOT matrix is depicted in Table 4.

Table 4. SWOT matrix related to ethanol [1, 7, 8, 9, 10, 11, 12, 14, 23, 24, 26, 39, 44, 53, 55, 61]

STRENGTHS (helpful in achieving market position)	WEAKNESSES (harmful in achieving market position)
+ Biodegradability, renewability → eco-friendly character, exploitation of plant waste or cellulosic material; + Oxygenated nature of molecule and low C:H ratio: • relative cleaner emissions than from gasoline; • reduced mass and number of emissions of particulates → efficient tool of fulfilling up-to-date Euro 6 PM/PN (DISI) standards; • octane rating → reduced probability of knocking combustion at high temperatures and pressures → the potential use in direct injection technology and working on stratified air-fuel mixtures; • possibilities of increasing the engine's. compression ratio (with a substantial increase in the combustion efficiency) proportional to the ethanol content in the blend; • perspectives of implementing the concept of engine downsizing and downspeeding in association with a high degree of turbocharging applied; + Proper solubility with gasoline → easiness of creation of blends with gasoline; + Overall physicochemical specifics of combustion and C:H ratio → reduction of HC, CO, CO$_2$, and some of the unregulated compounds like: benzene, toluene	– Reduced C content in the molecule → reduced calorific value relative to gasoline: • less stable combustion process → possible deteriorations in emissions (NO$_x$, methane, 1.3- butadiene etc.); • higher fuel consumption relative to gasoline → reduced range; – Acid-like character of ethanol, affinity to water, organic acids, chlorides impurities → corrosion risk: • higher probability of wear of engine components (injectors, fuel storage and delivery system); • necessity of using chemically inactive materials (which does not react chemically with ethanol) → cost increase; – Acid-like character of ethanol and water content → potential interaction with engine oil, oil oxidation, sludge formation and deterioration of lubrication quality; – Solvent nature of ethanol → swelling, softening and finally corrosion of materials mainly made from plastics rubber → necessity of using chemically inactive materials; – Increased deposits formation on intake valves and filters → necessity of usage of deposit control fuel additives; – Problems with starting up the engine, especially at sub-zero temperatures and high ethanol content due to combustion characteristics → necessity of implementing systems which support engine starting; – Aftertreatment systems' (ATS) compatibility with ethanol blends (accelerated ageing and reduced efficiency);

OPPORTUNITIES (helpful in achieving market position)	THREATS (harmful in achieving market position)
• Political significance of ethanol → establishment of the domestic energy independence strategy → lobbying power; • Empowerment from environmental protection agencies especially when switching to second generation bioethanol; • Broad possibilities of implementation in modern innovative engine technologies; • Promising and feasible substitute for gasoline; • More common switching to vehicles enabled for using ethanol fuels (even E85 in case of FFV); • Relatively easy implementation in modern SI engines but only in the case of low ethanol content blends	• Limited competitiveness with crude oil where government financial support is limited; • Need of restructuring and modernization of the fuel industry, distribution infrastructure and transport facilities → huge investment and ongoing costs; • Relatively unfavourable method of production in terms of exploiting edible crops and usage of substantial amounts of water; • Possible lack of social acceptance; • Substantial costs in terms of engine modifications when using high ethanol content blends; • Possible competition with other automotive solutions: hybrid and electric vehicles, hydrogen fuels and fuel cells

Possible future trends in the usage of ethanol in the automotive industry

In respect to biofuels and in particular ethanol fuels, some approximate trends can be seen and forecasts drawn, especially when analysing the visible political and economic factors. The most probable and common projections in this context can be stated as follows [12, 17, 36, 38, 44, 52, 55]:

- biofuels and ethanol are going to continuously increase in significance as fuels in the automotive sector, which is visible in persistently increasing volume of production and available size of supply on the fuel markets,
- ethanol is excepted to maintain its political lobbying significance as a major substitute for gasoline, especially in reference to the unstable political situation in the Middle East and possibilities of artificially inflated prices of crude oil per barrel controlled by the most influential exporters,
- increasing automotive usage of ethanol in the EU and the USA is excepted to be maintained in the short term, which is already reflected in the structure of the vehicle market and the rising share of ethanol-adopted vehicles and FFVs sold,

- alternative fuels (including ethanol) will probably not completely substitute the demand for gasoline fuel in the transportation sector in the long-term perspective, however they will certainly play a significant role,
- recalling some details, long-term projections issued by the US Energy Information Administration show that E85 will take a 37% share of US domestic ethanol production by 2035 and FFVs are expected to represent the largest share of all vehicles, at 17% of all new vehicle sales in US [52, 53],
- a gradual change in ethanol production methods and efforts striving for greater production of 2nd generation bioethanol are excepted as they are deemed more sustainable and non-invasive for agriculture focused on food production; such projections concern mostly the US and the EU,
- usage of ethanol-gasoline blends with volumetric proportions of ethanol ranging from 3% to 10% is already widespread in the EU and the US, however a slow but progressive switch to a more expanded usage of intermediate ethanol content blends is expected,
- it is highly expected that in the near future a strong need of establishment of a feasible sustainable energy policy at a more international level will occur, to include the issues of synergistic production of biofuels and energy together with simultaneous reduction of green gas emissions (GHG) and protection of the environment and its resources, including ground and surface waters.

CONCLUSIONS & SUMMARY

The issue of usage of ethanol as fuel for SI engines presented in this paper reveals complex and multidimensional specifics which involve a range of crucial aspects from the political, economic, technical and environmental points of view. The overview presented here includes the most important points and comments related to these aspects in the context of the past, present and future of ethanol as a fuel, which can be summarized in a few general conclusions:

- interest in usage of ethanol in SI engines dates back to the early part of the 20th century, and since then the issue has been developed and popularized significantly in the automotive sector,

- in the long-term perspective, ethanol will probably retain its political lobbying power remaining the major substitute to gasoline, however it will not completely replace demand for gasoline in the transportation sector,
- ethanol, as a 'new' alternative fuel, must be appropriately marketed, legislated and supported by governmental support and incentives in order to gain market advantage and receive social acceptance,
- ethanol's advantages are inherently related to its physicochemical characteristics and the favourable combustion specifics making it favourable when used in SI engines, notably in the area of emissions (benefits in emissions of HC, CO, PM and PN), engine performance and superior knocking resistance,
- ethanol's superior characteristics amongst alternative fuels can be successfully used as a effective marketing tool for both FFVs and ethanol blended fuels, however the implementation processes should not be taken uncritically due to some obstacles to be solved,
- the eco-friendly character of ethanol together with benefits in emissions of HC, CO, PM and PN when used low-to-mid ethanol blends makes its usage in the automotive sector likely to be highly valued and possibly substantially supported by environmental protection entities,
- ethanol and its blends with gasoline reveal a great potential in application with innovative engine technologies that enable full exploitation of ethanol's. favorable characteristics; the concepts taken into consideration are: downsizing associated with a high degree of turbocharging, variable compression ratio, DISI engines,
- ethanol's physicochemical properties and combustion characteristics of its blends with gasoline also determine some disadvantages that could be possibly harmful for durability, performance and operational parameters of the engine and conventional aftertreatment systems; these issues must be carefully investigated and successively solved at reasonable cost,
- interestingly, some of ethanol's. disadvantages could be possibly compensated by its advantages – for instance, ethanol's. lower volumetric energy density could be compensated in some degree by its high octane rating but only when suitable engine technology is applied,
- there are still many challenges and constraints in the context of usage of high ethanol content blends in the automotive sector, especially in terms of popularisation of FFVs and restructuring and adaptation of distribution

infrastructure; however, as experience shows, many countries such as Brazil and Sweden have successfully coped with such obstacles,

- usage of ethanol-gasoline blends in modern passenger cars without modifications to the engine or fuel delivery system is feasible, but only to a certain ethanol content, above which some modifications are unavoidable.

In summary, ethanol and ethanol-gasoline blends can be perceived as perspective alternative fuels for the automotive sector. In the overall pros and cons described here, analysis shows that the advantages of this fuel and its blends – together with the potential future benefits – outweigh the possible risks and disadvantages which already can be mitigated or reduced completely by numerous solutions. However, in reference to this point there are still plenty of research priorities that are highly required to enhance both the engineering and political decision-making processes. These priorities have been described in detail elsewhere [12, 11].

ABBREVIATIONS AND DEFINITIONS

λ	Lambda
AKI	Anti-knock index [AKI=(MON+RON)/2]
ATS	Aftertreatment System
CO	Carbon monoxide
CO_2	Carbon dioxide
DISI	Direct Injection Spark Ignition engines
ε	Compression ratio
E5	Fuel blend with 5% ethanol content
ECU	Engine Control Unit
EPA	Environment Protection Agency
EU	European Union countries
Ex	Fuel blend with x % ethanol content
FFV	Flex-Fuel-Vehicle
GHG	Green Gas Emissions
HC	Hydrocarbons
MON	Motor octane number
NO_x	Oxides of nitrogen

PFI	Port-fuel Injection
PM	Particulate Matter
PN	Particulate Number
RON	Research octane number
SI	Spark ignition
TWC	Three-way catalyst

REFERENCES

[1] Agarwal, A. K.: *Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines*. Progress in Energy and Combustion Science, 33, 233-271, 2007, doi:10.1016/j.pecs.2006.08.003.

[2] Aggarwal S., Naha S.: *Effect of fuel blends on pollutant emissions in flames*. Combustion Science and Technology. 12/2004, No. 177(1), 183-220, doi:10.1080/00102200590883822.

[3] Ambrozin A. R. P., Kuri S. E.: *Corrosão Metálica Associada ao Uso de Combustíveis Minerais e Biocombustíveis*. Quim. Nova, Vol. 32, No. 7, 1910-1916, 2009.

[4] Ando N., et al.: *The Permeation Effect of Ethanol-containing Fuels on Fluoropolymers*. SAE paper 2007-01-2035, 2007, doi:10.4271/2007-01-2035.

[5] Bayraktar, H.: *Experimental and theoretical investigation of using gasoline–ethanol blends in spark-ignition engines*. Renewable Energy 30, 1733-1747, 2005, doi: 10.1016/j.renene.2005.01.006.

[6] Bergstrom K., Jones C.: *The New Ecotech Turbo Biopower Engine from GM Powertrain*. EAEC paper, 2009.

[7] Bielaczyc P., et al.: *The alternative fuels powertrain technology evolution*. Polish Society of Combustion Engines paper PTNSS–2009–SC–162, 2009.

[8] Bielaczyc P., Klimkiewicz D., Szczotka A., Woodburn J.: *A Comparison of the Exhaust Emission of a Vehicle Fuelled with Different Ethanol-Petrol Blends*. Combustion Engines, No. 2/2012, http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-LOD6-0031-0062.

[9] Bielaczyc P., Szczotka, A., Woodburn, J.: *The Effect of Various Petrol-ethanol Blends on Exhaust Emissions and Fuel Consumption of an Unmodified Light-Duty SI Vehicle*. SAE Technical Paper 2011-24-0177, 2011, doi:10.4271/2011-24-0177.

[10] Bielaczyc P., Szczotka, A., Woodburn, J.: *The Impact of Different Petrol-Ethanol Blends on the Exhaust Emissions from a Modern Light-Duty Petrol Engine*. EAEC 2011 Conference paper, in press.

[11] Bielaczyc P., Woodburn J.: *The usage of bioethanol in light-duty SI vehicles - a brief overview*. Combustion Engines, No. 3/2011, http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-LODC-0001-0052.

[12] Bielaczyc P.: *The Impact of Fuel Containing Ethyl Alcohol on the Operation of Automotive Spark Ignited Engines (Wpływ Zastosowania Paliw Zawierających Alkohol Etylowy na Wskaźniki Pracy Silników Samochodowych o Zapłonie Iskrowym)*. Wyd. Politechniki Poznańskiej, Poznań, 2015, in press.

[13] Biello D.: *Intoxicated on Independence: Is Domestically Produced Ethanol Worth the Cost?* Scientific America, 2011, online access [09. 02. 2015]: http://www.scientificamerican.com /article/ethanol-domestic-fuel-supply-or-environmental-boondoggle/

[14] Bonnema G., et al.: *Use of Mid-Range Ethanol/Gasoline Blends in Unmodified Passenger Cars and Light Duty Trucks*. Minnesota Center for Automotive Research Report, 1999.

[15] Brentebraten J.: *Ford Motor Company Experiences with FFV/E85 in Sweden and European developments*. New Zealand Biofuels Conference presentation, April 2008.

[16] Caretta G., et al.: *Challenges and Impacts of Gasoline and Diesel Biofuels on Injection and Engine Management Systems*.

[17] Clark W.: *Intermediate Ethanol Blends: Plans and Status, National Renewable Energy Laboratory presentation to the US Department of Energy*, 2008.

[18] Demirbas A.: *Emission Characteristics of Gasohol and Diesohol*. Energy Sources, Part A, 31:1099-1104, 2009.

[19] Dias de Oliveira M. E., et al.: *Ethanol as Fuel: Energy, Carbon Dioxide Balances, and Ecological Footprint*. Bioscience, Vol. 55, No. 7, 2005.

[20] Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009. Official Journal of the European Union, 05. 06. 2009, L140, 88-113.

[21] DuMont R. J., et al.: *Controlling Induction System Deposits in Flexible Fuel Vehicles Operating on E85*. SAE paper 2007-01-4071, 2007, doi:10.4271/2007-01-4071 .

[22] Durbin T. D., et al.: *Effects of Ethanol and Volatility Parameters on Exhaust Emissions*. CRC Project No. E-67, 2006.

[23] Ertekin A., Sridhar N.: *Performance of Elastomeric Materials in Gasoline - Ethanol Blends - A Review*. NACE 2009 Corrosion Conference and Expo, 2009.

[24] Eyidogan M., et al.: *Impact of alcohol–gasoline fuel blends on the performance and combustion characteristics of an SI engine*. Fuel, 89, 2010, p. 2713-2720, doi:10.1016/j.fuel.2010.01.032.

[25] Goldemburg J.: *Ethanol for a Sustainable Energy Future*. Science, 315, 2007, p. 808-810.

[26] Graham L. A., et al.: *Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85*. Atmospheric Environment, 42, 4498-4516, 2008, doi:10.1016/j.atmosenv.2008.01.061.

[27] Hochhauser A.M.: *Review of Prior Studies of Fuel Effects on Vehicle Emissions*. SAE paper 2009-01-1181, 2009, doi:10.4271/2009-01-1181.

[28] Intensive Field Trial of Ethanol/Petrol Blend in Vehicles, Energy Research & Development Corporation Project No. 2511, 1998.

[29] Karavalakis G., Short D., Russell R., Jung H., et. al.: *Assessing the Impacts of Ethanol and Isobutanol on Gaseous and Particulate Emissions from Flexible Fuel Vehicles*. Environmental Science & Technology 2014, 48, 14016–14024, DOI: 10.1021/es5034316.

[30] Knoll K., et al.: *Effects of Mid-Level Ethanol Blends on Conventional Vehicle Emissions*. SAE paper 2009-01-2723, 2009, doi:10.4271/2009-01-2723.

[31] Kohse-Hoinghaus K., et al.: *Biofuel Combustion Chemistry: From Ethanol to Biodiesel*. Angew. Chem. Int. Ed., 49, 3572-3597, 2010.

[32] Kousoulido M., et al.: *Effect of biodiesel and bioethanol on exhaust emissions*. European Topic Centre on Air and Climate Change Technical Paper 2008/5, 2008.

[33] Marinov N. M.: *A detailed chemical kinetic model for high temperature ethanol oxidation*. International Journal of Chemical Kinetics, No. 01/1999, Vol. 31(3), p. 183-220, doi:10.1002/ (SICI)1097-4601(1999)31:33.0.CO;2-X.

[34] Mid-Level Ethanol Blends Catalyst Durability Study Screening. Coordinating Research Council Report: E-87-1, June 2009.

[35] Naidenko O. V.: *Ethanol-Gasoline Fuel Blends May Cause Human Health Risks and Engine Issues*. Environmental Working Group Review, 2009.

[36] Naik P. N., Goud V. V., Rout P. K., Dalai A. K., et al.: *Production of first and second generation biofuels: A comprehensive review*. Renewable and Sustainable Energy Reviews, 2010. Vol. 14(2), p. 578–597, doi:10.1016/j.rser.2009.10.003

[37] Negurescu N., et al.: *Aspects of Using Ethanol in SI Engines*. Fisita paper F2006P294, 2006.

[38] Nigam P. P., Singh A.: *Production of liquid biofuels from renewable resources*. Progress in Energy and Combustion Science, 2011, Vol. 37, p. 52–68, doi:10.1016/j.pecs.2010.01.003.

[39] Niven R. K.: *Ethanol in gasoline: environmental impacts and sustainability review*. Renewable and Sustainable Energy Reviews, 9, 535-555, 2005, doi:10.1016/j.rser.2004.06.003.

[40] Osiak J., Golisz E., Wielewska I., Kupczyk A.: *Wybrane aspekty funkcjonowania sektora bioetanolu w Polsce*. Energetyka, No. 12, 2013.

[41] Parag S., et al.: *Emissions from ethanol blended fossil fuel flames*. Experimental Thermal and Fluid Science, in press.

[42] Partial Grant of Clean Air Act Waiver Application Submitted by Growth Energy to Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator, United States Environmental Protection Agency, 2011.

[43] Prakash C.: *Use of Higher than 10 volume percent Ethanol/Gasoline Blends in Gasoline Powered Vehicles*. Report submitted to Canada's Air Pollution Prevention Directorate, 1998.

[44] Renewable Fuels Association (ed.). Ethanol facts: Environment, Last updated March 2015, RFA. Online access [02. 09. 2015]: http://www.ethanolrfa.org/pages/ethanol-facts-environment.

[45] Review of fuel ethanol impacts on local air quality. Bioethanol for Sustainable Transport report No. D9.14, 2008.

[46] Roberts M. C.: *E85 and fuel efficiency: An empirical analysis of 2007 EPA test data*. Energy Policy, Vol. 36, Issue 3, p. 1233-1235, 2008, doi:10.1016/j.enpol.2007.11.006.

[47] Smokers R., Smit R.: *Compatibility of Pure and Blended Biofuels with Respect to Engine Performance, Durability and Emissions – A Literature Review*. GAVE Report 2GAVE04.01, 2004.

[48] Strong R. M.: *Commercial deductions from comparisons of gasoline and alcohol tests on internal combustion engine*. United States Geological Survey Bulletin, Vol. 392, 1909, Online access [02. 09. 2015]: http://pu bp.usgp.gov/bul/0392/report.pdf

[49] Technical Assessment of the Feasibility of Introducing E15 Blended Fuel in U.S. Vehicle Fleet, 1994 to 2000 Model Years. Ricardo project FE405, 2010.

[50] Turner D., et al.: *Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine*. Fuel, article in press, 2011.

[51] Turner J. W. G., et al.: *Alcohol-Based Fuels in High Performance Engines*. SAE paper 2007-01-0056, 2007, doi:10.4271/2007-01-0056.

[52] U.S. Energy Information Administration (ed.), Annual Energy Outlook 2012 with Projections to 2035. EIA, June, 2012, Access on-line [09. 09. 2015]: http://www.eia.gov/forecasts/aeo/pdf/0383(2012).pdf.

[53] U.S. Energy Information Administration (ed.), Annual Energy Outlook 2013 with Projections to 2040. EIA, April, 2013, Access on-line [09. 09. 2015]: http://www.eia.gov/forecasts/aeo/pdf/0383(2013).pdf.

[54] Vancoillie J., Verhelst S.: *Modeling the Combustion of Light Alcohols in SI Engines: a Preliminary Study*. Fisita paper F2010-SC-O-04, 2010.

[55] Vierhout R. (ed.): *Renewable ethanol: driving jobs, growth and innovation throughout Europe*. State of the Industry Report, ePure European Renewable Ethanol Association, 2014.

[56] Vilardo J. S., et al.: *A Comprehensive Examination of the Effect of Ethanol-Blended Gasoline on Intake Valve Deposits in Spark-Ignited Engines*. SAE paper 2007-01-3995, 2007, doi:10.4271/2007-01-3995.

[57] Wallner T., et al.: *Impact of ethanol and butanol as oxygenates on SIDI engine efficiency and emissions using steady-state and transient test procedures*. 16th DEER Conference, Detroit, USA, September 27-30, 2010.

[58] West B. H., et al.: *Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 Biopower*. SAE paper 2007-01-3994, 2007, doi:10.4271/2007-01-3994.

[59] West B., et al.: *Mid-Level Ethanol Blends Test Program. US Department of Energy Presentation to 2010 U.S.* DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, 2010.

[60] www.fueleconomy.gov, US EPA and Department of Energy website, 2010.

[61] Yuksel F., Yuksel B.: *The use of ethanol–gasoline blend as a fuel in an SI engine*. Renewable Energy 29, p. 1181–1191, 2004, doi:10.1016/j.renene.2003.11.012.

[62] Yusaf T., et al.: *Theoretical and experimental investigation of SI engine performance and exhaust emissions using ethanol-gasoline blended fuels*. 3rd International Conference on Energy and Environment (ICEE2009), 7-8 December 2009, Malacca, Malaysia.

Environmental impacts connected with the use of ethanol-gasoline blends

Oddziaływania na środowisko związane ze stosowaniem mieszanek etanol-benzyna

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Abstract

As a summary of work in the project "Influence of bioethanol fuels treatment for operational performance, ecological properties and GHG emissions of spark ignition engines (Biotreth)", evolving around the effects from bioethanol blending, this paper summarizes the findings from the 3-year long project. These are 1) attributional life cycle assessment (LCA) of the environmental impact connected with the blended fuels, and 2) molecular dynamics simulations of exhaust from the blended fuels.

Bioethanol has been increasingly applied as a renewable energy component in combination with gasoline for the reduction of emissions and to reduce the release of climate gases into the atmosphere. Here the environmental and health impacts resulting from introducing bioethanol blended into fossil fuels are assessed. This bio-blended fuel is an alternative to fossil fuels, and their multivariate results are presented with the potential environmental impacts of the production (well-to-tank) of certain multifunctional detergent additive packages (MDAPs) combined with different ethanol-gasoline blends. Moreover the effect of feedstock for ethanol in Switzerland and Poland on end-

-point modelling results is explored. The resulting combustion products, as a result of adding these new MDAP to the ethanol-gasoline blends, are measured and added to the well-to-wheel LCA focused on GWP100, Cumulative Energy Demand and Eco-indicator'99. MDAP production eco-environmental impacts are estimated based on their chemical structure.

To assess the potentials for new types of emission compounds we have used molecular dynamics simulations. The combination of bioethanol and gasoline introduces two leading toxic components in the urban atmosphere as potentially toxic mixtures: acetaldehyde and poly aromatic hydrocarbons (PAHs) were established. The PAHs are found in combusted gasoline and are virtually absent in emissions of bioethanol. Bioethanol however, contributes with acetaldehyde, which is a potential carcinogen. In this study, we have studied the dynamics of particle formation between acetaldehyde and phenanthrene, which is a PAH found at high concentrations in generic fossil fuel emissions. Our analysis resolves the interaction of these two main emission toxic components at the molecular level in virtual chambers of 300 to 700K, under standard atmospheric conditions and under high pressure and temperature from the engine and exhaust pipe and also reveals their interaction with environmental humidity, modelled as single-point charged water molecules. The results show so far that PAHs and phenanthrene can combine in the water phase and form aqueous nanoparticles, which can be easily absorbed in the lungs through respiration. Water droplets in moisture become potential carriers of PAHs to the exposed subjects by forming non-covalent bonds with acetaldehyde, which in turn binds phenanthrene via its hydrophobic group.

Introduction

Blending of biofuels into fossil fuels is a much-used strategy for phasing in renewable energy in the transport sector. This is mainly motivated by the goal of reducing greenhouse gas emissions (GHGs), thus mitigating climate change. However, the efficiency of this strategy in terms of its effect on reducing the emission of GHGs is not clear-cut, and this form of renewable energy implementation has unintended consequences [1].

The life-cycle carbon dioxide emissions and other environmental and health impacts resulting from introducing biofuels have been studied via numerous attributional and consequential life cycle assessments (LCAs) [14, 7]. Especially climate change and land use have gotten much attention, whereas other eco-environmental impacts including the health consequences from emissions are less understood. Ethanol-gasoline blends, compared to gasoline, are well analysed in this context, but again, the potential for the emission of new toxic compounds have not been assessed, such as has been the case for biodiesel blended into fossil diesel [2].

Problems for assessing the environmental impact mentioned in existing literature are that different upstream feedstock (e.g. corn grain or lingocellulosic) for ethanol manufacturing implies different relative contribution to the climate change environmental impact category. Additionally, the share of process chemicals and enzymes of the total ethanol production eco-environmental impact vary (3-30%), depending on the ethanol. Moreover, previous research claim that more acetaldehyde and ethanol emissions result from the combustion of ethanol-gasoline blends than from gasoline.

Another loophole is that the overall environmental effects of multifunctional detergent additive packages (MDAP) used in bioethanol gasoline blends are not well assessed. These MDAPs are developed in the project "Influence of bioethanol fuels treatment for operational performance, ecological properties and GHG emissions of spark ignition engine (Biotreth)".

Compared to the state-of-the-art, the new MDAP compounds must improve the combustion and reduce harmful engine emissions as well the overall well-to-wheel eco-environmental impacts. To do this, an integrated platform is used, where research and development of additives provide primary data to the LCA.

Exhaust emissions from automotive fuel combustion represents one of the major public health-threats of modern times and is the major cause of world-wide incidents of cardiac problems, pulmonary complications, stroke, allergies, asthma and cancer [9, 5].

Bio-blended fuels contain a fossil fuel fraction (e.g. gasoline, diesel), which is mixed with a biofuel fraction (e.g. ethanol, biodiesel) at various ratios (e.g. B10, E5, E85), see [8].

Molecular dynamics simulations (MDS) have been used to model and predict the particle-formation properties in exhaust emissions [2, 11, 13]. MDS give results on the distribution of molecules in nanoparticles and applies chemical parameters of high accuracy. In this project, we have studied the chemical properties of nanoparticles formed by acetaldehyde emissions (from ethanol) and the PAH phenanthrene (from gasoline) in the exhaust of bio-blended gasoline.

A review of emission products from bioethanol and its blends with gasoline has been conducted to provide a background for new guidelines for emission control [12]. The review also included the effects from additives on the pollution profile, and a thorough chemical analysis of the environmental and transformation of the given compounds. It was showed that the main issue of importance for toxicity and pollution profiling for bioethanol is connected to acetaldehyde emissions, and that acetaldehyde generated in bioethanol-gasoline blends can remain in circulation in confined areas of up to a week, before being fully oxidized and transformed into innocuous organic forms.

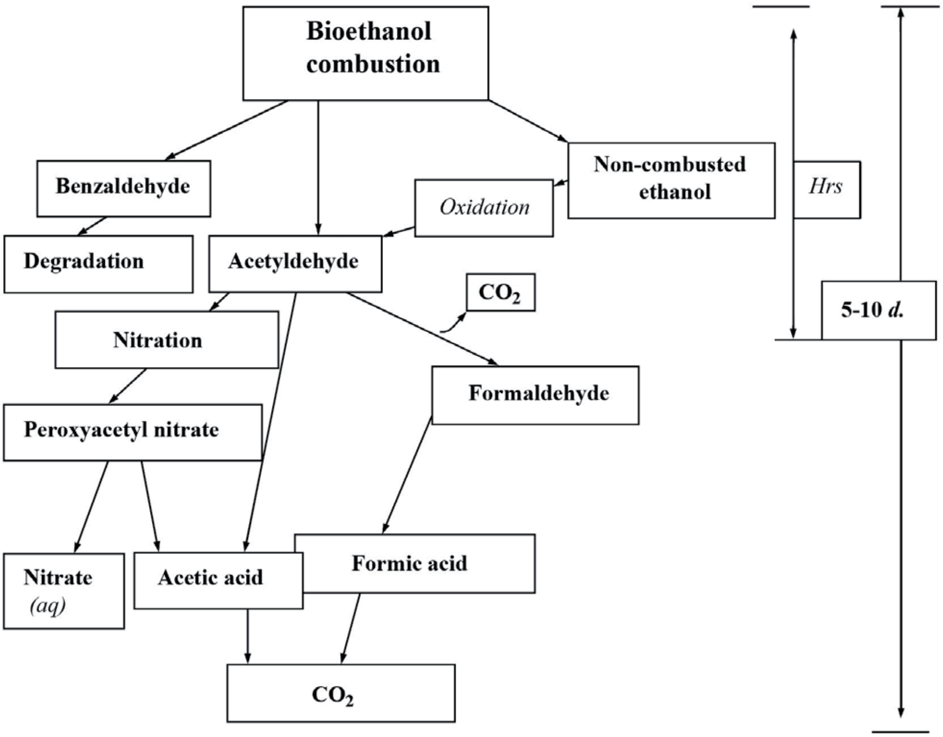

Figure 1. Degradation chart for bioethanol-blends, excluding HC, CO, NO_x, nanoparticles and polycyclic aromatic compounds from gasoline, and additive-derivatives. From top to bottom, chemical conversion path through atmospheric oxidation of acetaldehyde and its successors [10] and benzaldehyde [6]. Parts of the reactions derive from the work by Sauer & Ollis [16]. Right bars: Time periods (estimated from reviewed literature [17, 10, 6, 16,12]

The review also showed that there are only a few studies performed about the effects of acetaldehydes on animals, and that more toxicity assessments of acetaldehyde are required. The contribution of additives was also classified into types and products of the combustion process and showed that amine-based additives deserve particular attention in toxicological profiling of bioethanol blends with gasoline, as these have a higher probability of forming health-hazardous products during combustion. The cycle and production of adverse health- products is shown in Figure 2 of the respective study.

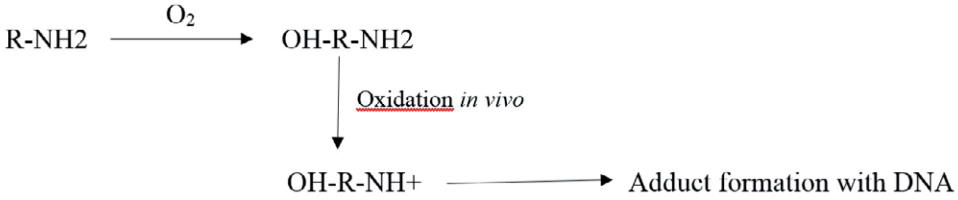

Figure 2. Reaction-path of aliphatic amines and polyether-amines from environmental release to cell intoxication. R: poly-butene, polyether chain. The functional NH2 depicts the key group with genotoxic properties, based on their triggering of liver oxidase and formation of the nitrenium form (NH+) which readily forms adducts with the DNA [12]

Methods

To predict the life cycle environmental impact of organic compounds that are MDAP constituents and for which no LCI data are available, the method of Wernet et al. [19, 20] is used.

Due to the fact that the development of the MDAPs in the Biotreth project has been occurring in Switzerland and Poland, literature analyses were used to find the most appropriate feedstock for ethanol for these two countries. The SimaPro 8 LCA software tool, with its Eco-invent commercial life cycle inventory database, as well as the Argonne National Laboratory GREET model, were used for the LCA data. Sensitivity and uncertainty analyses included comparison of ethanol types in the Eco-invent database.

Two main MDAPs were developed in Biotreth. The first, called NOR 15, containing a detergent-dispersant DEM1 of N-alkylated benzoxazine derivative structure, possessing a hydrogenated heterocyclic ring and an aromatic ring substituted by an alkyl and a synthetic carrier oil of oxy-alkylated alkyl phenol structure and an aromatic solvent.

The other main MDAP, the NOR20, contains a detergent-dispersant DEM2 of a diamine structure, a derivative of alkyl phenol possessing secondary and tertiary amines and a synthetic carrier oil of oxy-alkylated alkyl phenol structure, and an aromatic solvent. In both NOR15 and NOR20, detergent-dispersant additives are used at a concentration of 600 mg/kg.

The molecular dynamics simulations were conducted as described in [12].

Results

The novelty of this work is in the use of the end-point weighting method to express environmental impact, which provided some interesting results. But, as a vast amount of studies have been published about biofuels and bioethanol impacts, this is not obvious. Figures 3-5 show the main finding about MDAPs and feedstocks.

MDAP packages contribute between 0.07-1.17% of total ethanol production (well-to-tank) impacts (Figure 3).

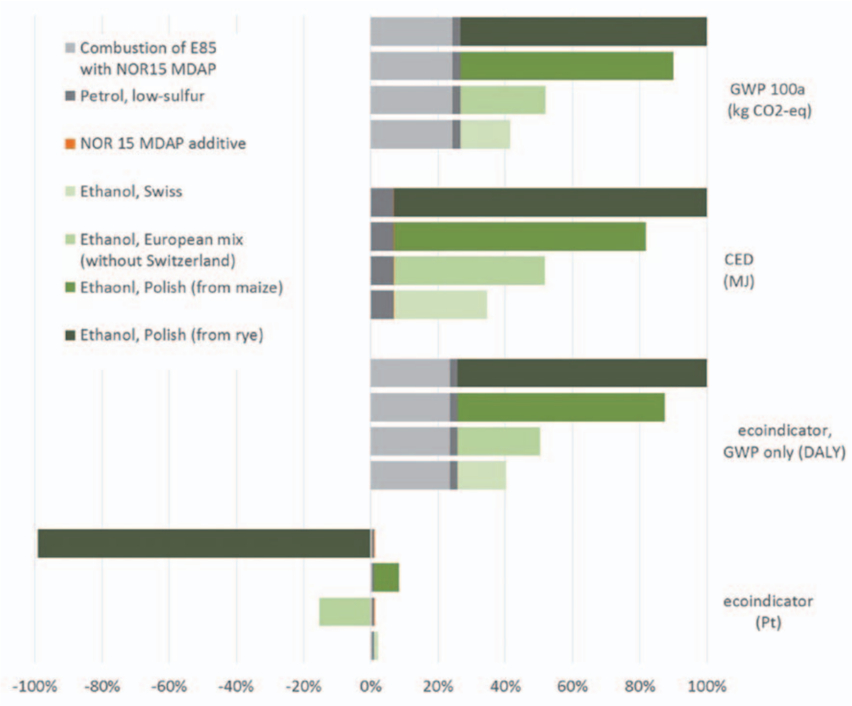

Figure 3. The impact categories GWP 100a, CED, and ecoindicator for E85, with NOR15, petrol, NOR15 alone, ethanol (Swiss and Polish), normalized against the maximum result

With adapted Polish bioethanol from rye, their contributions are less than 1% of total well-to-wheel emissions (Figure 3).

In the case of the environmental impact of MDAPs it should be stated that, the solvent component contributes the most, with the carrier oil and the active compound contributing somewhat less (Figure 4).

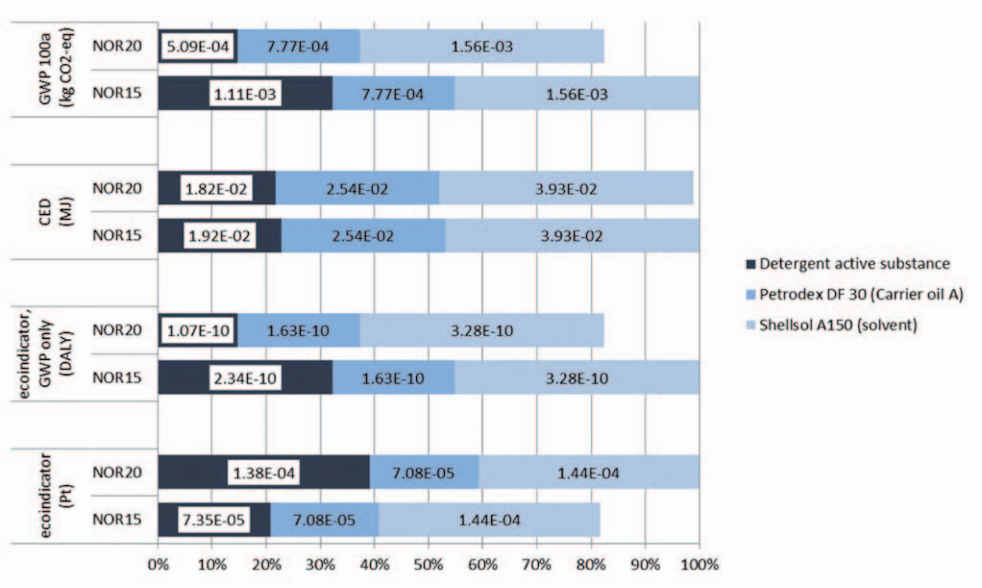

Figure 4. The relative contribution to environmental impacts by the content of the MDAPs

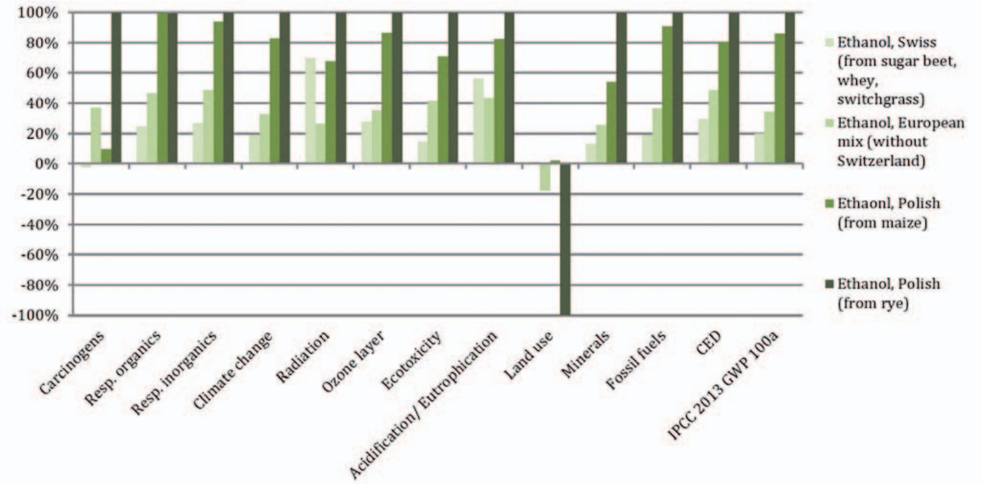

Figure 5. Environmental impacts from the various types of ethanol (well-to-tank), taking into account the feedstocks

There is a large span in impact ranges for different ethanol types based on feedstock (Figure 5). Negative values, specifically for land use, result from only one of the land use changes and are accounted for in the eco-indicator impact method, thus a "one-sided" land use impact.

Visual analysis of the triple gas-phase simulations with a higher ratio of phenanthrene to acetaldehyde show that the formed nanoparticles engulf and trap acetaldehyde molecules inside their clusters shapes at a higher rate, when fossil fuel emitted PAH content is higher in the blend (Figure 6).

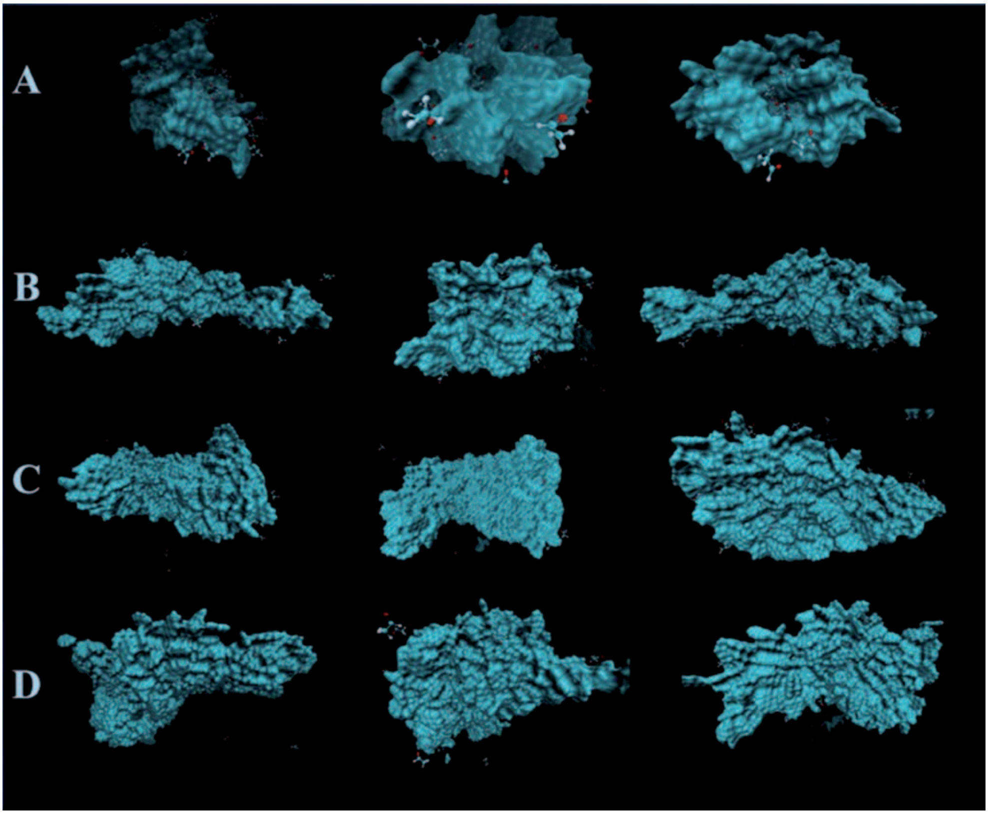

Figure 6. A-row: Formed nanoparticles from three separate simulations of 50% acetaldehyde (ACD) molecules and 50% phenanthrene (PHN) molecules. B-row: 33% ACD molecules and 67% PHN molecules. C-row: 20% ACD, 80% PHN. D-row: 13% ACD, 87% PHN. Triple simulations provide higher probability and show repetitive patterns of clustering acetaldehyde inside phenanthrene nanoparticles [11]

The radial distribution function (Figure 7) is in agreement with Figure 6 and shows that the formed nanoparticles of equal ratio contain more phenanthrene in the core and more acetaldehyde on the surface of the formed nanoparticles.

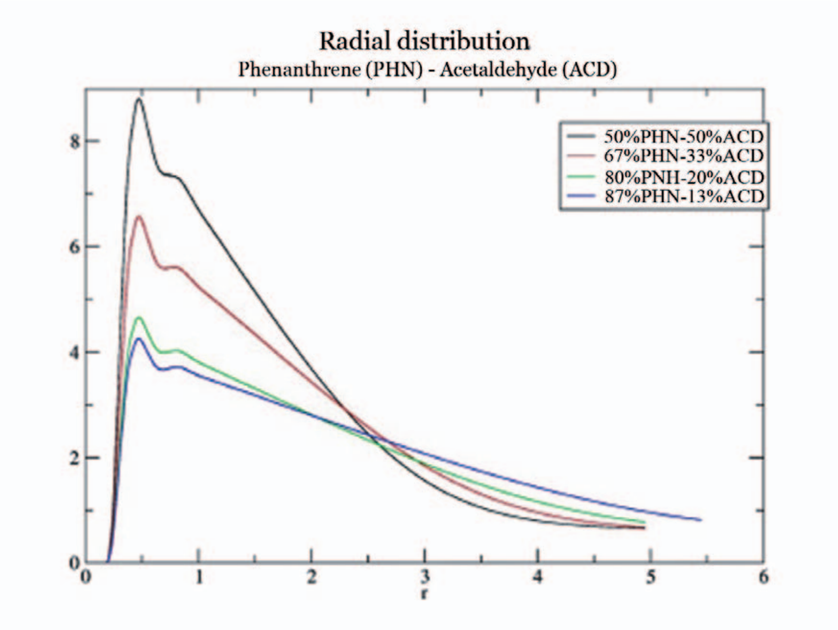

Figure 7. Radial distribution function. The plot shows the relative positions of the two molecules in respect to the nanoparticle radius (x-axis). The black plot shows that the probability of finding PHN at the core (low x-axis value) is high (y-axis), when the mixture is 50% PHN and 50% ACD. When this ratio changes and PHN increases in concentration, the probability of finding it at the core of the nanoparticles is reduced (lower y-axis value) as the ACD molecules are increasingly entrapped in the particle and compete with PHN on the probability value of being localized at the core of the nanoparticles [11]

When phenanthrene levels increase, acetaldehyde accesses the core of the particles more frequently, which yields absorption of acetaldehyde by phenanthrene. This shows that higher fossil fuel-deriving PAHs in the emissions from combustion of bio-blends provide a chemistry that forms nanoparticles, which capture acetaldehyde and encapsulates it in the formed nanoparticles. Acetaldehyde is a suspected carcinogen, and the results of this gas-phase study show that PAHs can preserve and carry acetaldehyde inside their agglomerates through its "sticky" chemistry. This sticky chemistry of PAHs from the fossil fuel component of the blend, can therefore introduce an additional health-hazard: the encapsulation and preservation of genotoxic compounds from the ethanol component in ultra small nanoparticles and their delivery to the pulmonary system.

Effects from atmospheric gases

The resolved nanoparticles have been studied also for interaction with atmospheric gases at nanometer resolution by adding a proportional quantity of nitrogen, oxygen and carbon dioxide to the simulated systems from Figure 6 and Figure 7. The proportions reflect the atmospheric concentrations of N_2, O_2 plus 20% of CO_2, reflecting the exhaust pipe environment. The effects presented in Figure 8 show that the nanoparticles remain stable in shape and size, absorb acetaldehyde as well as atmospheric gases.

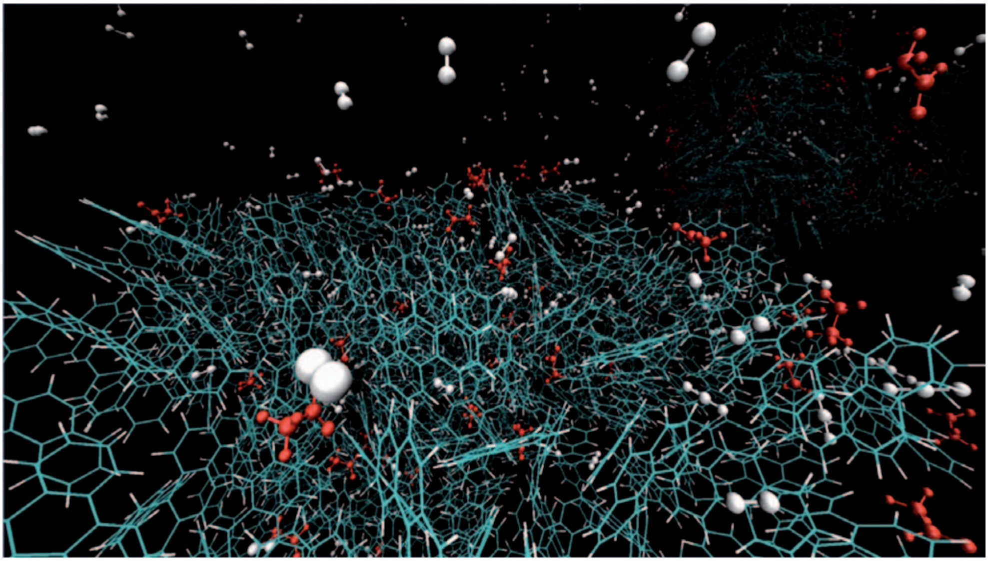

Figure 8. The surface of a formed nanoparticle from the interaction of ACD and PHN (width, 1nm), under chemospheric influence. Red: Acetaldehyde; Blue: Phenanthrene; White: N_2, O_2 and CO_2. The internal parts of the nanoparticle show acetaldehyde and chemospheric molecules encapsulated [11]

Nanocluster properties under atmospheric influence

The stability and size of the particles were assessed in single simulations of 10 nanoseconds each. This was carried out to determine the patterns of chemical stability of the formed nanoparticles towards CO_2, O_2 and N_2. The analysis was carried out by calculating the average radius and count of the nanoparticles. Four systems were assessed for interaction with atmospheric gases: 50/50, 67/33, 80/20 and 87/13% phenanthrene and acetaldehyde.

Conclusions

The new MDAPs have a negligible effect on the well-to-tank and tank-to-wheel emissions both regarding type and amount. On the other hand, the source of ethanol is hugely important for overall well-to-wheel studies.

Blending of bioethanol and gasoline has not been studied from a toxicological perspective earlier, and this study shows that it can contribute to increased toxicity in urban atmospheres. It has been shown that there is a likelihood of nanoparticles formed by polyaromatic hydrocarbons and acetaldehyde, providing toxic properties of concern. The study shows also that the interaction of the formed nanoparticles with the atmosphere reduces their surface tension, and makes them more hydrophilic. The feature has implications for chemical interaction with water droplets in the air, and shows that particle growth catalyzed by CO_2 absorption also gives a higher transfer potential to individuals exposed, via water and moist in the air.

The results also imply that the nanoparticles may more rapidly be transferred to the water phase during rain and heavy waterfall by sorption to water particles. However, the growth of the nanoparticles catalyzed by the chemical and the physical properties of the CO_2 molecule, allow study of nanoparticle formation under different cetane conditions. A new topic for study is the selective measurement of particle size in bioethanol-gasoline combustion at various CO_2 levels. This can be important for the research of nanoparticle generation in the combustion process of bioethanol and gasoline blends.

Outlook

Weighting methods in LCA, such as Eco-indicator'99, should be enhanced with added damage factors derived from present toxicity simulations and transport modeling [18]. Market based LCA should also be attempted for the 1st tier markets in the functional unit [3]. This means that the change of actual or predicted sales of some of the upstream products or materials, are included in a sensitivity analysis. In the present research, these sales could be for the different feedstocks (e.g. maize and rye) for the bioethanol, and for the different fuels (gasoline, bioethanol).

Acknowledgement

The work reported here is resulting from the project "Influence of bioethanol fuels treatment on the operational performance, ecological properties and GHG emissions of spark ignition engines (Biotreth). The project was financed by the European Economic Area (EEA) Grants / Norway Grant, contract no. Pol-Nor/199100/6/2013.

List of Abbreviations

GHG	Greenhouse gas
Biotreth	Influence of bioethanol fuels treatment for operational performance, ecological properties and GHG emissions of spark ignition engines
LCA	Life cycle assessment
MDS	Molecular dynamics simulations
MDAP	Multifunctional detergent additive package
GWP100	Global warming potential in a 100 year perspective
CED	Cumulative energy demand
PAH	Polycyclic aromatic hydrocarbon
LCI	Life cycle inventory
ACD	Acetaldehyde
PHN	Phenanthrene

References

[1] Andersen O.: (2013a). *Unintended Consequences of Renewable Energy. Problems to be Solved*. Springer London, London.

[2] Andersen O.: (2013b). *Biodiesel and its Blending into Fossil Diesel. In: Unintended Consequences of Renewable Energy*. Problems to be Solved. Springer London, London, pp. 55–70.

[3] Andrae A. S.: (2015). *Method based on market changes for improvement of comparative attributional life cycle assessments*. The International Journal of Life Cycle Assessment, 20(2), 263-275.

[4] Argonne National Laboratory, GREET model, http://greet.es.anl.gov/

[5] Brook R. D., Rajagopalan S., Pope C. A.: (2010) *Particulate matter air pollution and cardiovascular disease: an update to the scientific statement from the American Hearth Association*. Circulation, 121: 2331–2378.

[6] Costagliola M. A., De Simio L., Iannaccone S., Prati M. V.: (2013) *Combustion efficiency and engine out emissions of a S.I. engine fueled with alcohol/gasoline blends*. Appl Energy 111:1162–71.

[7] Daystar J., Treasure T., Reeb C., Venditti R., Gonzalez R., Kelley S.: (2015) *Environmental impacts of bioethanol using the NREL biochemical conversion route: multivariate analysis and single score results*. Biofuels, Bioproducts and Biorefining.

[8] Hammond G. P., Kallu S., McManus M. C.: (2008). *Development of biofuels for the UK automotive market*. Applied Energy, 85:506–515.

[9] Hong Y. C., Lee J. T., Kim H., Kwon H. J.: (2002). *Air pollution: a new risk factor in ischemic stroke mortality*. Stroke, 33:2165–2169.

[10] López-Aparicio S., Hak C.: (2013). *Evaluation of the use of bioethanol fuelled buses based on ambient air pollution screening and on-road measurements*. SciTotal Environ, 452:40–9.

[11] Manzetti S., Andersen O.: (2015a). *A molecular dynamics analysis of the nanoparticle-forming dynamics of acetaldehyde and phenanthrene from bioethanol fuel combustion. Implications for lung toxicity from bioethanol fuel blends*. Submitted.

[12] Manzetti S., Andersen O. (2015b). *A review of emission products from bioethanol and its blends with gasoline. Background for new guidelines for emission control*. Fuel 140:293–301.

[13] Manzetti S., Andersen O., Czerwinski J.: (2011). *Biodiesel, Fossil Diesel and their Blends: Chemical and Toxicological Properties*. In: Biodiesel: Blends, Properties and Applications. Nova Publishers, pp. 41–68.

[14] Martin E. W., Chester M. V., Vergara S. E.: (2015). *Attributional and Consequential Life-cycle Assessment in Biofuels: a Review of Recent Literature in the Context of System Boundaries*. Current Sustainable/Renewable Energy Reports, 2(3), pp. 82–89.

[15] Pronk S., Páll S., Schulz R., Larsson P., Bjelkmar P., Apostolov R., et al.: (2013). *GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit*. Bioinformatics, 29:845–854.

[16] Sauer M. L., Ollis D. F.: (1996). *Photocatalyzed oxidation of ethanol and acetaldehyde in humidified air*. J Catal, 158:570–82.

[17] Seinfeld J. H., Pandis SN (2012). *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons.

[18] Tang L., Nagashima T., Hasegawa K., Ohara T., Sudo K., Itsubo N.: (2015). *Development of human health damage factors for PM2.5 based on a global chemical transport model*. The International Journal of Life Cycle Assessment, pp. 1–11.

[19] Wernet G., Hellweg S., Fischer U., Papadokonstantakis S., Hungerbühler K.: (2008). *Molecular-structure-based models of chemical inventories using neural networks*. Environmental science & technology, 42(17), pp. 6717–6722.

[20] Wernet G., Papadokonstantakis S., Hellweg S., Hungerbühler K.: (2009). *Bridging data gaps in environmental assessments: Modelling impacts of fine and basic chemical production*. Green Chemistry, 11(11), pp. 1826–1831.

Zagrożenia eksploatacyjne stwarzane przez paliwa etanolowe dla silników o zapłonie iskrowym

Operational threats for positive ignition engines caused by ethanol fuels

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Abstract

Ethanol blends can present a plethora of technical challenges to positive ignition engine operation because ethanol differs from petroleum in some key properties.This leads to operational threats for positive ignition engines that are as various as they are complex what describes this paper. Extensive experimental investigation by using simulate dynamometer engine testing has been carried out to study the solubility of various additive compositions in E85 fuels and detergent effects on deposits formation in a FlexFuel engine running in special devised in-house test method. As a result two high effective multifunctional fuel additive packages properly formulated for use in high ethanol-gasoline blends were developed and optimized. Simultaneously, the great importance of modern deposit control additives specially formulated to be compatible with high ethanol fuels for providing control and counteracting deposit formation has been proved.

Keywords: High-ethanol fuels, additives, deposits, spark ignition engines

Streszczenie

Mieszanki etanolowe mogą stwarzać liczne problemy techniczne, a zarazem wyzwania podczas eksploatacji tego rodzaju paliw w silnikach ZI, ze względu na różnice właściwości etanolu i benzyny. Prowadzi to do opisanych w artykule różnych złożonych zagrożeń eksploatacyjnych dla silników. W celu zbadania rozpuszczalności różnych kompozycji dodatków w paliwie E85 i oceny wpływu poszczególnych detergentów na formowanie osadów na elementach silnika Flex-Fuel wykonano szerokie badania doświadczalne przy wykorzystaniu symulowanych testów silnikowych prowadzonych według specjalnie przygotowanej własnej metody badawczej. W rezultacie opracowano i zoptymalizowano dwa wysokoefektywne, wielofunkcyjne pakiety dodatków uszlachetniających przeznaczone do stosowania w paliwach wysokoetanolowych. Równocześnie wykazano ogromne znaczenie specjalnie opracowanych nowoczesnych dodatków detergentowych kompatybilnych z paliwami o wysokiej zawartości etanolu w kontroli i przeciwdziałaniu tworzeniu się osadów w silniku.

Słowa kluczowe: paliwa wysokoetanolowe, dodatki uszlachetniające, osady, silniki z zapłonem iskrowym

Wstęp

Biopaliwo E85 jest na rynku europejskim w dalszym ciągu nowym, mało rozpowszechnionym gatunkiem paliwa i wymaga dalszego rozwoju poprzez prowadzenie prac badawczych. Ze względu na konieczność dywersyfikacji paliw wobec zmniejszających się zasobów ropy naftowej, przy równoczesnym wzroście zapotrzebowania na paliwa i coraz ostrzejszych wymaganiach w zakresie ograniczenia emisji CO_2, paliwa alternatywne nabierają coraz większego znaczenia. Zasadniczym kryterium decydującym o możliwości stosowania paliwa jako alternatywnego dla obecnie używanych pojazdów są jego właściwości proekologiczne, a takimi charakteryzują się paliwa etanolowe [1, 2, 3]. Jednak uzyskanie wymaganych właściwości użytkowo-eksploatacyjnych mieszanek etanolu z benzyną i pełne wykorzystanie ich walorów jako paliwa proekologicznego stanowią trudne wyzwanie i wiążą się z pokonaniem wielu problemów, zwłaszcza w zakresie opracowania składu i sposobu uszlachetniania takich paliw. Wynika to w szczególności ze znacznych różnic właściwości fizykochemicznych etanolu i benzyny (tabela 1). W rezultacie także właściwości fizykochemiczne paliw silnikowych zawierających w swym składzie znaczny udział etanolu różnią się istotnie od tych, jakimi charakteryzują się tradycyjne benzyny, a różnice narastają wraz ze zwiększającą się zawartością etanolu. Do najważniejszych cech należy zaliczyć obniżanie się wartości opałowej biopaliwa wraz z rosnącym udziałem etanolu, przy równoczesnym wzroście liczb oktanowych (LOB i LOM). Wynika to z tego, że w samym etanolu jest około 30–35% (*m/m*) tlenu, w związku z czym ma on wartość opałową o ponad 30% mniejszą niż benzyna. Szybko wzrastające ciepło odparowania biopaliwa w miarę podwyższania zawartości etanolu (który charakteryzuje się ciepłem parowania około 280% większym niż benzyna) powoduje o około 250% wydajniejsze chłodzenie ładunku mieszanki paliwowo-powietrznej w silniku i związane z tym konsekwencje. Ponadto przy niskich zawartościach etanol powoduje nieaddytywny wzrost prężności par paliwa, a przy wysokich zawartościach – jej obniżanie [1, 2]. Etanol to dobry rozpuszczalnik, często też jest niekompatybilny z różnymi materiałami konstrukcyjnymi, a jego wysoka higroskopijność sprawia, że łatwo pochłania wodę.

Tabela 1. Najważniejsze różnice pomiędzy benzyną silnikową a etanolem

Właściwość	Benzyna zgodna z PN-EN 228	Etanol
Gęstość [kg/m^3]	720–775	794
Wartość opałowa [MJ/kg]	42,3–43,5	26,8
Temperatura wrzenia [°C]	20–220	77,8
LOB	95 min.	120–135
LOM	85 min.	100–106
Temperatura zapłonu [°C]	– 42	12,8
Ciepło odparowania [kJ/kg]	350	855–870

Powyższe zmiany właściwości fizykochemicznych paliw zawierających etanol mają istotny wpływ na ich właściwości użytkowo-eksploatacyjne, tym większy, im. większy jest udział etanolu w paliwie (tabela 2).

Tabela 2. Wpływ właściwości fizykochemicznych etanolu na właściwości użytkowo-eksploatacyjne mieszanek benzyny z etanolem

Właściwości fizykochemiczne mieszanek etanol–benzyna		Właściwości użytkowo-eksploatacyjne mieszanek etanol–benzyna
Wpływ korzystny		
Wzrost liczb oktanowych (LOB, LOM)	→	Możliwość stosowania wyższych stopni sprężania, większych kątów wyprzedzenia zapłonu oraz wyższego ciśnienia doładowania, co zwiększa moc użyteczną
Wyższe ciepło parowania		Większy stopień napełnienia cylindrów, podwyższenie stopnia sprężania
Wpływ niekorzystny		
Mniejsza wartość opałowa	→	Zwiększenie zużycia paliwa dla zachowania porównywalnej mocy użytecznej
Wyższe ciepło parowania		Większy gradient temperatury w głowicy, który nakłada się na inne naprężenia wynikające z obciążenia mechanicznego, podwyższonego ciśnienia spalania, i resztkowe naprężenia cieplne, co może prowadzić do pęknięć powstających w najbardziej obciążonych strefach głowicy silnika
Nieaddytywny przyrost prężności par		Wyższa prężność par paliwa i obniżona temperatura końca jego parowania sprzyjają powstawaniu korków parowych w układzie zasilania, a tym samym trudnościom rozruchu silnika i niestabilności jego pracy, zwłaszcza na biegu jałowym
Obniżanie prężności par w przypadku wysokiej zawartości etanolu		Problemy z rozruchem zimnego silnika w niskiej temperaturze otoczenia
Pogarszanie właściwości smarnych na skutek obniżania się ilości tworzonej sadzy podczas spalania		Osiadanie gniazd zaworowych

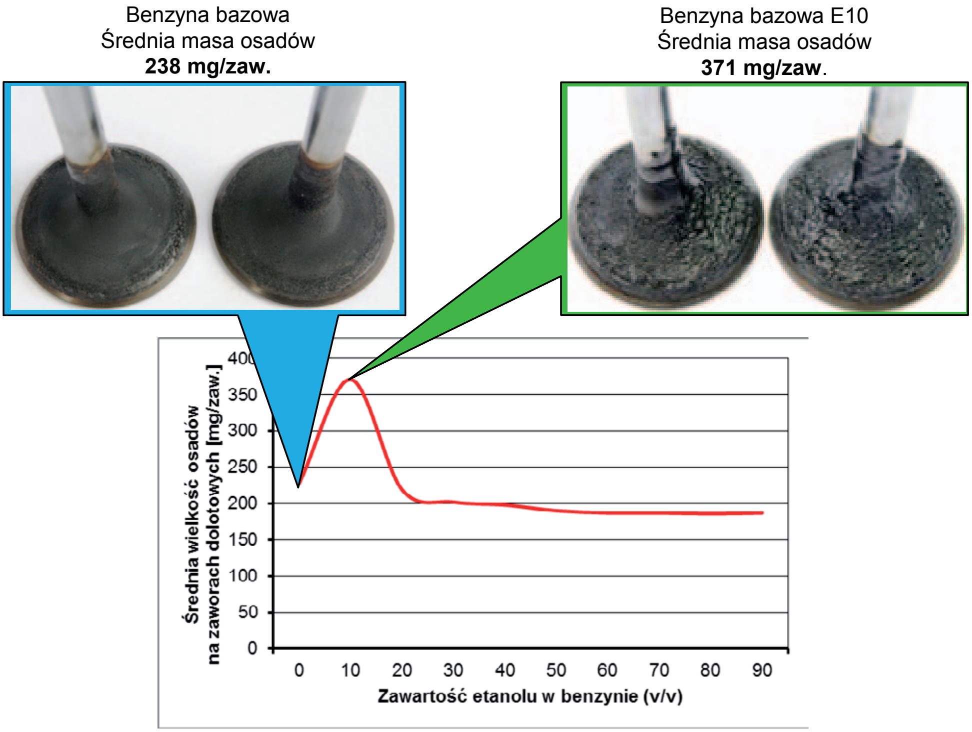
Właściwości fizykochemiczne mieszanek etanol–benzyna		Właściwości użytkowo-eksploatacyjne mieszanek etanol–benzyna
Intensyfikacja działania jako rozpuszczalnik	→	Wymywanie osadów z elementów oraz części składowych układu paliwowego i przenoszenie ich do filtrów i podzespołów układów wtrysku paliwa. Pogorszenie warunków smarowania poprzez wypłukiwanie i zmywanie oleju z powierzchni smarowanych silnika, w tym złożenia tłok–cylinder
Podwyższona higroskopijność paliwa i zawartość siarczanów		Zatykanie filtrów paliwowych i zalewanie odstojników. Po osiągnięciu zawartości około 5% (V/V) wody w paliwie następuje jego rozwarstwienie, a woda wraz z etanolem, jako oddzielna faza, osiada na dnie zbiornika paliwa, powodując zaburzenia procesów spalania lub unieruchomienie silnika. Intensyfikacja procesów korozyjnych
Możliwa niekompatybilność z niektórymi materiałami konstrukcyjnymi		Możliwość uszkodzenia uszczelnień, elementów układów paliwowych, jak: zbiorniki paliwa, przewody paliwowe, elementów wtryskiwaczy i pomp paliwa itp.

Zagrożenia stwarzane przez paliwa etanolowe dla silnika

Zawarty w paliwie etanol, niezależnie od jego poziomu, może stwarzać zagrożenia dla poprawnej pracy silnika, a także wpływać na pogorszenie jego osiągów w miarę przebiegu eksploatacji. Zagrożenia te występują zarówno w przypadku eksploatacji konwencjonalnych silników na benzynie zawierającej, zgodnie z normą PN-EN 228:2013, do 10% (*V/V*) etanolu, jak i w przypadku silników przystosowanych do zasilania paliwami wysokoetanolowymi (zazwyczaj do 85% (*V/V*) etanolu) w pojazdach typu *Flex-Fuel Vehicles* (FFV). Do najważniejszych zagrożeń należy zaliczyć tworzące się w silniku osady, a w szczególności te na zaworach dolotowych w komorach spalania, lecz również te na i we wtryskiwaczach oraz w przewodach i kanałach dolotowych silnika. Osady te powodują zaburzenia procesów ilościowego i jakościowego tworzenia mieszanki palnej w cylindrach silnika oraz spalania, co prowadzi do pogarszania osiągów i właściwości użytkowo-eksploatacyjnych silnika, a także do zwiększenia zużycia paliwa i emisji składników szkodliwych w gazach spalinowych [1–7].

Osady na zaworach dolotowych

Standardowe dodatki detergentowe stosowane do benzyn silnikowych najczęściej oparte są na poliizobutylenie (PIB) lub aminie polieterowej (PEA). PIB łatwo rozpuszcza się w węglowodorach, natomiast w alkoholu nie, co może być jedną z przyczyn zwiększonej ilości osadów tworzonych na elementach silnika, a szczególnie na zaworach dolotowych. W przypadku paliw zawierających etanol, nawet na poziomie 10% (*V/V*), dodatki takie kumulują się w powstających osadach, intensyfikując ich przyrost, co powoduje tzw. *hump effect*, czyli efekt garbu, a więc zwiększenia ilości tworzonych osadów w porównaniu do paliwa nieuszlachetnionego (rysunek 1).



Rys. 1. Przyrost osadów na zaworach dolotowych silnika Mercedes M102E zasilanego paliwem E10 (*hump effect*)

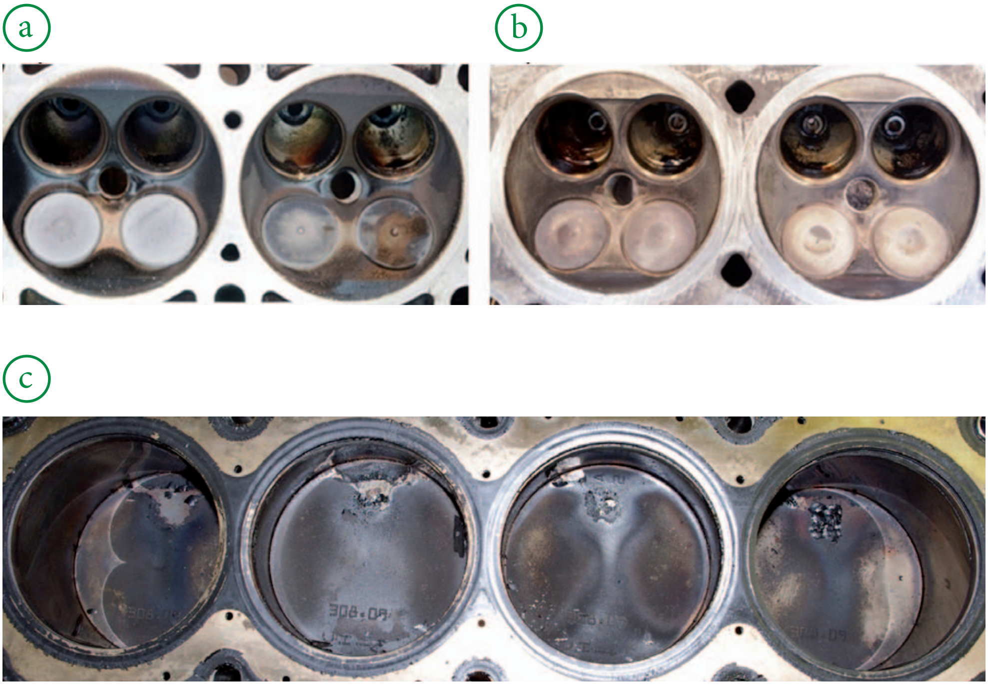
W przypadku nieuszlachetnionych mieszanin paliw zawierających etanol w miarę wzrostu jego udziału w paliwie ilość osadów powstających na zaworach dolotowych i w komorach spalania silnika stopniowo, nieznacznie maleje w porównaniu do wielkości osadów tworzonych przez nieuszlachetnione benzyny bez etanolu. Po osiągnięciu około 50–60% (*V/V*) udziału etanolu w mieszaninie z benzyną ilość powstających osadów stabilizuje się i nie zmienia w miarę dalszego zwiększania zawartości etanolu [6].

Paliwa E85 zazwyczaj mogą być komponowane przy zastosowaniu 15% (*V/V*) standardowo uszlachetnionej, handlowej benzyny silnikowej i 85% (*V/V*) etanolu. W rezultacie małe stężenie standardowych dodatków detergentowych pochodzących z benzyny, słabo rozpuszczających się w etanolu, sprawi, że nie utworzą one na powierzchni elementów silnika ochronnego filmu zapobiegającego osadzaniu się osadów, a podobnie jak w przypadku paliw niskoetanolowych ulegną kumulacji w powstających osadach, przyspieszając ich tworzenie. Dodatkowym elementem przyczyniającym się do tworzenia osadów są zawarte w paliwach etanolowych siarczany, stanowiące zanieczyszczenia pochodzące z procesu produkcji bioetanolu lub z pewnych typów inhibitorów korozji stosowanych w E85 [1, 2, 6]. Duża ilość i lepka konsystencja osadów na zaworach dolotowych, a zwłaszcza na ich trzonkach, może powodować zawieszanie się zaworów, szczególnie podczas procesów wychładzania silnika (rys. 2).

Rys. 2. Osady na zaworach dolotowych silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego nieuszlachetnionym paliwem E85. Masy osadów na zaworach kolejno od lewej: 160 mg, 152 mg, 135 mg, 127 mg

Osady w komorach spalania

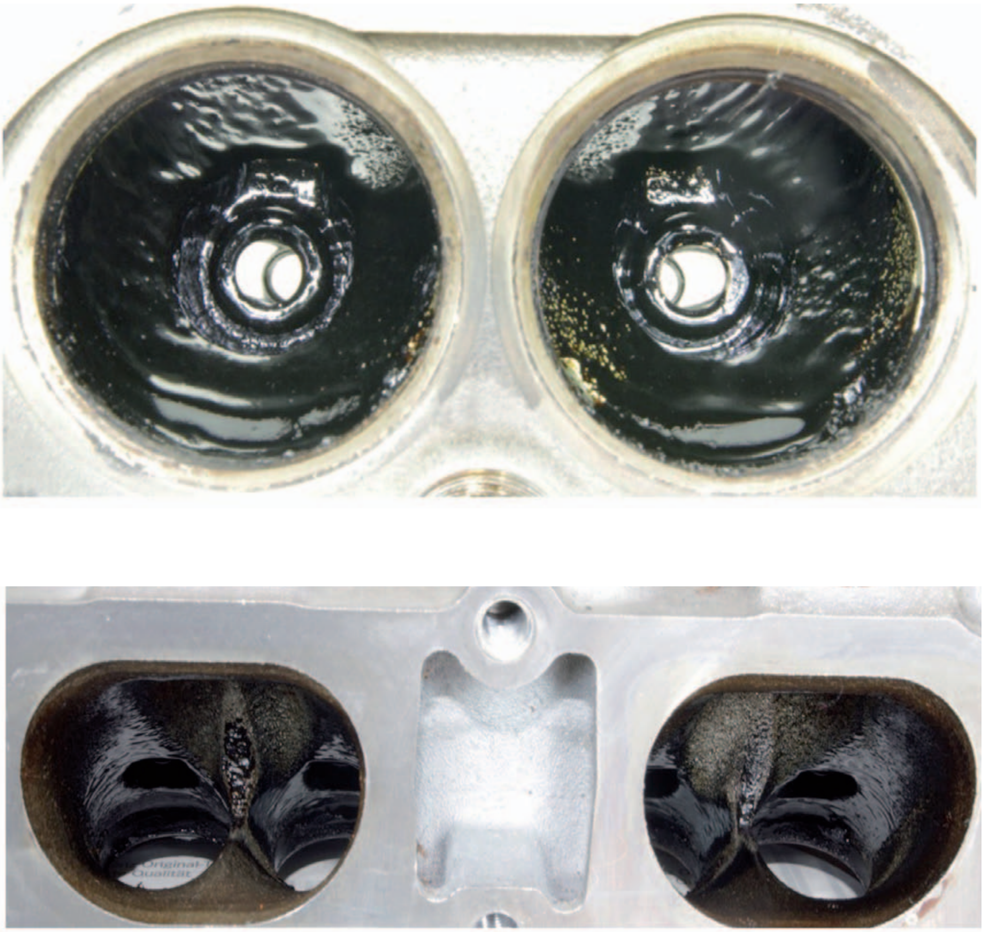
Paliwa wysokoetanolowe są paliwami, które spalają się, tworząc małą ilość sadzy, jednak osady mogą nadal powstawać w silnikach, w tym w kanałach dolotowych i w komorach spalania. W przypadku komór spalania wzrost zawartości etanolu, zarówno przy spalaniu paliwa nieuszlachetnionego, jak i uszlachetnionego, powoduje zazwyczaj obniżanie się ilości tworzonych osadów (rysunek 3). Ponadto wielkości masy osadów powstających przy stosowaniu paliw etanolowych są niższe względem analogicznych utworzonych przy zasilaniu silnika konwencjonalną benzyną niezawierającą biokomponentów. W rezultacie w przypadku paliw zawierających etanol osady w komorach spalania silnika nie stanowią takiego zagrożenia jak powstające przy zastosowaniu benzyn silnikowych niezawierających etanolu.



Rys. 3. Osady w komorach spalania silnika:
a) Mercedes M111 zasilanego nieuszlachetnionym paliwem E10 (całkowita masa osadów w 4 komorach: 2771 mg),
b) Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego nieuszlachetnionym paliwem E85 (całkowita masa osadów w 4 komorach: 1046 mg),
c) osady na denkach tłoków silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego nieuszlachetnionym paliwem E85

Osady w kanałach dolotowych

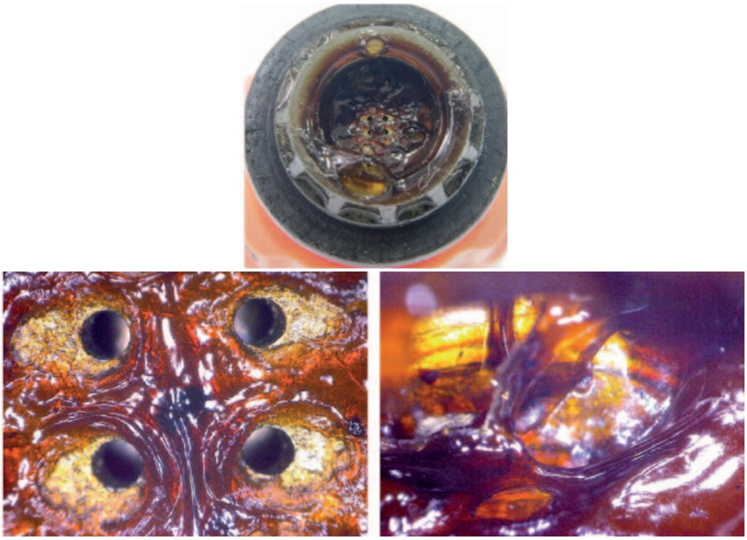
W przypadku paliw stanowiących mieszanki etanol–benzyna obserwuje się znaczną ilość lepkich osadów powstających w kanałach dolotowych silnika – zarówno w przypadku paliw nieuszlachetnionych, jak i uszlachetnionych. Duża ilość osadów pokrywających prowadnice zaworów dolotowych wraz z osadami powstałymi na trzonkach zaworów dolotowych często powoduje ich zawieszanie, zwłaszcza po pozostawieniu silnika unieruchomionego przez kilkadziesiąt godzin (rysunek 4).



Rys. 4. Osady w kanałach dolotowych silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego nieuszlachetnionym paliwem E85

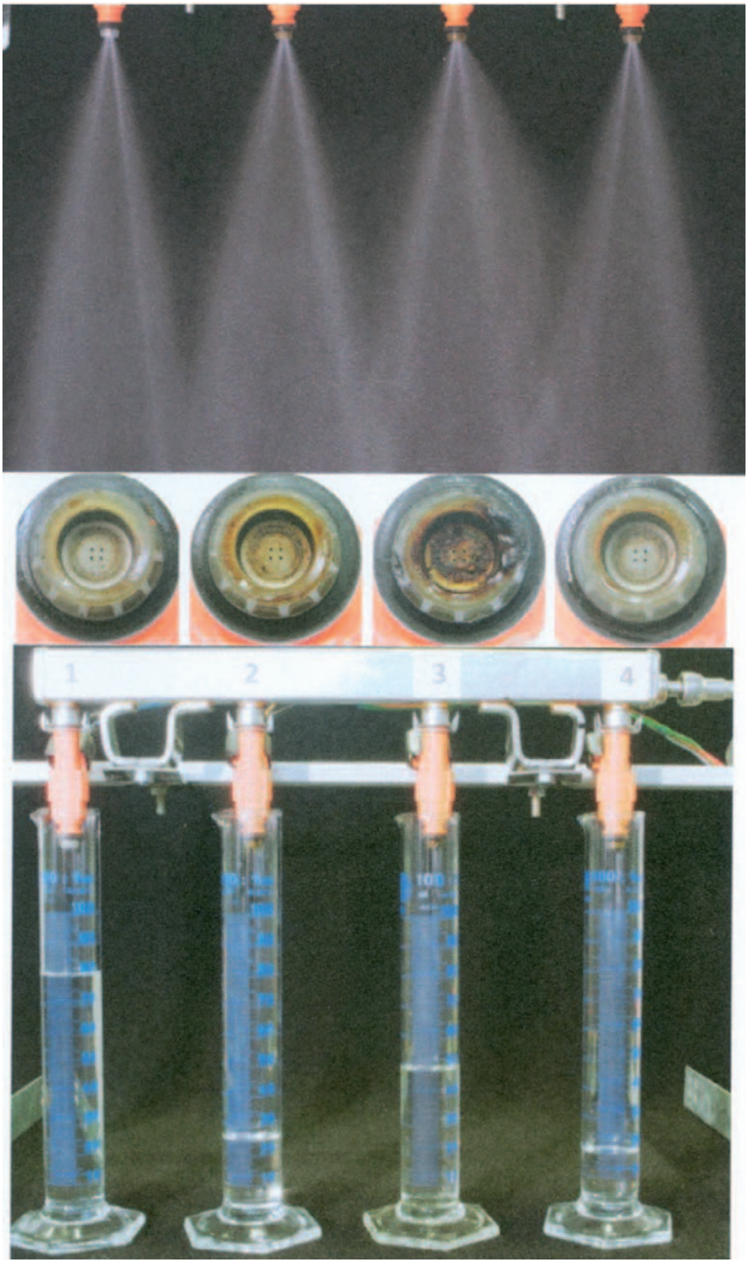
Osady wewnętrzne i zewnętrzne wtryskiwaczy paliwa – badania INiG – PIB

W silnikach typu *Flex-Fuel* zasilanych paliwami wysokoetanolowymi, w tym E85, osady tworzone na i we wtryskiwaczach paliwowych stanowią duży problem, a zarazem zagrożenie dla poprawnego funkcjonowania i osiągów silnika. Spośród warunków eksploatacji samochodu sprzyjających powstawaniu wyżej wymienionych osadów należy wymienić: krótkie odcinki jazdy (wielokrotne rozgrzewanie i chłodzenie silnika) oraz jazdę w warunkach *stop and go* [6, 7, 8] (rysunek 5).



Rys. 5. Widok osadów na końcówce rozpylacza silnika Ford 1.8L Duratec-HE PFI FFV (125PS) zasilanego niewłaściwie uszlachetnionym paliwem E85

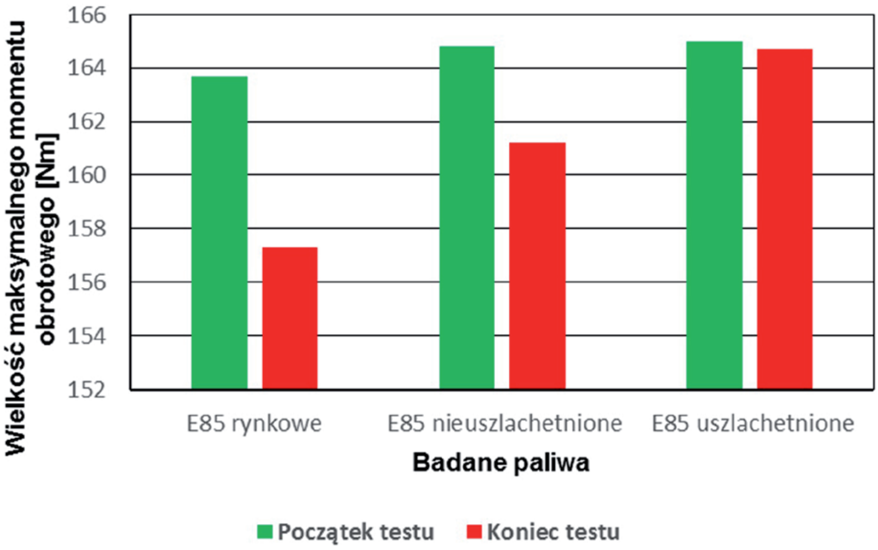
Przeprowadzone w INiG – PIB szerokie badania na stanowiskach silnikowych potwierdzają, że np. eksploatacja silnika typu *FlexFuel* na paliwie E85, składającym się w 15% (*V*/*V*) z uszlachetnionej, dostępnej na rynku benzyny silnikowej i w 85% (*V*/*V*) z bioetanolu, ma znaczący wpływ na tworzenie się zarówno wewnętrznych, jak i zewnętrznych osadów we wtryskiwaczach paliwa. Już po 100 godzinach pracy silnika w symulowanych warunkach jazdy miejskiej można zaobserwować wpływ osadów zewnętrznych na kształt i jakość rozpylanej strugi paliwa (rysunek 6).



Rys. 6. Wpływ osadów wewnętrznych i zewnętrznych wtryskiwaczy na jakość rozpylanej strugi i ilość wtryskiwanego paliwa

Równocześnie po zmianie czasu przesterowania (czas otwarcia) wtryskiwaczy zamontowanych na stanowisku badawczo-pomiarowym bezpośrednio po przeprowadzonym teście silnikowym widoczne są znaczące różnice w ilości dozowanego paliwa przez poszczególne wtryskiwacze w czasie. Osady wewnętrzne, w różnym stopniu obciążające wtryskiwacze, po teście silnikowym powodują zupełny brak wtrysku paliwa przez wtryskiwacze oznaczone w dolnej części rysunku 6, na listwie paliwowej, jako 2 i 4 przy czasie wtrysku dawki paliwa ustawionym na 1,5 ms. Po wydłużeniu czasu otwarcia wtryskiwaczy o 0,1 do 0,2 ms następuje ich stopniowe odblokowywanie, jednak taka dysfunkcja ich pracy wpływa znacząco na ilość dozowanego paliwa przez poszczególne wtryskiwacze w czasie, co widoczne jest w górnej części rysunku 6.

Zanieczyszczanie wtryskiwaczy powstającymi w nich osadami wewnętrznymi, jak i zewnętrznymi wpływa nie tylko na zaburzenia procesu jakościowego i ilościowego wtrysku paliwa, ale w konsekwencji powoduje też ograniczenie osiągów silnika. Na rysunku 7 przedstawiono wyniki pomiarów wielkości maksymalnego momentu obrotowego silnika Ford 1.8L Duratec-HE PFI FFV (125PS) zasilanego w 100-godzinnych testach kolejno: rynkowym paliwem E85, nieuszlachetnionym paliwem E85 i paliwem E85 uszlachetnionym pakietem dodatków przeznaczonym do tego rodzaju paliwa.



Rys. 7. Zmiany wielkości momentu obrotowego silnika zasilanego różnymi paliwami podczas prowadzonych testów

Jak widać, zastosowane do zasilania silnika paliwo miało wyraźny wpływ na zachowanie jego osiągów (maksymalnego momentu obrotowego) w czasie. Największy spadek momentu obrotowego wystąpił podczas zasilania silnika w teście rynkowym paliwem E85, tzn. skomponowanym z 15% (*V/V*) standardowej, handlowej, uszlachetnionej benzyny i 85% (*V/V*) etanolu. Uszlachetnienie bazowego paliwa E85 specjalnie zoptymalizowanym pakietem dodatków przeznaczonym do tego typu paliwa pozwoliło znacznie ograniczyć spadek maksymalnego momentu obrotowego w czasie testu.

Oddziaływanie na smarowy olej silnikowy

Problemy eksploatacyjne związane ze stosowaniem do zasilania silników ZI mieszanek etanol–benzyna związane są też ze zwiększonym rozcieńczaniem smarowego oleju silnikowego w skrzyni korbowej poprzez przedostające się z komór spalania biopaliwo. Intensyfikacji tego zjawiska sprzyjają niektóre warunki eksploatacji pojazdu, a zwłaszcza duża częstotliwość zimnych rozruchów silnika (szczególnie w niskich temperaturach otoczenia), związana z wykorzystywaniem pojazdu na krótkich dystansach [2, 4, 6, 8]. Agresywne oddziaływanie bioetanolu zarówno na materiały konstrukcyjne silnika, jak i na smarowy olej silnikowy wynika ogólnie z zawartej w nim (łatwo pochłanianej) wody, kwasów organicznych (tworzonych podczas procesu spalania bioetanolu w silniku) i innych zanieczyszczeń. Przeprowadzone dotychczas badania przez producentów samochodów mających największe doświadczenie w konstrukcji silników typu *FlexFuel* (GM, Ford, Saab), a także badania INiG – PIB wskazują, że stosowanie paliwa E85 powoduje zmniejszenie szybkości przyrostu lepkości smarowego oleju silnikowego w stosunku do występującej przy zasilaniu silnika konwencjonalną benzyną. Można to wyjaśnić tworzeniem się mniejszej ilości reaktywnych składników procesu spalania bioetanolu w silniku w porównaniu ze spalaniem benzyny. W konsekwencji mniej reaktywne gazy spalinowe przedmuchiwane do skrzyni korbowej silnika w mniejszym stopniu wpływają na postępujące procesy starzenia (utlenianie) oleju smarowego i przyrost jego lepkości aniżeli w przypadku spalania benzyny silnikowej. Równocześnie przy stosowaniu paliwa E85 zaobserwowano przyśpieszoną utratę rezerwy alkalicznej, a więc zdolności oleju smarowego do neutralizacji kwaśnych produktów spalania, przejawiającą się w szybszym niż podczas spalania benzyny silnikowej spadku całkowitej liczby zasadowej. Koresponduje to z szybszym wyczerpywaniem się potencjału stosowanych w oleju smarowym dodatków detergentowych i dyspergujących [8–11]. Warto podkreślić, że zdaniem niektórych producentów silników typu *FlexFuel* stanowi to podstawę do skrócenia (nawet o połowę) okresów między wymianami oleju smarowego w silniku.

Oddziaływanie na łożyska ślizgowe

Etanol ma znacznie większe właściwości korozyjne aniżeli konwencjonalna benzyna silnikowa. Jeżeli etanol wraz z paliwem przedostanie się do smarowego oleju silnikowego korozyjnie oddziałuje na różne elementy silnika, zwłaszcza gdy wyczerpane są dodatki przeciwutleniające w oleju. Ponadto w wyniku spalania paliw zawierających etanol powstają takie kwasy jak: kwas mrówkowy, kwas octowy oraz aldehydy, jak: aldehyd octowy i formaldehyd, które agresywnie oddziałują na stopy metali używane do wytwarzania panewek łożysk ślizgowych, jak: Cu-Sn-P, Cu-Sn-Pb, Al-Sn, powodując korozję Sn i Pb oraz tworząc siarczki miedzi [12, 13] (rysunek 8).

Rys. 8. Skutki agresywnego oddziaływania bioetanolu przedostającego się do smarowego oleju silnikowego na panewki łożysk wału korbowego [13]

Przeciwdziałanie zagrożeniom

W projekcie finansowanym ze środków funduszy norweskich w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju, w INiG – PIB opracowano i przebadano kilkanaście wielofunkcyjnych pakietów dodatków uszlachetniających o zoptymalizowanych właściwościach detergentowych przeznaczonych zwłaszcza do paliw wysokoetanolowych (E85). Ostateczne oceny, weryfikacje składu i jakościowe kwalifikacje przedmiotowych pakietów dodatków były dokonywane na podstawie specjalnie opracowanych do tego celu symulowanych testów silnikowych. Pakiety dodatków optymalizowano pod kątem maksymalnego ograniczenia tendencji do tworzenia osadów na elementach silnika typu *FlexFuel*. Szczególny nacisk położono na przeciwdziałanie tworzeniu się osadów na zaworach dolotowych oraz wewnętrznych i zewnętrznych osadów na wtryskiwaczach paliwa. Jak stwierdzono w obszernych silnikowych badaniach wstępnych, w przypadku paliw wysokoetanolowych te osady stanowią największe zagrożenia dla procesów jakościowego i ilościowego tworzenia mieszanki w cylindrach oraz zakłócają procesy spalania. Powoduje to nierównomierną pracę silnika na biegu jałowym, opóźnioną reakcję na ruch pedału przyspieszenia, wzrost zużycia paliwa i emisji szkodliwych składników spalin. W rezultacie paliwa uszlachetnione opracowanymi pakietami dodatków były oceniane pod kątem efektywności przeciwdziałania tworzeniu się osadów *keep-clean*, zmywania utworzonych osadów *cleanup*, a także wpływu na wielkość emisji składników szkodliwych do atmosfery oraz emisji GHG.

Bazowe paliwo E85 (niezawierające dodatków) przygotowywano w INiG – PIB, stosując etanol o właściwościach podanych w tabeli 3 oraz benzynę bazową (tabela 4).

Tabela 3. Wybrane wyniki analiz właściwości etanolu

Parametr	Etanol (wyniki analiz)	Wymagania wg Rozporządzenia*
Zawartość etanolu i wyższych alkoholi nasyconych [% (*m*/*m*)]	99,852	min. 98,7
Zawartość wyższych alkoholi (C3–C5) [% (*m*/*m*)]	<0,001	maks. 2,0
Zawartość metanolu [% (*m*/*m*)]	<0,001	maks. 1,0
Zawartość wody [% (*m*/*m*)]	0,137	maks. 0,300
Zawartość nieorganicznych chlorków [mg/l]	<4,0	maks. 20,0
Zawartość miedzi [mg/kg]	<0,1	maks. 0,100
Całkowita kwasowość (w przeliczeniu na kwas octowy) [% (*m*/*m*)]	0,004	maks. 0,007

Parametr	Etanol (wyniki analiz)	Wymagania wg Rozporządzenia*
Zawartość fosforu [mg/l]	<0,15	maks. 0,50
Zawartość substancji nielotnych [mg/100 ml]	<10,0	maks. 10
Zawartość siarki [mg/kg]	<5,0	maks. 10,0
Parametry dodatkowe:		
Gęstość [kg/m^3]	793,4	–
DVPE [kPa]	15,1	–
Destylacja:		
Temp. początku destylacji [°C]	77,8	–
Temp. końca destylacji [°C]	87,3	–
Pozostałość [% (*V*/*V*)]	0,1	–
Straty [% (*V*/*V*)]	1,5	–

* Rozporządzenie Ministra Gospodarki z dnia 17 grudnia 2010 r. w sprawie wymagań jakościowych dla biokomponentów, metod badań jakości biokomponentów oraz sposobu pobierania próbek biokomponentów (Dz. U. z 2010 r. Nr 249, poz. 1668)

Tabela 4. Wybrane wyniki analiz właściwości benzyny bazowej E95

Parametr	E95 (wyniki analiz)	Wymagania wg normy PN-EN 228
Liczba oktanowa RON	98,8	min. 95,0
Liczba oktanowa MON	89,6	min. 85,0
Gęstość [kg/m^3]	725,6	720–775

Parametr	E95 (wyniki analiz)	Wymagania wg normy PN-EN 228
Prężność par [kPa]	57,8	45,0–60,0
Destylacja:		
E70 [% (*V*/*V*)]	21,1	20,0–48,0
E100 [% (*V*/*V*)]	52,5	46,0–71,0
E150 [% (*V*/*V*)]	93,1	min. 75,0
Temp. końca destylacji [°C]	181,9	maks. 210
Pozostałość [% (*V*/*V*)]	1,0	maks. 2
Zawartość zw. tlenowych [% (*V*/*V*)]	brak	jak w normie PN-EN 228
Zawartość benzenu [% (*V*/*V*)]	0,25	maks. 1,0
Zawartość metanolu [% (*V*/*V*)]	<0,1	maks. 3,0
Zawartość etanolu [% (*V*/*V*)]	<0,1	maks. 5,0
Zawartość siarki [mg/kg]	<3	maks. 10
Korozja Cu, klasa korozji	1	klasa 1
Okres indukcyjny [min]	>360	min. 360
Zawartość żywic [mg/100 ml]:		
– nieprzemywane	7,1	–
– obecne	0,2	maks. 5
Skład grupowy FIA [% (V/V)]:		
– parafino-nafteny	55,0	–
– olefiny	14,6	maks. 18,0
– aromaty	30,4	maks. 35,0

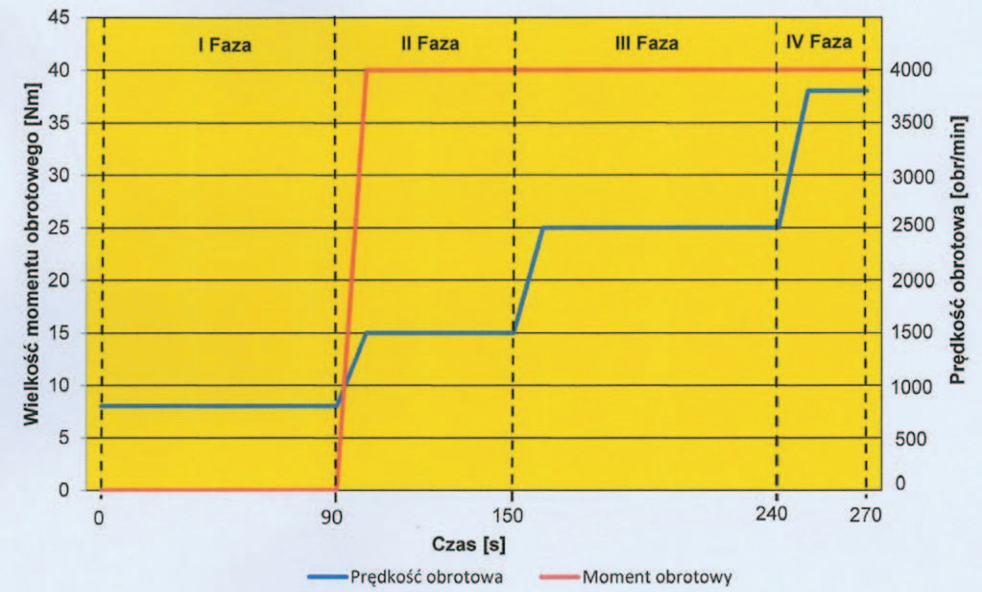
Badania przeprowadzono na stanowisku badawczym z silnikiem typu *FlexFuel* (Ford 1.8L Duratec-HE PFI FFV (125PS) MI4) fabrycznie przystosowanym do zasilania biopaliwem o zawartości do 85% (*V/V*) etanolu (tabela 5).

Tablica 5. Wybrane parametry techniczne silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4

Obieg pracy	czterosuwowy, z zapłonem iskrowym
Typ wtrysku paliwa	pośredni wtrysk paliwa sterowany elektronicznie – systemem Visteon
Układ cylindrów	rzędowy, pionowy
Liczba cylindrów	4
Kolejność wtrysku paliwa do cylindra	1-3-4-2
Typ układu rozrządu	DOHC/4 VPC
Średnica cylindra	83,0 mm
Skok tłoka	83,1 mm
Pojemność skokowa	1798 cm^3
Moc maksymalna	125 KM (92 kW) przy 6000 obr./min
Maks. moment obrotowy	165 Nm przy 4000 obr./min
Stopień sprężania	10,8
Średnie zużycie paliwa (E85)	10,5 l/100 km
Luz zaworowy	Regulacja hydrauliczna
Pojemność układu smarowania z filtrem	4,3 dm^3
Spełniana norma w zakresie wielkości emisji składników szkodliwych do atmosfery	Euro IV

Silnik połączony był z hamulcem elektrowirowym AVL Alpha 160 z programowanym działaniem, umożliwiającym realizację i powtarzanie różnych sekwencji (cykli) wcześniej opracowanych testów.

Oceny efektywności przygotowanych pakietów dodatków pozwalające na weryfikację ich składu i optymalizację poziomu dozowania prowadzono w symulowanych testach silnikowych według własnej procedury badawczej. Procedura testowa obejmowała czterofazowy, powtarzalny cykl badawczy symulujący przeciętne warunki pracy silnika podczas eksploatacji pojazdu w ruchu miejskim o małym natężeniu (rysunek 9). Testy były prowadzone przez 100 godzin poprzez powtarzanie cyklu badawczego.



Rys. 9. Powtarzany cykl badawczy składający się na testy silnikowe

Utworzone w czasie testów osady na zaworach dolotowych i w komorach spalania były fotografowane, a następnie oceniane wagowo przy wykorzystaniu znanej metodyki opisanej w procedurze CEC F-20-98 (Mercedes Benz M111). Osady w kanałach dolotowych głowicy oraz na końcówkach wtryskiwaczy oceniano optycznie i dokumentowano fotograficznie. Wewnętrzne i zewnętrzne osady wtryskiwaczy były oceniane na stanowisku przepływowym opartym na układzie wtrysku paliwa silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 pod względem wpływu na jakość rozpylania, zasięg i wzór strugi paliwa oraz równomierność dawkowania paliwa.

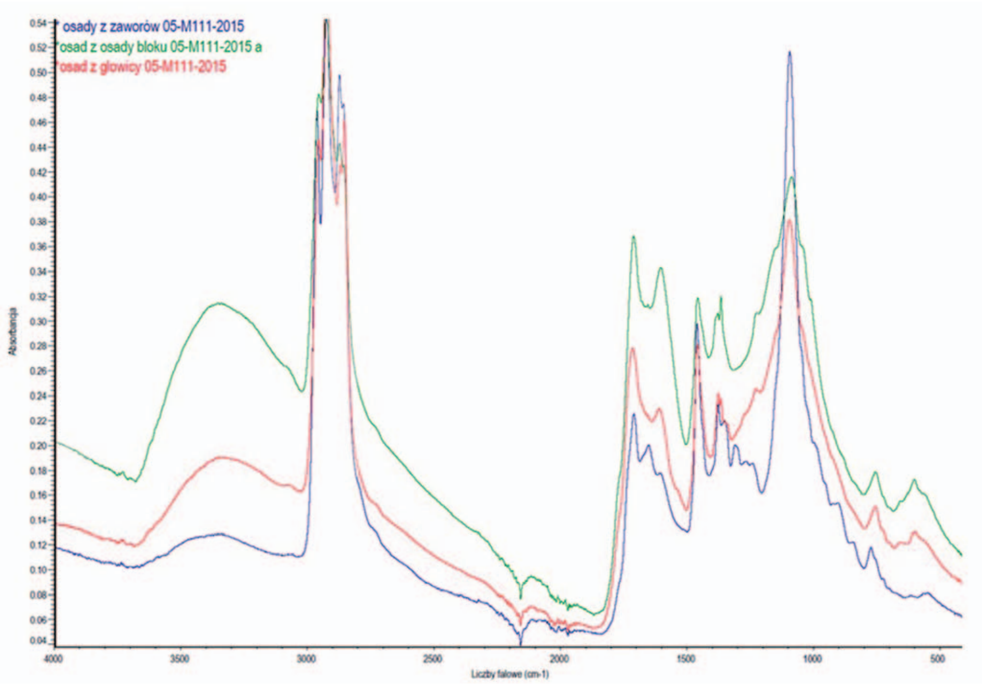
Wyniki badań

Przeprowadzone wielokierunkowe testy na stanowiskach silnikowych w różnych warunkach pracy silników potwierdziły, że zastosowanie paliw wysokoetanolowych do zasilania silników ZI typu *FlexFuel* wiąże się z problemem tworzenia szkodliwych osadów na elementach układu dolotowego, w komorach spalania, na zaworach dolotowych oraz na powierzchniach wtryskiwaczy paliwa silnika. Osady takie nie są niczym nowym, jako że występują też w silnikach zasilanych paliwami węglowodorowymi, jednak w przypadku paliw zawierających duży udział etanolu czynniki, jak i uwarunkowania sprzyjające ich powstawaniu są w dużej mierze inne niż przy stosowaniu paliw konwencjonalnych. Paliwo etanolowe stwarza nieco inne warunki spalania w silniku niż tradycyjna benzyna silnikowa, ponieważ w silniku następuje szybkie odparowanie paliwa, w czasie uniemożliwiającym ustalenie się warunków równowagi termicznej. Szczególnie w zimnym klimacie lub przy uruchamianiu zimnego silnika ciepło potrzebne do odparowania paliwa jest ograniczone, dlatego też ciekłe paliwo pozostaje w systemie dolotowym. Etanol charakteryzuje się znacznie wyższym ciepłem parowania w porównaniu z węglowodorami, co powoduje, że odparowanie azeotropów etanol–węglowodory jest utrudnione w zimnym silniku. Ma to też wpływ na procesy nagrzewania się powierzchni, na których powstają osady. Biorąc pod uwagę, że zasadnicze znaczenie dla tworzenia osadów węglowych mają składniki paliwa o najwyższej temperaturze wrzenia, temperatura nagrzewania się powierzchni, na której mogą odkładać się osady ma wpływ na szybkość i wielkość ich powstawania. Duże znaczenie dla tworzenia osadów mają też zanieczyszczenia zawarte w etanolu, w tym w szczególności siarczany i pierwiastki metaliczne, a także brak lub stosowanie niekompatybilnych z etanolem dodatków detergentowych w aktualnie dostępnych na rynkach światowych paliwach E85 [2].

W rezultacie istnieje potrzeba opracowania przeznaczonych do paliw etanolowych pakietów dodatków uszlachetniających o zoptymalizowanych właściwościach detergentowych.

Początkowe badania wpływu różnych kompozycji pakietów dodatków w paliwach E10 na tworzenie i skład osadów na zaworach dolotowych i w komorach spalania prowadzono na stanowisku hamowni z silnikiem Mercedes M111, według procedury CEC F-20-98. W wyniku spalania uszlachetnionej benzyny E10 tworzą się osady odkładające się na elementach układu paliwowego. Analizując w podczerwieni widma (FTIR-ATR po korekcie matematycznej) osadów oraz stosowanych do uszlachetniania benzyny dodatków, można stwierdzić, że w osadach, oprócz skoksowanej pozostałości i produktów utleniania wysokocząsteczkowych węglowodorów obecnych w niewielkich ilościach w benzynie, obserwowane są produkty degradacji składników polimerycznych pakietu uszlachetniającego, takich jak np. acylowane eteroaminy czy polialkoksylowane alkilofenole. Struktury estrowe, amidowe (dodatki), karboksylowe i karbonylowe (utlenianie węglowodorów i dodatków), struktury aminowe i eterowe (degradacja dodatków) najwyraźniej obserwowane są w osadach z zaworów. Wraz ze wzrostem temperatur w poszczególnych elementach układu paliwowego rośnie ilość trudnych do identyfikacji produktów degradacji dodatków oraz sadzy/bezpostaciowego węgla.

Na rysunku 10 przedstawiono widma osadów zebranych po jednym z testów przeprowadzonych na stanowisku z silnikiem Mercedes M111.



Rys. 10. Widma FTIR osadów z zaworów dolotowych, głowicy i denek tłoków silnika badawczego Mercedes M111

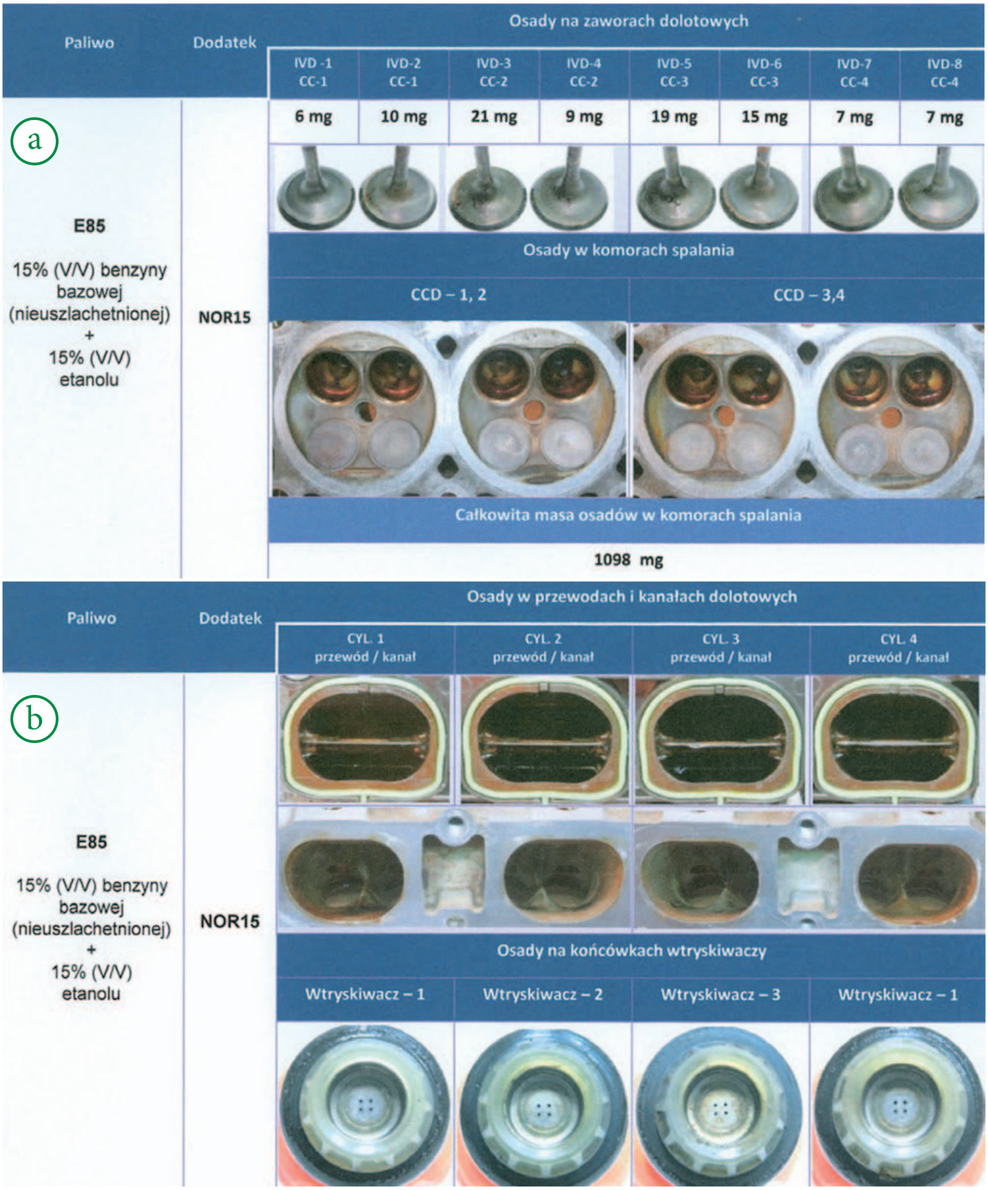
W widmie osadów z zaworów (kolor niebieski) widać wyraźnie pasma w zakresie 1100–1000 cm^{-1}, związane z obecnością oleju wynośnikowego, natomiast podwójne pasmo w zakresie 1400–1350 cm^{-1} wskazuje na obecność struktur polibutenowych typowych dla dyspergatorów stosowanych w dodatkach uszlachetniających do benzyn. Silne pasmo ok. 1700 cm^{-1} związane jest z obecnością produktów utleniania o charakterze kwasów karboksylowych. W przypadku osadów z komór spalania silnika (głowica i denka tłoków) w widmie obserwuje się więcej pasm struktur typowych dla produktów utleniania (~3500 cm^{-1} –OH i 1700 cm^{-1} –COOH), bardzo szerokie nałożone pasma w zakresie 1200–900 cm^{-1}, pochodzące zarówno od z produktów utleniania, jak i degradacji stosowanych dodatków). Za obserwowane podniesienie tła odpowiada sadza obecna w osadzie.

Finalne badania dotyczyły opracowania i optymalizacji pakietów dodatków przeznaczonych do paliwa E85.

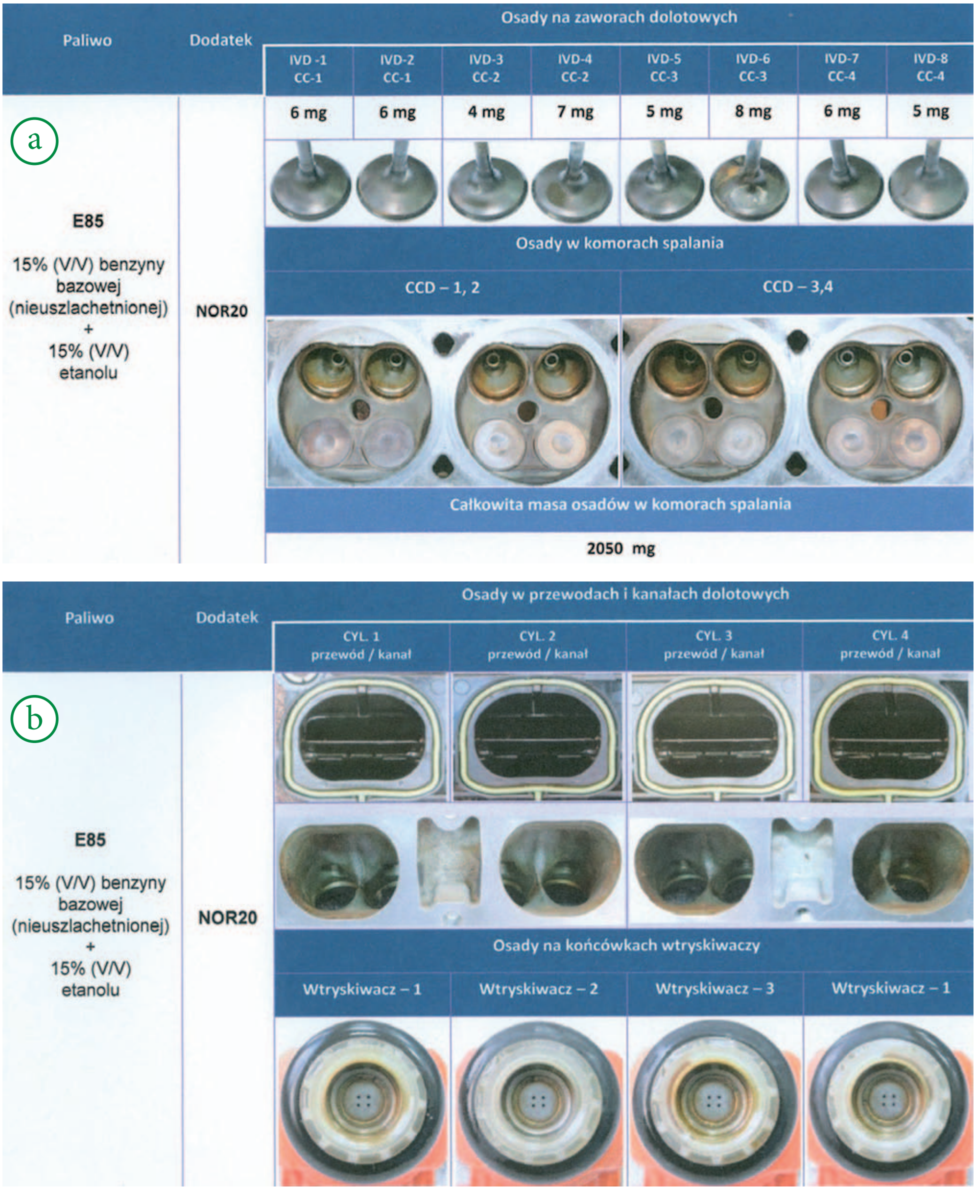
Na rysunkach 11 i 12 przedstawiono wyniki ocen silnikowych dwóch wybranych wielofunkcyjnych pakietów dodatków uszlachetniających o zoptymalizowanych właściwościach detergentowych, przeznaczonych zwłaszcza do paliw wysokoetanolowych (E85). Dodatki zostały opracowane w INiG – PIB w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju. Oznaczono je jako NOR15 i NOR20.

NOR15 to pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM1, o strukturze N-alkilowanej pochodnej benzoksazyny uwodornionej w pierścieniu heterocyklicznym, dodatkowo podstawionej resztą alkilową w pierścieniu aromatycznym, oraz syntetyczny olej nośny o strukturze oksyalkilowanego alkilofenolu i rozpuszczalnik aromatyczny. Z kolei NOR20 to pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM2, o strukturze diaminy, pochodnej alkilofenolu, zawierającej struktury II- i III-rzędowej aminy, oraz syntetyczny olej nośny o strukturze oksyalkilowanego alkilofenolu i rozpuszczalnik aromatyczny.

W przypadku pakietu NOR15 średnia masa osadów na zaworach dolotowych wynosiła około 12 mg/zawór, a całkowita masa osadów w komorach spalania była równa 1098 mg (rysunek 11a). Zarówno powierzchnie grzybków zaworów dolotowych, jak i komór spalania pokrywały bardzo cienkie warstwy równomiernie rozłożonych, suchych, dobrze przywierających do powierzchni jasnych osadów, niewykazujących tendencji do łuszczenia się. W kanałach dolotowych widoczne były niewielkie, tłuste, smołowate osady, nierównomiernie pokrywające powierzchnie kanałów i przewodów dolotowych (rysunek 11b). Większa ilość osadów, które spłynęły na dolną część kanałów dolotowych, bezpośrednio przed zaworami dolotowymi (podczas robienia zdjęć głowica silnikowa opierała się w pozycji pionowej na ściance wyprowadzenia kanałów wylotowych), pozwala przypuszczać, że były one skutecznie rozpuszczane przez uszlachetnione paliwo E85 (rysunek 11a). Na uwagę zasługują czyste końcówki wtryskiwaczy (rysunek 11b). Przeprowadzone oceny przepływowe wtryskiwaczy nie wykazały wpływu osadów wewnętrznych na zakłócenia pracy wtryskiwaczy, poprzez



Rys. 11. Widok osadów na elementach silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego paliwem E85 uszlachetnionym pakietem dodatków NOR15: a) osady na zaworach dolotowych i w komorach spalania, b) osady w przewodach i kanałach dolotowych oraz na końcówkach wtryskiwaczy



Rys. 12. Widok osadów na elementach silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4 zasilanego paliwem E85 uszlachetnionym pakietem dodatków NOR20: a) osady na zaworach dolotowych i w komorach spalania, b) osady w przewodach i kanałach dolotowych oraz na końcówkach wtryskiwaczy

oddziaływanie na ich czas przesterowania, powodowanie podciekania lub zmiany równomierności dawkowania paliwa czy też początkowych utrudnień we wtrysku dawek paliwa po kilkudziesięciogodzinnej przerwie w pracy silnika.

Pakiet NOR20 był optymalizowany pod kątem dalszego zmniejszenia osadów na zaworach dolotowych przy zachowaniu czystości wtryskiwaczy. W rezultacie zredukowano średnią masę osadów na zaworach dolotowych do około 6 mg/zawór, równocześnie znacznie zmniejszając ilość osadów w kanałach i przewodach dolotowych (rysunki 12a i 12b). Niestety wpłynęło to niekorzystnie na całkowitą masę osadów w komorach spalania, która uległa podwyższeniu do 2050 mg. Jednak jest to w dalszym ciągu bardzo dobry wynik w porównaniu do analogicznego w przypadku zasilania silnika konwencjonalną, handlową benzyną silnikową (około 3600–4200 mg, w zależności od producenta paliwa dla silnika Ford *FlexFuel*).

Nie wykazano różnic w zakresie oddziaływania paliwa E85 uszlachetnionego pakietem dodatków NOR15 lub NOR20 na funkcjonowanie wtryskiwaczy paliwa (rysunek 12b). W obydwu przypadkach osady wystąpiły jedynie w śladowych ilościach.

Podsumowując, obydwa wielofunkcyjne pakiety dodatków, tzn. NOR15 i NOR20, przeznaczone do uszlachetniania paliw wysokoetanolowych, odznaczają się wysoką efektywnością w zakresie właściwości detergentowych i są produktami w pełni konkurencyjnymi z podobnymi opracowanymi przez renomowanych producentów światowych.

Wnioski

1) Różnice właściwości fizykochemicznych etanolu i benzyny mają duży wpływ na właściwości użytkowo-eksploatacyjne mieszanek etanol–benzyna.
2) Zasilanie silnika ZI typu *FlexFuel* nieuszlachetnionym biopaliwem stanowiącym mieszaninę 85% (*V/V*) etanolu i 15% (*V/V*) benzyny bazowej powoduje powstawanie dużej ilości osadów na elementach układu dolotowego i wtryskowego silnika, mogących zagrażać jego poprawnemu funkcjonowaniu poprzez zakłócenie procesów tworzenia mieszanki i jej spalania.
3) Duży wpływ na powstawanie osadów mają zanieczyszczenia zawarte w etanolu, w tym w szczególności siarczany i pierwiastki metaliczne, a także brak lub stosowanie niekompatybilnych z etanolem dodatków detergentowych pochodzących z 15% (*V/V*) uszlachetnionej standardowej benzyny handlowej, zazwyczaj obecnej w dostępnych na rynku paliwach E85.

4) Zastosowanie specjalnie opracowanego i zoptymalizowanego pakietu dodatków uszlachetniających przeznaczonych do paliw wysokoetanolowych, zawierającego efektywny dodatek detergentowy, stanowi skuteczny sposób znacznego ograniczenia ilości osadów tworzonych na elementach układu dolotowego i wtryskowego silnika.

Artykuł opracowano na podstawie projektu realizowanego w INiG – PIB i finansowanego ze środków funduszy norweskich w ramach programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju.

Literatura

[1] Pałuchowska M., Stępień Z., Żak G.: *The prospects for the use of ethanol as a fuel component and its potential in the reduction of exhaust emissions – Perspektywy wykorzystywania etanolu jako składnika paliwa i jego potencjał w redukcji emisji szkodliwych składników spalin*. Combustion Engines 2014, vol. 158, no. 3, PTNSS-2014-309, PL ISSN 0138-0346.

[2] Stępień Z.: *Multidirectional investigations of high-ethanol fuels on deposit formation in spark ignition engines – Wielokierunkowe badania wpływu paliw wysoko-etanolowych na tworzenie osadów w silnikach z zapłonem iskrowym*. Combustion Engines 2015, vol. 162, no. 3, PTNSS-2015-3418, PL ISSN 2300-9896.

[3] *Life Cycle Emissions*. http://www.afdc.energy.gov/afdc/vehicles/emissions_e85.html, dostęp: 3.02.2014.

[4] Hauet B., Grand J. G., Jouron C., Tran-Dinh C.: *E85: Impact of the fuel properties on „flex fuel" engine tuning*. 31 Internationales Wiener Motorensymposium 2010. Wiedeń 2010.

[5] Grant L. J., Mason R. L.: *SwRI-BMW N.A. Intake Valve Deposit Test – A Statistical Review*. SAE Paper No. 922215.

[6] Schwahn H., Lutz U.: *Deposit Formation of Flex Fuel Engines Operated on Ethanol and Gasoline Blends*. SAE Paper No. 2010-01-1464.

[7] Stępień Z.: *Intake valve and combustion chamber deposits formation – the engine and fuel related factors that impacts their growth*. Nafta-Gaz 2014, nr 4, s. 28–34. ISSN 0867-8871.

[8] Bergström H., Melin S. A., Coleman J.: *The New ECOTEC Turbo Bio Power Engine from GM Power train – Utilizing the Power of Nature's. resources*. 28 Internationales Wiener Motorensymposium 2007. Wiedeń 2007.

[9] Bennett J.: *Specific bioethanol issues for the automotive industry.* International Conference on Biofuels Standards, 27-28 February 2007, Brussels

[10] Kalghatgi G.: *Fuel/Engine Interactions*. SAE International, 2013. ISBN 978-0-7680-6458-2.

[11] Urzędowska W., Stępień Z.: *Oddziaływanie paliwa na zmiany właściwości użytkowych oleju smarowego w silniku z ZI typu FlexFuel*. Nafta-Gaz 2012, nr 6, s. 377–387. ISSN 0867-8871.

[12] Tomanik E.: *Some tribological issues on flex-fuel engines*. Int. Workshop on Ethanol ICE, S. Paulo, 4/Oct/2012.

[13] *MAHLE Systems with optimized friction properties for greater fuel efficiency and lower CO_2 Emission*. MAHLE Performance 2009.

[14] Altin O., Eser S.: *Carbon Deposit Formation From Thermal Stressing of Petroleum Fuels*. Preprint Papers – American Chemical Society, Division of Fuel Chemistry 2004, vol. 49, no. 2, s. 764–766.

[15] *Ethanol Guidelines*. Worldwide Fuel Charter Committee. March 2009.

Ocena właściwości detergentowych mieszanek benzyny z wysoką zawartością etanolu w zależności od zastosowanych formulacji pakietów dodatków

Evaluation of detergent properties of high ethanol- gasoline blends depending on applied formulations of additive packages

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Abstract

The problem of the application of detergent-dispersant additives for gasolines with the low and high content of ethanol were discussed. The results of the detergent properties assessment of high ethanol content gasoline (E85) treated by evaluated in Oil and Gas Institute – National Research Institute additive package formulations had been presented. The research was financed by Norwegian founds and carried out in the frame of the Polish-Norwegian Research Programme realized by the National Center for Research and Development.

Streszczenie

Omówiono problem stosowania dodatków detergentowo-dyspergujących w benzynach węglowodorowych z niewielką zawartością etanolu i benzynach wysokoetanolowych. Zaprezentowano wyniki oceny właściwości detergentowych benzyny z wysoką zawartością etanolu (E85) uszlachetnionej opracowanymi w Instytucie Nafty i Gazu – Państwowym Instytucie Badawczym formulacjami pakietów dodatków. Badania wykonano w ramach projektu finansowanego ze środków funduszy norweskich będącego częścią programu Polsko-Norweska Współpraca Badawcza, realizowanego przez Narodowe Centrum Badań i Rozwoju.

Wprowadzenie

Ze względu na konieczność sprostania wyzwaniom idei zrównoważonego rozwoju oraz zapewnienia bezpieczeństwa energetycznego, a także poprzez przyjęcie regulacji prawnych ograniczających emisję CO_2 wprowadzone zostały obecnie w wielu krajach świata polityki promujące wykorzystanie energii ze źródeł odnawialnych, w tym również w transporcie, a wśród nich stosowanie paliw etanolowych. Wprowadzenie na rynek paliwa etanolowego wymaga wielu kosztownych badań – zarówno w zakresie konstrukcji silników, projektowania systemów komputerowych obsługujących pracę pojazdów samochodowych, budowy infrastruktury niezbędnej w systemie dystrybucji tego paliwa, jak również rozwiązywania problemów eksploatacyjnych związanych ze specyficznymi właściwościami fizykochemicznymi etanolu.

Powszechnie wiadomo, że korzystanie z kompozycji etanolu z benzyną silnikową może powodować wiele trudności technicznych dotyczących pracy silnika, ponieważ etanol różni się od benzyny silnikowej w niektórych kluczowych właściwościach, co skutkuje tworzeniem osadów na zaworach dolotowych, w komorach spalania, w układzie dolotowym i na końcówkach wtryskiwaczy, wzrostem tendencji do zawieszania zaworów, utrudnionym rozruchem w warunkach niskich temperatur, korozją układu paliwowego, zatykaniem filtra paliwa, wzrostem zużycia paliwa oraz podwyższeniem emisji toksycznych składników spalin [1].

W przypadku benzyn silnikowych znane są bardzo skuteczne dodatki detergentowe zapewniające praktycznie całkowitą czystość zarówno zaworów dolotowych, jak i wtryskiwaczy paliwa oraz gwarantujące zgodność z wymaganiami Światowej Karty Paliw [2] w zakresie całkowitej ilości nagarów i osadów gromadzących się w komorach spalania. Dodatki detergentowe do benzyn silnikowych stosowane są już od ponad 50 lat, a ich receptury były rozwijane w miarę wzrostu wymagań w stosunku do silników o zapłonie iskrowym (ZI). Można mówić o co najmniej czterech generacjach dodatków do benzyn silnikowych, różniących się od siebie typem substancji chemicznych zastosowanych jako substancje aktywne o działaniu detergentowym oraz rodzajem tzw. olejów nośnych (mineralnych bądź syntetycznych).

Rozwój dodatków do benzyn silnikowych przebiegał od wykorzystania pochodnych kwasów tłuszczowych do zaawansowanych polibutenoamin i polieteroamin, otrzymywanych z zastosowaniem reaktywnych polibutenów [3].

Po wprowadzeniu wtrysku paliwa w silnikach ZI pojawiła się konieczność podwyższenia poziomu dozowania dodatków detergentowych w celu zapewnienia odpowiedniej czystości wtryskiwaczy, co jednakże przełożyło się na wzrost poziomu nagarów i zanieczyszczeń na zaworach dolotowych i w komorach spalania silników testowych, a w efekcie skutkowało również zwiększeniem zapotrzebowania oktanowego [4–6]. Wzrost poziomu dozowania dodatków detergentowych sięgał 1000 mg/kg paliwa wobec początkowych 100 mg/kg. Zaistniała sytuacja zmusiła producentów dodatków zarówno do poszukiwań nowego typu związków o działaniu detergentowym, jak również do poprawy właściwości termicznych substancji aktywnych o działaniu detergentowym oraz stosowania syntetycznych olejów nośnych o określonej strukturze chemicznej (początkowo polialfaolefin, a ostatecznie alkilopolieterów i pochodnych karbaminianów). W efekcie opisanych zmian w charakterze dodatków do benzyn silnikowych pojawiły się tzw. *Gasoline Performance Additives* (GPA), w skład których z definicji wchodziły co najmniej: substancja aktywna o działaniu detergentowym, syntetyczny olej nośny i rozpuszczalnik o zdefiniowanym składzie chemicznym. Zadaniem tego typu dodatków było:

- dyspergowanie prekursorów osadów i nagarów;
- zapobieganie blokowaniu się zaworów w prowadnicach;
- niedopuszczanie do wzrostu ilości osadów i nagarów w komorach spalania, (w porównaniu z benzyną silnikową niezawierającą dodatków detergentowych).

W skład tego typu dodatków detergentowych mogły również wchodzić inne komponenty, np.:

- demulgatory;
- dodatki przeciwkorozyjne;
- antyoksydanty;
- dodatki smarnościowe.

Konieczne jest, jak wspomniano, stosowanie w pakiecie dodatków odpowiedniego rozpuszczalnika, który ma na celu nie tylko ułatwienie operacji logistycznych (właściwości niskotemperaturowe, pompowalność, łatwość dozowania itp.), ale przede wszystkim zapewnienie odpowiedniej kompatybilności składników pakietu, często wykazujących antagonistyczne tendencje związane z ich właściwościami powierzchniowo-czynnymi.

Dalszy rozwój dodatków detergentowych związany był z wprowadzeniem silników benzynowych z wtryskiem bezpośrednim (DIG – *Direct Injection Gasoline*), w których temperatura pracy wtryskiwaczy była wyższa od temperatury pracy wtryskiwaczy w silnikach PFI (*Port Fuel Injection*), co stanowiło powód wzrostu stopnia ich zanieczyszczenia. Fakt ten zmusił producentów benzyn i dodatków do zwiększenia poziomów ich dozowania lub poprawy skuteczności ich działania.

Wprowadzenie etanolu do benzyn silnikowych również skomplikowało stosowanie dodatków detergentowych [7, 8]. W przypadku korzystania z benzyn o niskiej zawartości etanolu (do 10% (*V*/*V*)) może nastąpić wzrost ilości tworzących się nagarów i osadów, ale również zmiana ich charakteru. Niskie zawartości etanolu w benzynie wykazują jednak zazwyczaj ograniczony wpływ na efektywność dodatków przeznaczonych do benzyn węglowodorowych [3]. Gdy zawartość etanolu w benzynie silnikowej jest wyższa (do 85% (*V*/*V*)), problem związany ze zwiększeniem ilości i rodzajem osadów i nagarów może być znacznie poważniejszy. W przypadku benzyn wysokoetanolowych główną przyczyną spadku efektywności działania dodatków detergentowych może być ograniczona rozpuszczalność zastosowanych substancji aktywnych o działaniu detergentowym, syntetycznych olejów nośnych i innych składników dodatków detergentowych do benzyn[3]. Zjawisko ograniczonej rozpuszczalności może się manifestować zminiejszoną przeźroczystością uszlachetnionego paliwa, którą można wyznaczać z wykorzystaniem metod nefelometrycznych [3]. Stosowanie dodatków detergentowych typu PIBA (polibutenoamin) w porównaniu z dodatkami typu PEA (polieteroamin) powoduje znaczne różnice w efektywności, co wynika z bardzo dużych różnic ich rozpuszczalności w benzynach o wysokiej zawartości etanolu.

Opracowanie i zastosowanie dodatków detergentowych skutecznych w benzynach o wysokiej zawartości etanolu wydaje się realne, problemem jednak jest ich efektywność w wypadku zmieszania benzyn węglowodorowych i benzyn o wysokiej zawartości etanolu. W takim przypadku prawdopodobne będzie wystąpienie braku kompatybilności dodatków przeznaczonych do obu rodzajów benzyn silnikowych (z niską i wysoką zawartością etanolu) oraz wystąpienie braku rozpuszczalności dodatków przeznaczonych do stosowania w benzynach o niskiej zawartości etanolu w alkoholu oraz dodatków przeznaczonych do benzyn z wysoką zawartością etanolu w węglowodorach, co z pewnością doprowadzi do poważnych problemów eksploatacyjnych.

Wyzwaniem dla technologów nie jest zatem tylko opracowanie efektywnych dodatków detergentowych przeznaczonych do tych dwóch rodzajów benzyn (węglowodorowej, z niewielką zawartością etanolu, i benzyn wysokoetanolowych), ale rozwiązanie problemów z kompatybilnością i rozpuszczalnością, sprzyjających powstawaniu osadów i nagarów w silnikach eksploatowanych na mieszanym paliwie, co w warunkach eksploatacyjnych jest sytuacją trudną do uniknięcia.

Część doświadczalna

Paliwo wykorzystane w badaniach

Do badań wykorzystano benzynę silnikową, o właściwościach zamieszczonych w tabeli 1, zawierającą 85% (*V/V*) etanolu i 15% (*V/V*) benzyny węglowodorowej. Paliwo przeznaczone do badań silnikowych uszlachetniano przygotowanymi w INiG – PIB formulacjami pakietów dodatków.

Tabela 1. Właściwości fizykochemiczne paliwa bazowego stosowanego do badań

	Wymagania	Wynik badania	Wymagania wg PKNCEN/TS 15293	Metoda badania wg
1.	Gęstość (w temperaturze 15°C) [kg/m^3]	784	760,0–800,0	EN ISO 12185
2.	Okres indukcyjny [min]	>360	min. 360	EN ISO 7536
3.	Zawartość żywic obecnych [mg/100 ml]	<1	maks. 5	EN ISO 6246
4.	Działanie korodujące na płytce miedzianej (3 h w temperaturze 50°C) [klasa]	1A	klasa 1	EN ISO 2160
5.	Całkowita kwasowość (w przeliczeniu na kwas octowy) [% (*m/m*)]	<0,003	maks. 0,005	EN ISO 15491
6.	Przewodność elektryczna [µS/cm]	1,0	maks. 1,5	EN 15938
7.	Zawartość metanolu [% (*V/V*)]	<0,17	maks. 1,0	EN 1601

	Wymagania	Wynik badania	Wymagania wg PKNCEN/TS 15293	Metoda badania wg
8.	Zawartość wyższych nasyconych alkoholi jednowodorotlenowych, (C3–C5) [% (*V*/*V*)]	2,5	maks. 6,0	EN 1601
9.	Zawartość eterów (z pięcioma lub więcej atomami węgla) [% (*V*/*V*)]	<0,17	maks. 11,0	EN 1601
10.	Zawartość wody [% (*m*/*m*)]	0,118	maks. 0,400	EN 15489
11.	Zawartość chlorków nieorganicznych [mg/kg]	<1,0	maks. 1,2	EN 15492
12.	Zawartość miedzi [mg/kg]	<0,05	maks. 0,10	EN 15837
13.	Zawartość fosforu [mg/l]	<0,15	maks. 0,15	EN 15487
14.	Zawartość siarki [mg/kg]	<5,0	maks. 10,0	EN 15486
15.	Zawartość siarczanów [mg/kg]	2,7	maks. 4,0	EN 15492
16.	Prężność par [kPa]	45,2	35,0–60,0 klasa a	EN 13016-1

Badane dodatki

Przygotowane do badań formulacje pakietów dodatków zawierały zsyntezowane w INIG – PIB substancje o właściwościach detergentowo-dyspergujących, oleje nośne (handlowy i zsyntezowany w INiG – PIB) oraz rozpuszczalnik.

Substancje detergentowo-dyspergujące:

DEM 1 – N-alkilowana pochodna benzoksazyny uwodorniona w pierścieniu heterocyklicznym, dodatkowo podstawiona resztą alkilową w pierścieniu aromatycznym.

DEM 2 – diamina, pochodna alkilofenolu, zawierająca struktury II- i III-rzędowej aminy.

Oleje nośne:

Petrotex DF-30 – oksyalkilowany alkilofenol.

Olej nośny CR 10 – toluenodikarbaminian dialkilowy.

Rozpuszczalnik:

Shellsol A150 – rozpuszczalnik aromatyczny.

Pakiety:

NOR 11:

Pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM 1, o strukturze N-alkilowanej pochodnej benzoksazyny uwodornionej w pierścieniu heterocyklicznym, dodatkowo podstawionej resztą alkilową w pierścieniu aromatycznym, oraz syntetyczny olej nośny o strukturze toluenodikarbaminianu dialkilowego i rozpuszczalnik aromatyczny.

NOR 12:

Pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM 2, o strukturze diaminy, pochodnej alkilofenolu, zawierającej struktury II- i III-rzędowej aminy, oraz syntetyczny olej nośny o strukturze toluenodikarbaminianu dialkilowego i rozpuszczalnik aromatyczny.

NOR 15:

Pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM 1, o strukturze N-alkilowanej pochodnej benzoksazyny uwodornionej w pierścieniu heterocyklicznym, dodatkowo podstawionej resztą alkilową w pierścieniu aromatycznym, oraz syntetyczny olej nośny o strukturze oksyalkilowanego alkilofenolu i rozpuszczalnik aromatyczny.

NOR 20:

Pakiet dodatków zawierający substancję detergentowo-dyspergującą DEM 2, o strukturze diaminy, pochodnej alkilofenolu, zawierającej struktury II- i III-rzędowej aminy, oraz syntetyczny olej nośny o strukturze oksyalkilowanego alkilofenolu i rozpuszczalnik aromatyczny.

Metodyka badań

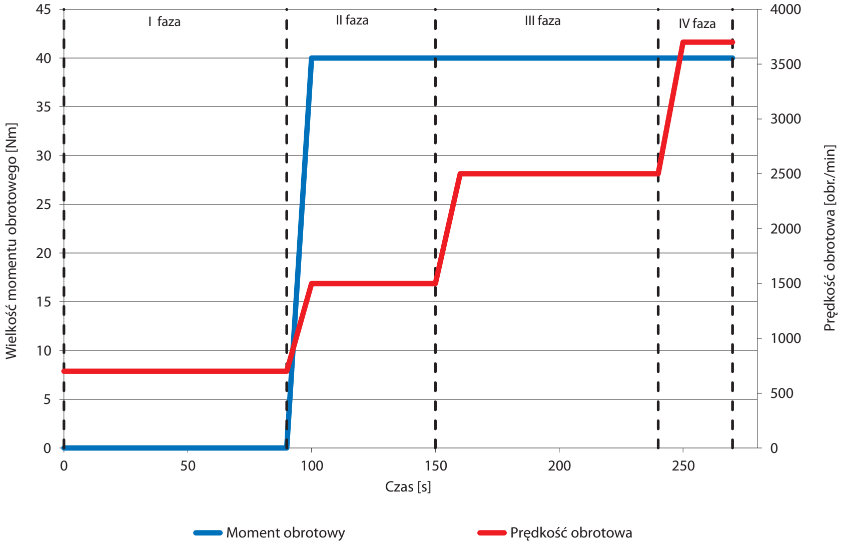
Badania przeprowadzono na stanowisku badawczym z silnikiem typu FlexiFuel (Ford 1.8L Duratec-HE PFI FFV (125PS) MI4) fabrycznie przystosowanym do zasilania biopaliwem o zawartości do 85% (*V/V*) etanolu. W tabeli 2 zamieszczono wybrane parametry techniczne silnika Ford 1.8L.

Tabela 2. Wybrane parametry techniczne silnika Ford 1.8L Duratec-HE PFI FFV (125PS) MI4

Obieg pracy	czterosuwowy, z zapłonem iskrowym
Typ wtrysku paliwa	pośredni wtrysk paliwa sterowany elektronicznie – systemem Visteon
Układ cylindrów	rzędowy, pionowy
Liczba cylindrów	4
Kolejność wtrysku paliwa do cylindra	1–3–4–2
Typ układu rozrządu	DOHC/4 VPC
Średnica cylindra	83,0 mm
Skok tłoka	83,1 mm
Pojemność skokowa	1798 cm^3
Moc maksymalna	125 KM (92 kW) przy 6000 obr./min
Maks. moment obrotowy	165 Nm przy 4000 obr./min
Stopień sprężania	10,8
Średnie zużycie paliwa (E85)	10,5 l/100 km
Luz zaworowy	regulacja hydrauliczna
Pojemność układu smarowania z filtrem	4,3 dm^3
Spełniana norma w zakresie wielkości emisji składników szkodliwych do atmosfery	Euro IV

Silnik połączony był z hamulcem elektrowirowym AVL Alpha 160 z programowanym działaniem, umożliwiającym realizację i powtarzanie różnych sekwencji (cykli) wcześniej przygotowanych testów.

Oceny efektywności opracowywanych pakietów dodatków, pozwalające na weryfikację ich składu i optymalizację poziomu dozowania, prowadzono w symulowanych testach silnikowych. Procedura testowa obejmowała czterofazowy, powtarzalny cykl badawczy symulujący przeciętne warunki pracy silnika podczas eksploatacji pojazdu w ruchu miejskim o małym natężeniu – rysunek 1. Testy były prowadzone przez 100 h poprzez powtarzanie cyklu badawczego.



Rys. 1. Powtarzalny cykl badawczy symulujący warunki pracy silnika podczas eksploatacji pojazdu w ruchu miejskim o małym natężeniu

Wyniki badań

Przeprowadzone badania miały na celu ocenę właściwości detergentowych mieszanek benzyny z wysoką zawartością etanolu w zależności od użytych formulacji pakietów dodatków. Do badań wytypowano pakiety dodatków różniące się zastosowaną substancją detergentową (DEM 1 w pakietach NOR 11 i NOR 15 i DEM 2 w pakietach NOR 12 i NOR 20) oraz wykorzystanym olejem nośnym (CR 10 w pakietach NOR 11 i NOR 12 i DF-30 w pakietach NOR 15 i NOR 20).

W tabeli 3 zamieszczono wyniki przeprowadzonych testów w silniku Ford FlexiFuel (ilości osadów na zaworach dolotowych i w komorach spalania). Światowa Karta Paliw podaje wymagania odnośnie do badanych parametrów (osadów na zaworach dolotowych i w komorach spalania) w silnikach M102E i M111 zasilanych benzyną węglowodorową lub z niską zawartością etanolu (do 10% (*V*/*V*)), natomiast brak jest w niej kryteriów dotyczących paliw wysokoetanolowych. Badania prowadzono zatem w silniku Ford FlexiFuel według własnej metodyki badawczej opracowanej na podstawie procedury badawczej przeznaczonej do badań w silniku Mercedes-Benz M111.

Tabela 3. Wyniki badań eksploatacyjnych w silniku Ford FlexiFuel

NOR 15 (DEM 1 + DF-30 + Shellsol A150)									NOR 20 (DEM 2 + DF-30 + Shellsol A150)								
Nr zaworu	1	2	3	4	5	6	7	8	Nr zaworu	1	2	3	4	5	6	7	8
Masa osadu [mg]	6	10	28	9	19	15	7	7	Masa osadu [mg]	7	11	3	2	6	15	4	8
Średnia ilość osadów – zawory [mg]	12,6								Średnia ilość osadów – zawory [mg]	7,0							
Średnia ilość osadów – komory spalania [mg]	1098								Średnia ilość osadów – komory spalania [mg]	2133							
NOR 11 (DEM 1 + CR 10 + Shellsol A150)									NOR 12 (DEM 2 + CR 10 + Shellsol A150)								
Nr zaworu	1	2	3	4	5	6	7	8	Nr zaworu	1	2	3	4	5	6	7	8
Masa osadu [mg]	1	1	16	5	17	0	3	1	Masa osadu [mg]	15	16	28	20	30	22	15	19
Średnia ilość osadów – zawory [mg]	5,5								Średnia ilość osadów – zawory [mg]	17,2							
Średnia ilość osadów – komory spalania [mg]	3772								Średnia ilość osadów – komory spalania [mg]	1967							

W przypadku zasilania silnika Ford FlexiFuel paliwem E85 uszlachetnionym pakietem zawierającym N-alkilowaną pochodną benzoksazyny (DEM 1) otrzymano, w zależności od zastosowanego oleju nośnego, odpowiednio 12,6 mg osadów na zawór (wynik średni) dla formulacji z DF-30 i 5,5 mg osadów na zawór (wynik średni) dla formulacji zawierającej olej nośny CR 10. W komorach spalania po zakończeniu testu stwierdzono obecność 1098 mg osadów w przypadku silnika zasilanego paliwem zawierającym pakiet z handlowym olejem nośnym DF-30 i 3772 mg osadów w przypadku silnika zasilanego paliwem etanolowym (E85) uszlachetnionym pakietem z zsyntezowanym olejem nośnym CR 10.

Wykorzystanie do badań silnikowych paliwa zawierającego diaminę, pochodną alkilofenolu, (DEM 2) w połączeniu z handlowym olejem nośnym DF-30 spowodowało, że na zaworach dolotowych zgromadziło się średnio 7 mg osadów na zawór, a w komorach spalania 2133 mg osad**ów**. Przy zastosowaniu tego samego dodatku detergentowo-dyspergującego w połączeniu ze zsyntezowanym olejem nośnym CR 10 zaobserwowano średnio 17,2 mg osad**ów** na zawór i 1967 mg osadów w komorach spalania.

W przypadku niektórych testów silnikowych wyliczanie średniej ilości osadów na zaworach może budzić wątpliwości. Przykładowo dla kompozycji NOR 11 na zaworze nr 6 nie zaobserwowano wzrostu masy zaworu spowodowanego występowaniem osadów, natomiast na zaworze nr 3 stwierdzono obecność aż 17 mg osadów. Podobnie w teście, w którym badano pakiet NOR 15, na zaworze nr 6 zidentyfikowano 6 mg osadów, natomiast na zaworze nr 3 aż 28 mg osadów. Rozbieżności w wynikach uzyskiwanych na różnych zaworach wynikają ze specyfiki testów silnikowych, ogromu zmiennych (nie wszystkich możliwych do kontrolowania) wpływających na pracę silnika i konstrukcji silnika.

Omówienie wyników badań

Dokonując analizy otrzymanych wyników, można stwierdzić, że o właściwościach detergentowych decydują łącznie dwa główne składniki formulacji pakietów dodatków: substancja detergentowo-dyspergująca oraz odpowiednio do niej dobrany olej nośny. Przykładowo zastosowanie jednej z badanych substancji detergentowych (N-alkilowana pochodna benzoksazyny) skutkuje mniejszą ilością osadów na zaworach dolotowych w kompozycji z olejem nośnym CR 10, natomiast w przypadku drugiej substancji detergentowo-dyspergującej (diamina, pochodna alkilofenolu) kompozycja z tym samym olejem nośnym (CR 10) daje znacznie gorsze wyniki niż po zastosowaniu oleju DF-30.

Przy komponowaniu pakietów do benzyn nie jest zatem możliwe klasyczne podejście do zestawiania pakietów, jak to ma miejsce np. w przypadku pakietów dodatków uszlachetniających do olejów napędowych, jest to złożona operacja mająca na celu połączenie substancji detergentowo-dyspergującej z odpowiednim olejem nośnym, co daje zadowalające rezultaty.

Na podstawie otrzymanych wyników we wszystkich analizowanych przypadkach zaobserwowano, że jeśli poprzez zmianę jednego ze składników badanych formulacji uzyskuje się poprawę jednego z badanych parametrów (np. ilość osadów na zaworach dolotowych) to równocześnie może nastąpić pogorszenie drugiego analizowanego parametru (ilość osadów w komorach spalania), co powoduje, że wybór najlepszej kompozycji nie jest oczywisty.

Podsumowanie

Benzyny węglowodorowe zawierające do 10% (*V/V*) etanolu uszlachetnione konwencjonalnymi, handlowymi dodatkami detergentowymi wykazują niską tendencję do tworzenia się i gromadzenia osadów na elementach silnika.

Benzyna o zawartości do 85% (*V/V*) etanolu uszlachetniona opracowanym w INIG – PIB dodatkiem detergentowym wykazała niską tendencję do tworzenia się i gromadzenia osadów i nagarów na elementach silnika.

Utrzymując uzyskaną efektywność działania opracowanego dodatku detergentowego w przypadku komór spalania (ok. 1000 mg osadów), należy dążyć do nieco wyższej efektywności w przypadku zaworów dolotowych (obniżenie ilości osadów z wartości 12 mg/zawór do poniżej 5 mg/zawór), co w świetle przeprowadzonych badań wydaje się realne. Konieczna jest dalsza optymalizacja składu i poziomu dozowania pakietu.

Problem wzajemnej kompatybilności uszlachetnionych odpowiednimi dodatkami detergentowymi benzyn o niskiej i wysokiej zawartości etanolu wymaga dalszych badań.

Wysoką skutecznością w zakresie właściwości detergentowych odznaczały się dodatki NOR 15 i NOR 20 podczas testu silnikowego zasilanego benzyną etanolową E85.

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Literatura

[1] Pałuchowska M., Stępień Z., Żak G.: *Perspektywy wykorzystania etanolu jako składnika paliwa i jego potencjał w redukcji emisji szkodliwych składników spalin*. Combustion Engines 2014, vol. 158, no. 3, s. 80–92.

[2] Worldwide Fuel Charter, Fifth Edition, September 2013.

[3] Bennett J.: *Advanced fuel additives for modern internal combustion engines*. [W:] R. Folkson (ed.): *Alternative Fuels and Advanced Vehicle Technologies for Improved Environmental Performance*. 2014, s. 165–194.

[4] Johansen L. C. R, Hemdal S.: *In cylinder visualization of stratified combustion of E85 and main sources of soot formation.* Fuel 2015, vol. 159, s. 392–411.

[5] Xu H., Wang Ch., Ma X., Sarangi A. K., Weall A., Krueger-Venus J.: *Fuel injector deposits in direct-injection spark-ignition engines.* Prog. in Energy and Comb. Sci. 2015, vol. 50, s. 63–80.

[6] DuMont R. J.: *Test and Control of Fuel Injector Deposits in Direct Injected Spark Ignition Engines*. SAE Technical Paper 2009-01-2641, 2009.

[7] Demirbas A.: *Bioalcohols as Alternatives to Gasoline*. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 2009, vol. 31, no. 12, s. 1056–1062.

[8] Frazier R. S.: *Ethanol Gasoline Blends – Problems or Benefits for Customers?* Energy Engineering 2008, vol. 106, no. 1, s. 62–70.

Non-Legislated Emissions of SI Passenger Car with Ethanol Blend Fuels E10 & E85

Nieregulowne emisje silników samochodów osobowych o zapłonie iskrowym zasilanych mieszankami paliw E10 i E85

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Abstract

The well-balanced use of alternative fuels worldwide is an important objective for the sustainable development of individual transportation.

Several countries have set objectives to substitute a part of the energy of traffic by ethanol as the renewable energy source.

The global share of Bioethanol used for transportation is continuously increasing.

Investigations of limited and unregulated emissions of a flex fuel vehicle with gasoline-ethanol blend fuel, have been performed in the present work according to the measuring procedures, which were established in the previous research, in the Swiss Network.

The investigated fuel contained ethanol (E), in portions of 10% and 85% by volume.

The investigated vehicle represented a newer state of technology and an emission level of Euro 5. The engine works with homogenous GDI concept and with 3-W-catalyst (3WC).

Since there is special concern about particle emissions of gasoline cars with direct injection, the nanoparticle counts measurements were systematically performed with Scanning Mobility Particle Sizer (SMPS) at stationary and with Condensation Particle Counter (CPC) at dynamic operation.

The non-legislated gaseous emissions were tested with Fourier Transform Infrared Spectroscopy (FTIR), with special focus on NH_3, N_2O and HCHO (Formaldehyde).

The main results to be mentioned are:

- the particle counts emissions are generally significantly reduced with Ethanol blend fuels at all operating conditions,
- in Worldwide Light-duty Test Cycle (WLTC) there is a clear increase of NH_3 with E85 and an insignificant tendency of increasing NH_3 with E10,
- with all fuels (E0, E10 & E85) there are no emissions of N_2O and no increase of HCHO (below 1 ppm) observed, in WLTC warm.

The present research did not address the durability aspects and cold startability in extreme conditions.

Gasoline/Ethanol operation – state of the art

The progress of development of very powerful and reliable electronic control systems in the last 20 years has enabled the introduction of Flex Fuel Vehicles (FFV) on the market. A FFV can be operated with fuel mixtures gasoline-Ethanol up to E85. The engine's electronic control unit recognizes automatically (by means of an Ethanol-sensor, [1]) the portion of Ethanol and adapts the parameterization of the engine, respectively to obtain the desired performances, and the emissions below the legal limits.

Several manufacturers introduced the FFV variants and published extensive information about their R&D and performances: GM / Saab [2, 3]; Toyota [4]; VW [5].

The durable operation with Ethanol needs several precautions: improvements of materials and surfaces of combustion chamber parts, all plastic materials having contact with fuel, fuel and injection system, functions of the electronic control of the engine, problems of lube oil degradation, [6–8], deposits formation, [9, 10] and cold startability [11].

Cold start and especially winter cold start, is more difficult with higher Ethanol content in the fuel. The solutions are: double-tank-system (Brasilian market), or electrical preheating of engine and of the fuel system (EU and US markets).

Several research institutes have been investigating the potentials of modern combustion systems, like stratified or downsized concepts, with Ethanol, [12–14]. There also are standard emissions measurements, [15, 16].

Non-legislated emissions of gasoline cars

The most important non-legislated emission components in present discussions are: the nanoparticles (NP), Ammonia (NH_3), nitrous oxide (N_2O) and Formaldehyde (HCHO).

In all previous research with Ethanol the questions of nanoparticle emissions NP were not addressed, since the particle emissions of spark ignition (SI) engines were not a legal topic.

This situation has changed with the first introduction of legal nanoparticle counts limits (Euro 5b) since the beginning of 2013.

In this new situation the NP and especially the metal oxides emissions from additive packages of lube oils and fuels, have become an important topic for all kinds of engines. The NP-emission also originates from lube oil and is increased particularly at cold start [17, 18, 19]. There is a necessity for an investigation into these new aspects with Ethanol blend fuels Exx.

Production of Ammonia (NH_3) in the exhaust of gasoline cars with 3WC was demonstrated in [20] and [21] – especially at transient operation with rich excursions of Lambda. The other components mentioned (N_2O & HCHO) were less investigated in connection with E85-operation.

Test vehicle and fuels

The tests were performed with a new (Euro 5) flex fuel vehicle, Volvo V60 (GDI), which is a reference vehicle for several projects concerning NP-research from gasoline engines, Fig. 1 & Tab. 1.

Figure 1. Gasoline vehicle (FFV) for research with E10 & E85

Table 1. Data of test vehicle Volvo V60

Vehicle	Volvo V60 T4F
Engine code	B4164T2
Number and arrangement of cylinder	4 / in line
Displacement cm^3	1596
Power kW	132 @ 5700 rpm
Torque Nm	240 @ 1600 rpm
Injection type	DI
Curb weight kg	1554
Gross vehicle weight kg	2110
Drive wheel	Front-wheel drive
Gearbox	a6
First registration	27.01.2012
Exhaust	EURO 5a

Fuels

The gasoline used was from the Swiss market, RON 95, according to SN EN228. For the tests a charge of fuel was purchased to keep the composition of the fuels always unchanged.

As further variants of fuels E10 and E85 were used. These are respectively blends with: 90% vol. gasoline and 10% vol. Ethanol, or with 15% vol. gasoline and 85% vol. Ethanol. Table 2 summarizes the most important parameters of the fuels.

Table 2. Parameters of used fuels

		Gasoline	Ethanol C_2H_5OH	E10	E85
density 15°C	[g/cm^3]	0.737	0.789	0.742	0.781
stoichiometric air/fuel ratio	[-]	14.6	9.0	14.0	9.8
lower calorific value	[MJ/kg]	43.0	26.8	41.3	28.9
boiling point	[°C]	30-200	78.5		
research octane Nbr.	[-]	95	110		
latent heat of evaporation	[kJ/kg]	420	900		
oxygen content	[%m]	<5	34.8		

Instrumentation

The tests were performed on a chassis dynamometer (Schenk 500 G5 60) with CVS-system (Horiba CVS-9500 T) and with the exhaust gas measuring system for legislated components (Horiba MEXA-9400H).

The non-legislated gaseous components were analyzed with FTIR.

FTIR (Fourier Transform Infrared) Spectrometer (AVL SESAM) offers the possibility of simultaneous, time-resolved measurement of approx. 30 emission components – among others: NO, NO_2, NO_x, NH_3, N_2O, HCN, HNCO, HCHO.

Nanoparticles were measured at stationary operation with SMPS (particle size distributions) and at transient operation with CPC (summary particle counts) – SMPS: DMA TSI 3081 & CPC TSI 3772 (9.8–429 nm).

For the dilution and sample preparation an ASET system from Matter Aerosol was used, (ASET… aerosol sampling & evaporation tube). This system contains:

- Primary dilution air – MD19 tunable minidiluter (Matter Eng. MD19-2E)
- Secondary dilution air – dilution of the primary diluted and thermally conditioned measuring gas on the outlet of evaporative tube.
- Thermoconditioner (TC) – sample heating at 300°C

Test procedures

The vehicle was tested on a chassis dynamometer in the dynamic driving cycles (WLTC) and at constant speeds (SSC). The braking resistances were set according to legal prescriptions i.e. responding to the horizontal road.

Driving cycles

In terms of the driving cycles, an approach to find a homogenized world-wide driving cycle was successfully finished, with the development of the homogenized WLTP world-wide light duty test procedure. The WLTC (world-wide light duty test cycle) should represent typical driving conditions around the world and was developed based on a combination of collected in-use data and suitable weighting factors by an expert group from China, EU, India, Japan, South Korea, Switzerland and USA. This cycle has been used also in this study, Fig. 2. It represents different driving situations, like city, over-land and speed-way.

The steady state cycle (SSC) consists of 20 min-steps at 95, 61, 45, 26 km/h and idling, performed in the sequence from the highest to the lowest speed.

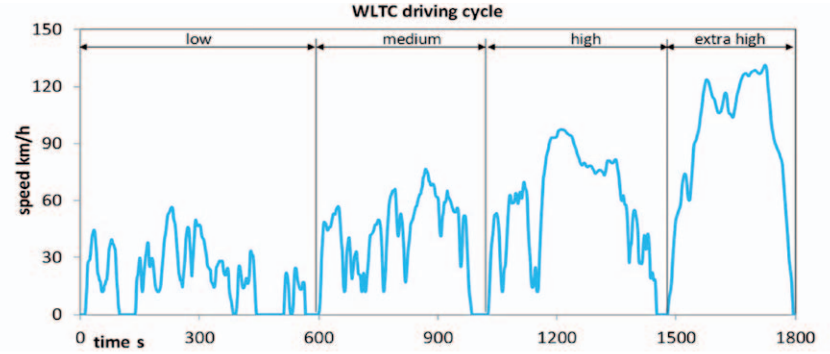

Figure 2. WLTC driving cycle

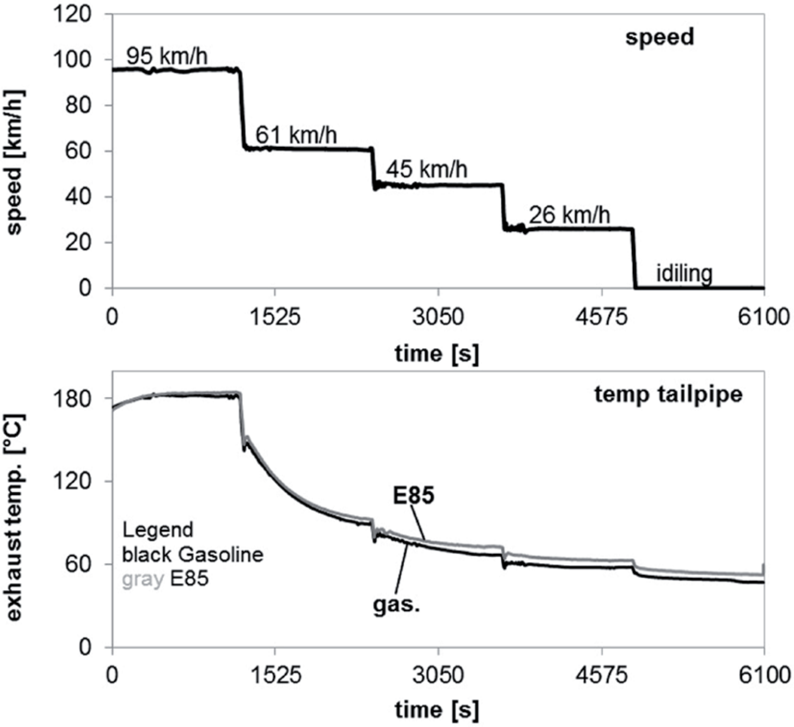

Figure 3. SSC steady state cycle and tailpipe temperature Volvo V60 T4F; 3WC

Results – stationary operation

Fig. 3 shows the steady state cycle (SSC) with the resulting tailpipe temperatures for gasoline & E85.

Fig. 4 represents the respective SMPS particle size distributions in all steps. The drastic reduction of NP count concentrations with E10 & E85 is demonstrated. It is interesting to note, that already the lower Ethanol content (E10) contributes significantly to the reduction of PC-concentrations at all driven vehicle speeds.

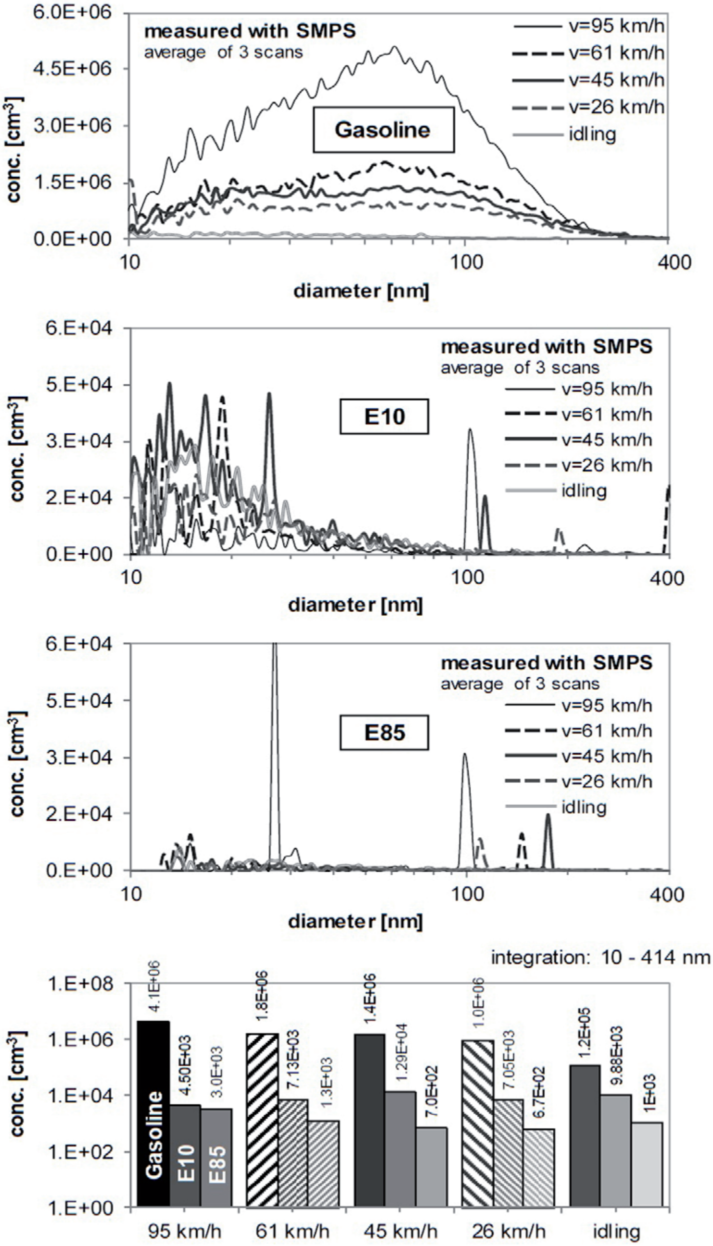

Figure 4. Particles size distributions (PSD) and integrated particle counts during the driving cycle SSC Volvo V60 T4F; 3WC

Results – dynamic operation

A comparison of emission time-plots in WLTC is given in Fig. 5. for legislated and in Fig. 6 for non-legislated components with two extreme variants of fuel E0 & E85.

In the time-intervals of acceleration, peaks of CO, CPC (NP) and sometimes of NO_x can be observed. Increase of CO & NP is a result of mixture enrichment and increase of NO_x is caused by Lambda-excursion to the lean domain (poor NO_x-conversion in the 3WC).

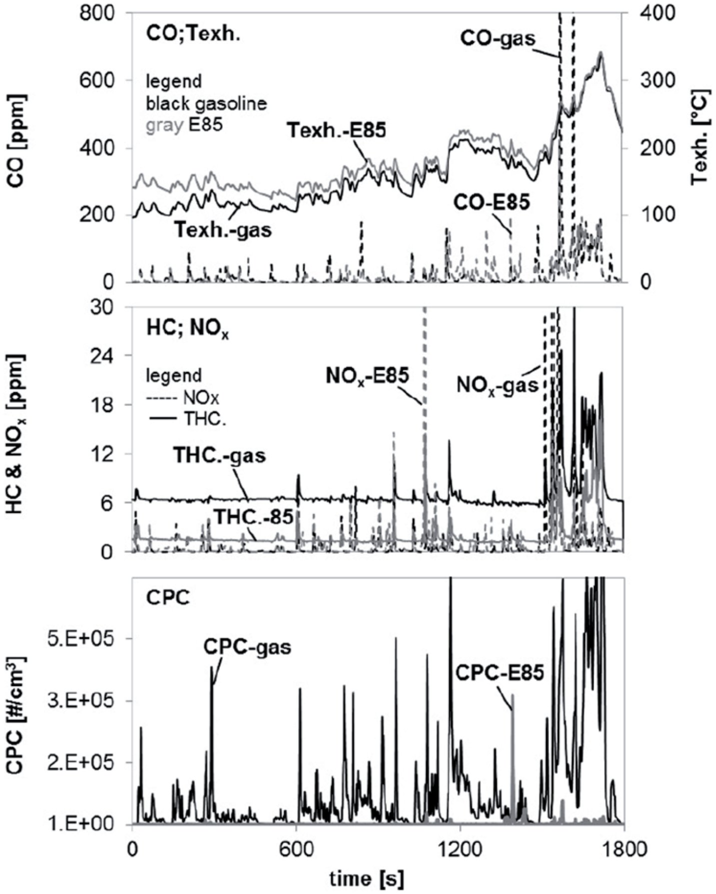

Figure 5. Particle counts, diluted exhaust emissions and exhaust gas temperature in WLTC warm, gasoline & E85

The more dynamic and power-demanding cycle parts cause more frequent and more pronounced CO-(enrichment) peaks.

With E85 there is higher level of t_{exh} at lower speeds and lower level of NO_x and of NPs, than with gasoline. There are remarkable concentrations of NH_3 from some 3 ppm to the short peaks up to 120 ppm. A repetition of WHTC with E85 shows the fluctuation of NH_3-results.

The concentrations of Formaldehyde HCHO with both fuels are very low (below 1 ppm) and the influence of a fuel cannot be seen. With both fuels there are no emissions of N_2O observed.

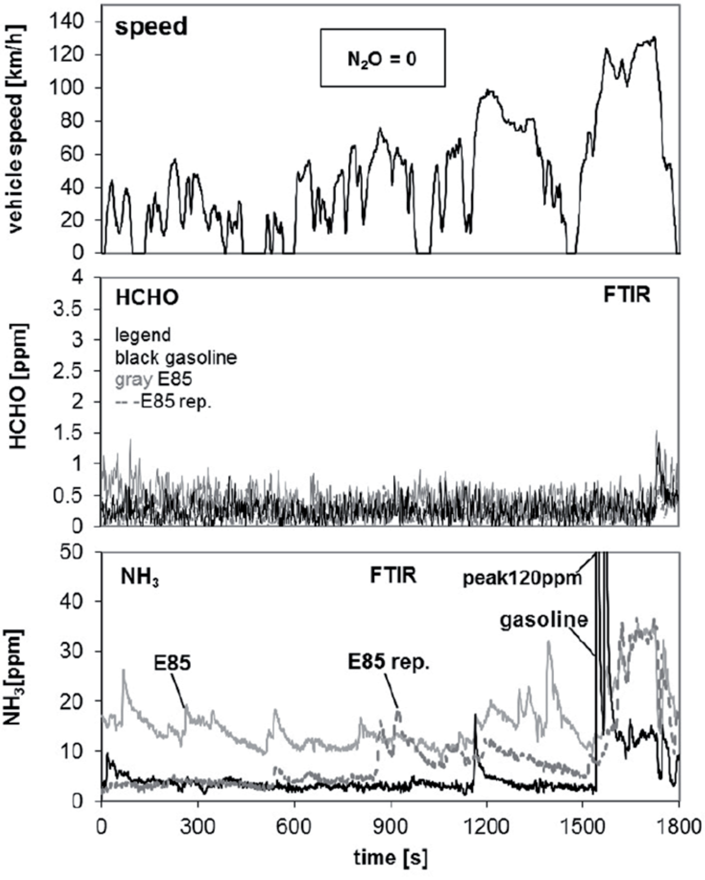

Figure 6. N_2O, HCHO and NH_3 emissions in WLTC warm, with gasoline & E85 Volvo V60 T4F; 3WC; raw exhaust measurement

The following Fig. 7 gives the comparisons of average emission values from the operation with gasoline, E10 and E85 in WLTC warm.

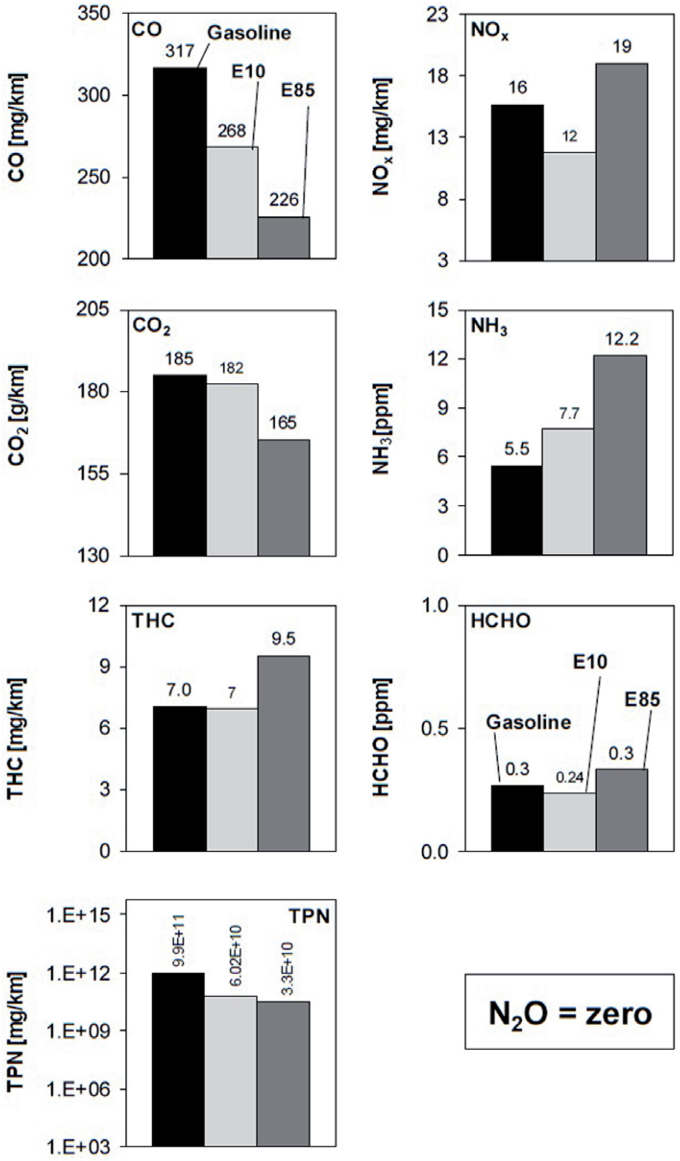

Figure 7. Average emissions in WLTC warm, with gasoline E10 & E85 Volvo V60 T4F, 3WC

The particle counts emissions are generally significantly reduced with Exx (more than 1 order of magnitude). There is a clear increase of NH_3 with E85 and an insignificant tendency of increasing NH_3 with E10.

There are no significant emissions and no increasing tendencies of average values HCHO (at a level of fraction of ppm).

CO-emissions are clearly reduced with increasing Exx-content. For HC- & NO_x no monotonous tendencies with E10 & E85 are visible. It can be stated, that with E10 there are no changes of HC & NO_x, but with E85 a slight increase of these compounds is remarkable. This nevertheless, especially NO_x is dependent very much on the electronic control of this FFV and the indicated differences of a few [ppm] can also be an effect of emitting dispersion.

Conclusions

With the present flex fuel vehicle there are the following influences of E85 on emissions in comparison with E0 and E10:

Stationary operation

- clear reduction of summary PCs after switching the fuel from gasoline to E10 & E85,
- no distributions (PSD), but only sporadic NP-peaks with E85 at all stationary operating points.

Dynamic cycles

- in the time-intervals of acceleration, peaks of CO, CPC (NP) and sometimes of NO_x can be observed,
- in higher-speed cycles there is mostly higher CO with E85,
- the particle counts emissions are generally significantly reduced with E10 & E85,
- in WLTC there is a clear increase of NH_3 with E85 and an insignificant tendency of increasing HCHO (below 1 ppm),
- emissions of NH_3 in the same cycle are fluctuating,
- with all fuels (EO, E10 & E85) there are no emissions of N_2O observed.

Regarding the results it might be kept in mind, that several influences of the ECU on the parameterization of the engine after a change of fuel, like setting of spark advance, injection timing or strategy and positioning of Vario Cams are not known.

Definitions/Abbreviations

AFHB	Abgasprüfstelle der Fachhochschule Biel, CH
ASET	Aerosol Sampling & Evaporation Tube
ASTRA	Amt für Strassen (CH)
BAFU	Bundesamt für Umwelt, (FOEN)
BfE	Bundesamt für Energie (FOE)
CADC	Common Artemis Driving Cycle
CLA	chemiluminescent analyzer
CLD	chemiluminescent detector
CPC	condensation particle counter
CS	cold start
CVS	constant volume sampling
DF	dilution factor
DI	Direct Injection
DMA	differential mobility analyzer
ECU	electronic control unit
EMPA	Eidgenössische Material Prüf- und Forschungsanstalt
EUDC	Extra Urban Driving Cycle
EV	Erdöl Vereinigung
FFV	flex fuel vehicle
FOE	Federal Office of Energy
FOEN	Federal Office of Environment
FTIR	Fourier Transform Infrared analyzer
HC	unburned hydrocarbons
HCHO	Formaldehyde
HCN	Hydrocyanic Acid
HNCO	Isocyanic Acid
INIG – PIB	Instytut Nafty i Gazu – Państwowy Instytut Badawczy, Krakow, PL
MD	minidiluter

MS	mass spectroscopy
NO	nitrogen monoxide
NO_2	nitrogen dioxide
N_2O	nitrous oxide
NH_3	Ammonia
NO_x	nitric oxides
NP	nanoparticles< 999 nm
OBD	on-board diagnostics
PC	particle counts (integrated)
PMP	Particle Measuring Program of the GRPE
PN	particle numbers
PSD	particle size distribution
SMPS	scanning mobility particle sizer
SP	sampling position
TC	thermoconditioner
TPN	total particle number
TTM	Technik Thermische Maschinen, Niederrohrdorf, CH
TWC	three way catalyst
ULSD	ultra low sulphur Diesel
VSS	Verband der Schweizerischen Schmierstoffindustrie
WLTC	worldwide harmonized light duty test cycle
WLTP	worldwide harmonized light duty test procedure
3WC	three way catalyst

References

[1] Fahrenbruch, A.; Bachmann, J.: Ethanolsensoren für den Flex-Fuel-Betrieb. MTZ Sept. 2008. p. 732.

[2] Bergström, K.; Melin, S.-A.; Jones, C.: The New ECOTEC Turbo BioPower Engine from GM powertrain – Utilizing the Power of Nature's resources. 28. Internationales Wiener Motoren-Symposium 2007, Bd.2, p. 47.

[3] Bergström, K.; Nordin, H.; Königstein, A.; Marriott, C.; Wiles, M.: ABC – Alcohol Based Combustion Engines – Challenges and Opportunities. 16. Aachener Kolloquium Fahrzeug- und Motorentechnik 2007, Bd.2, p. 1031.

[4] Kawai, T.; Tsunooka, T.; Chiba, F.; Uda, H.; Sonoda,Y.: Effect of High Concentration Ethanol on SI Engine Cold Startabillity and Emissions. 16. Aachener Kolloquium Fahrzeug- und Motorentechnik 2007, Bd.2, p. 1075.

[5] Hadler, J.; Szengel, R.; Middendorf, H.; Sperling, H.; Gröer, H-G.; Tilchner, L.: Der 1.4l 118kW TSI für E85 Betrieb – die Erweiterung der verbrauchsgünstigen Ottomotorenlinie von Volkswagen. 32. Internationales Wiener Motorensymposium 2011, Bd.1, p. 263.

[6] Schwarze, H.; Brouwer, L.; Knoll, G.; Longo, C.; Kopnarski, M.; Emrich, S.: Auswirkung von Ethanol E85 auf Schmier-stoffalterung und Verschleiss im Ottomotor. MTZ April 2010, p. 286.

[7] Artmann, Ch.; Rabl, H-P.; Faulstich, M.: Online-Ermittlung der Schmierölverdünnung bei Ottomotoren. MTZ Januar 2012, p. 70.

[8] Küpper, C.; Artmann, Ch.; Pischinger, S.; Rabl H-P.: Schmierölverdünnung von direkteinsprit-zenden Ottomotoren unter Kaltstartrandbedingungen. MTZ 09/2013, S.710

[9] DuMont, R. J.; Cunningham, L. J.; Oliver, M. K.; Studzinski, W. M.; Galante-Fox, J. M.: Controlling Induction System Deposits in Flexible Fuel Vehicles Operating on E85. SAE Technical Paper 2007-01-4071, Rosemont, Illinois, 2007.

[10] Galante -Fox, J. M.; Von Bacho, P.; Notaro, C.; Zizelman, J.: E-85 Fuel Corrosivity: Effects on Port Fuel Injector Durability Performance. SAE Technical Paper 2007-01-4072, Rosemont, Illinois, 2007.

[11] Greff, A.; Brandl, A.; Schulze, T.; Kapphan, F.: Extended range of optimal combustion in flex-fuel operation. MTZ September 2011, p. 668.

[12] Smith, J. D.; Sick, V.: The Prospects of Using Alcohol-Based Fuels in Stratified-Charge Spark-Ignition Engines. SAE Technical Paper 2007-01-4034, Rosemont, Illinois, 2007.

[13] Weinowski, R.; Sehr, A.; Rütten, O.; Thewes, M.; Nijs, M.: Impact of the Ethanol Fuel Content on Operation Parameters of Passenger Car Gasoline Engines. 17. Aachener Kolloquium Fahrzeug- und Motorentechnik 2008, Bd.1, p. 385.

[14] Schwaderlapp, M.; Adomeit, Ph.; Kolbeck, A.; Thewes, M.: Ethanol und sein Potenzial für Downsizing-Motorenkonzepte. MTZ Februar 2012, p. 120

[15] Bielaczyc, P.; Klimkiewicz, D.; Szczotka, A.; Woodburn, J.: A Comparison of the Exhaust Emission of a Vehicle Fuelled with Different Ethanol-Petrol Blends. Journal of the Polish Scientific Society of Combustion Engines, ISSN / 0138-0346, No. 2/2012 (149) p, 57. PTNSS-2012-SS2-107.

[16] Lomankiewicz, D.; Brodzik, K.; Bielaczyc, P.: GC-MS/FID Analysis of Aldehyde and Hydrocarbon Emissions from Exhaust Gases of a Spark Ignition Engine Fueled with Different Ethanol-Gasoline Blends. Journal of the Polish Scientific Society of Combustion Engines, ISSN / 0138-0346, No. 2/2012 (149) p, 30. PTNSS-2012-SS2-104.

[17] Chan, T.W.; Meloche, E.; Kubsh, J.; Brezny, R.; Rosenblatt, D.; Rideout, G.: Impact of Ambient Temperature on Gaseous and Particle Emissions from a Direct Injection Gasoline Vehicle and its Implications on Particle Filtration. SAE Technical Paper 2013-01-0527, Detroit, April 2013.

[18] Sonntag, D. B.; Bailey, Ch. R.; Fulper, C. R.; Baldauf, R.W.: Contribution of Lubricating Oil to Particulate Matter Emissions from Light-Duty Gasoline Vehicles in Kansas City. Environment Science & Technology, 27. Febr. 2012.

[19] Porter, S.: Particle Number Emissions of Gasoline Hybrid Electric Vehicle. MTZ 04/2012.

[20] Heeb, N.; Forss, A-M.; Brühlmann, S.; Lüscher, R.; Saxer, Ch.; Hug, P.: Three-Way Catalyst-Induced Formation of Ammonia – Velocity- and Acceleration-Dependent Emission factors. Elsevier, Atmospheric Environment, 40 (2006) 5986-5997.

[21] Heeb, N.; Saxer, Ch.; Forss, A-M.; Brühlmann, S.: Trends of NO-, NO_2-, and NH_3--Emissions from Gasoline-Fueled Euro-3- to Euro-4-Passenger Cars. Elsevier, Atmospheric Environment, 42 (2008) 2543-2554.

[22] Czerwinski, J.; Comte, P.; Reutimann, F.; Makkee, M.: Emissions of 2-Stroke Scooter with Ethanol Blends. SAE Technical Paper 2009-24-0143, Detroit, April 2009.Technical Paper 2011-01-2428, 2012, doi:10.4271/2011-01-2428.

Exhaust Emissions from Light Duty Vehicles Running on Petrol Ethanol Blends Measured under Laboratory Conditions

Emisja z silników samochodów osobowych i dostawczych zasilanych mieszankami benzyna-alkohol mierzona w warunkach laboratoryjnych

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Abstract

Ethanol is widely used in petrol-ethanol blends, including in the European Union. Since the fuel type has a great impact on emissions, blends of differing ethanol content can have a great impact on exhaust emissions. This paper presents a variety of data on regulated and unregulated exhaust emissions from European vehicles running on various petrol-ethanol blends tested under laboratory conditions at BOSMAL. Some fundamental phenomena are discussed and the reader is directed to sources of further information. Furthermore, some brief comparisons to other studies are made and general comments are made on emissions trends regarding petrol-ethanol blends.

Keywords: alternative fuel, ethanol, ethanol blend, emission, SI engine

Introduction

Ethanol an automotive fuel and fuel blend component

While the concept itself is not new, in recent years there has been growing interest in using ethanol as a fuel for spark ignition (SI) engines, particularly those fitted to passenger cars and other light-duty vehicles. Indeed, all standard petrol sold in the EU now contains at least 5% ethanol (by volume). When used as an automotive fuel, ethanol is most commonly splash blended with petrol to create blends such as E5, E10, E15, etc. The highest commonly used blend is E85, which is suitable for use only in specially adapted vehicles. The use of lower blends in unmodified vehicles has been the subject of intensive research efforts over the last 10–15 years.

The potential for fuel chemistry to affect engine operation and emissions is very well known. In the case of ethanol blends, this relationship is particularly interesting for two main reasons: firstly, the proportion of ethanol in ethanol blends is non-trivial, normally being *at least* a few % (by volume); secondly, the physicochemical characteristics of ethanol are very different from those of the majority of compounds which make up 'standard' petrol. Based on these two facts, the potential for ethanol blends to have a substantial impact on exhaust emissions is evident and the motivation for performing emissions testing is self-explanatory.

On the investigation of emissions from SI engines running on ethanol blends

The standard approach for determining exhaust emissions under laboratory conditions is to use the standard 'legislative' test method, using a chassis dynamometer, a constant volume sampler and special sample bags for collection of exhaust gas. Figure 1 shows such a setup, with an emissions testing system together with a chassis dynamometer.

A certain amount of research has been performed on the usage of ethanol blends at lower ambient temperatures. The climatic chamber shown in Figure 1 shows how the entire vehicle can be tested at a range of ambient temperatures.

Legislative testing is based on the prescribed driving cycle for a given piece of legislation, which differs from jurisdiction to jurisdiction. However, in the EU the most commonly used cycle is the new European Driving Cycle (NEDC) – although recent changes mean that this cycle will most likely be replaced soon.

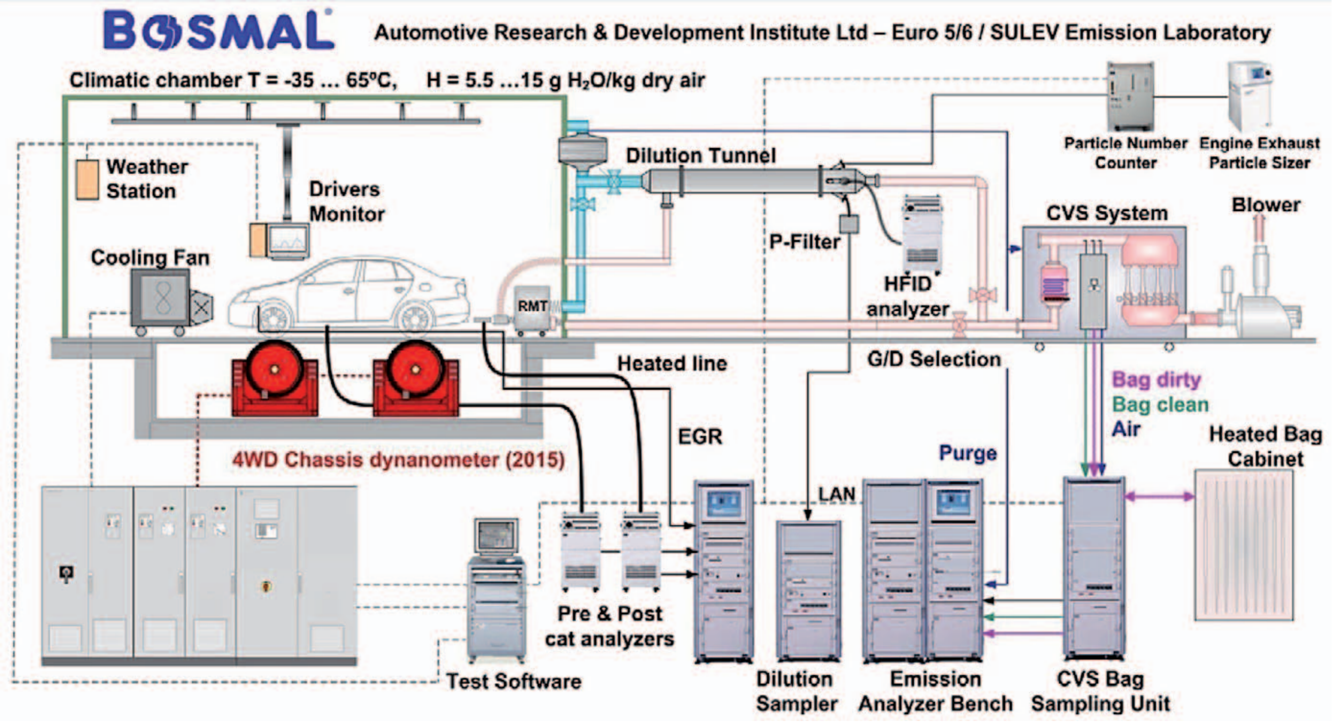

Figure 1. BOSMAL’s climate controlled Euro 5/6 / SULEV exhaust emissions laboratory as an example of a test facility for investigating a wide range of emissions from vehicles

Legislative testing produces results at low resolution, since limits are set per test. Additional analysers of the type shown in Figure 1 can be used to measure continuous emissions – both at the vehicle's tailpipe (exhaust or post-cat) and upstream of any TWC aftertreatment device (engine out or pre-cat).

In general, where emissions from ethanol blends are concerned, agreement between studies (and even between vehicles within the same study) can be relatively low. In addition to this, a wide range of results is typically observed, even in a laboratory environment; outlying data and exceptions to the rule are common [1]. Even where data from relatively large numbers of vehicles are considered, data distributions tend to be non-normal and results may or may not be statistically significant [1, 2]. Caution must be exercised in the extrapolation of results, as geometrically opposed trends have been observed, even under what appear to be very similar test conditions. Results presented in studies featuring a single test vehicle must be treated in a different way to studies conducted on larger samples. Hot start test cycles may be unable to differentiate between the emissions performance of ethanol blends with any real certainty. Furthermore, legislative cycles in general may be poor representations of the real-world performance of ethanol blends. However, standard laboratory techniques are for the most part appropriate for measuring emissions from ethanol blends, with the possible exception of certain types of organic molecules.

Regulated exhaust emissions

Regulated emissions can be defined as emissions for which limits exist in the EU's Euro 6 standard (namely HC, NMHC, CO, NO_x for all SI vehicles and particle mass and number (PM and PN) for SI vehicles featuring direct injection engines), in addition to CO_2 (subject to fleet average limits and covered under separate legislation). For legal purposes, emissions of the aforementioned compounds are quantified by testing a vehicle on a chassis dynamometer under laboratory conditions. At this point it is worthwhile identifying two broad categories of study: some studies have examined the effect of ethanol-petrol blends on regulated exhaust emissions from *unmodified* passenger cars; multiple authors have also reported on results obtained using vehicles with engines specially designed to enable usage of ethanol blends E0-E85 (termed 'Flex-Fuel Vehicles', FFVs).

A large number of studies have reported on the effect of using petrol-ethanol blends in unmodified vehicles – indeed the number of studies has become so large that numerous meta-analyses have been carried out to try and make sense of the available data. Due to start-up difficulties, drivability issues and material compatibility concerns, higher ethanol blends are not routinely tested in non-FFV engines. Most work has focused on the E5, E10, E15, E20, E25, E30 and E50 blends, although other blends have been investigated (E3, E6, E12, E40, etc). However, there are exceptions: e.g. [3–5]), tested E85 in an unmodified non-FFV; while execution of the NEDC under laboratory conditions was possible, some drivability issues were encountered and large excess emissions of HC were reported during the UDC.

Using unmodified small-displacement European passenger cars running over the NEDC, Bielaczyc and co-authors [3–6] present a range of data on regulated emissions, CO_2 and fuel consumption. In the 2011 study, as ethanol content increased from 5% to 50%, monotonic (if modest) decreases in exhaust emissions HC and CO were observed (see Figure 3); NO_x changed relatively little up to E25. A follow-up study [4] presented modal emissions data as well as showing that HC emissions were numerically close for blends E5, E10 and E25 and that the impacts on emissions were non-linear over the E5-E85 range. The 2012 study (6) presented regulated emissions alongside an analysis of unregulated emissions and failed to find any correlation between HC and CO emissions performance. The most recent study [5] confirmed some of these previous findings and concluded that for the test vehicle employed changes in regulated emissions were generally limited for ethanol blends up to E25.

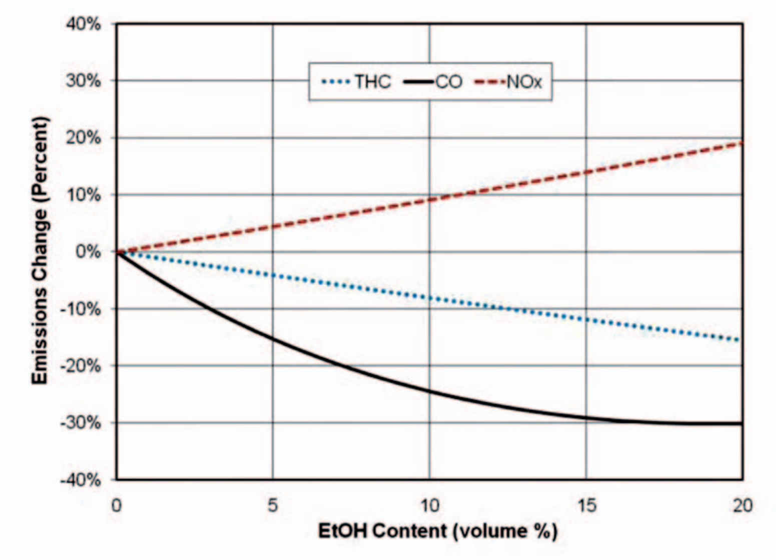

Figure 2. Trends of emissions of THC, CO and NO_x over the range E0-E20. Note that the figure shows trends, rather than raw results. Taken from [7]

In terms of the literature consensus, Crawford and co-authors [7] present an analysis of data obtained from testing modern vehicles for the E0-E20 range, shown in Figure 2. The decrease for THC and the increase for NO_x are linear; the logarithmic decrease for CO implies the onset of diminishing returns at 10%–15% v/v ethanol.

As suggested by Figure 2, one controversial area regarding the emissions performance of ethanol blends concerns increases in emissions of oxides of nitrogen. Any failure to adequately adjust the mixture to maintain stoichiometry would cause the oxygen in the fuel to create a lean mixture **($\lambda>1$), which would have a significant im**pact on the reduction of NO_x in the catalytic converter. Particularly for non-FFV test vehicles, at higher loads the injectors may be unable to deliver enough fuel to maintain a stoichiometry conducive to effective NO_x emission control. Here it should be evident that the driving cycle chosen for emissions testing can have a large impact on the NO_x exhaust emission results.

On the other hand, there are certain theoretical reasons to expect exhaust emissions of NO_x to decrease with increasing ethanol content, as long as the NO_x reduction effectiveness of the aftertreatment system is not compromised (briefly discussed in [3]). This trend was in fact observed in [3].

Since CO_2 is always measured when performing automotive emissions testing, most emissions studies report CO_2 emissions and fuel consumption results. The chemistry and density of ethanol is sufficiently different from that of standard petrol that the carbon balance formula must be adapted. Two opposing effects exist: the carbon weight fraction of E85 is much lower than that of E0 (so CO_2 emissions should be lower), but the energy content of E85 is also lower (so a greater quantity of fuel should be required to obtain the same power output from the engine). These two counteracting effects mean that differences in CO_2 emissions are limited. For fuel consumption, on the other hand, the controlling factor appears to be the energy density of the blend in question. A study investigating fuel consumption for blends up to E85 on an unmodified passenger car [3] showed that fuel consumption increased in direct proportion to the decreasing energy content of the blend, but the highest blend (E85) caused significant 'excess' fuel consumption, due to combustion difficulties (reflected in high HC and CO emissions – see Figure 3), as shown in Figure 4. This same trend we later re-confirmed [5].

Regarding FFVs running on high ethanol blends (typically E85), Yanowitz & McCormick [1] reviewed a wide range of data to arrive at conclusions on the relative change in emissions resulting from usage of E85 compared to standard petrol in FFVs and non-FFV vehicles. The authors concluded that E85 in FFV caused NMHC emissions to reduce by 10%, CO by 10%, NO_x by 18% and CH4 emissions to increase by around 100%.

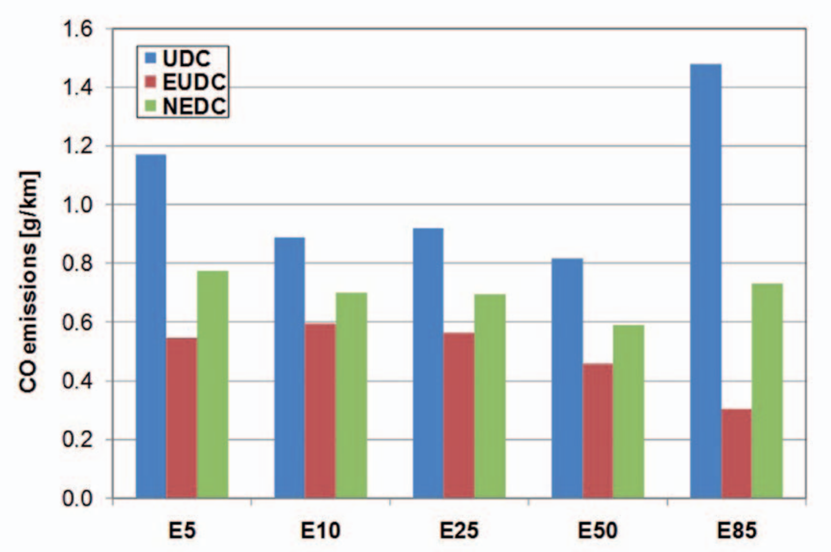

Figure 3. Exhaust emissions of CO from an unmodified car running over the NEDC on various ethanol blends [3]

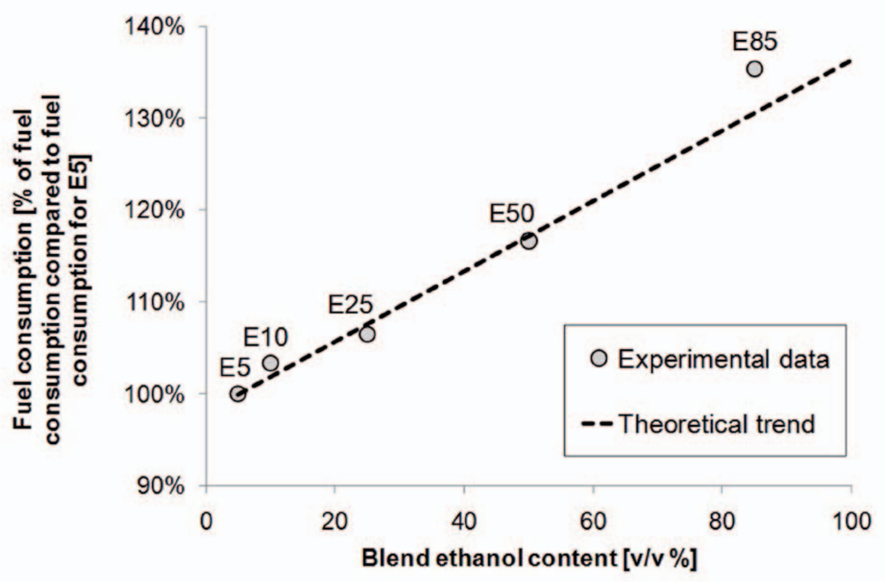

Figure 4. Fuel consumption for an unmodified car running over the NEDC on various ethanol blends [3]

Exhaust emissions of particulate matter

Vehicles featuring direct injection SI engines (SIDI) have been subject to mass-based PM emissions limits since the entry into force of the Euro 5 standard. Following the introduction of a particle number limit for vehicles featuring compression ignition (Diesel) engines, a particle number limit for SIDI vehicles has been confirmed for Euro 6 (Commission Regulation (EU) No 459/2012), to be followed by a limit an order of magnitude more stringent limit three years later. In light of this, particulate matter emissions from SI engines are currently partially regulated. Bielaczyc et al. [8] compared PM and PN emissions from several ethanol blends in a European SIDI vehicle tested over the NEDC. Under standard laboratory conditions, any decreases in PM and PN with increasing ethanol content were "small to non-existent" (although when tested at -7°C, there was some evidence of an appreciable decrease in PM emissions). Maricq et al. [9] measured PM and PN emissions (as well as particle size distributions) from a SIDI pick-up truck running on the FTP75 test cycle on various fuels. They found questionable reductions in PM and PN as ethanol content increased from 0% to 20%; concrete reductions were only observed where ethanol content was greater than 30%.

Regarding emissions of particulate matter from vehicles featuring indirect injection SI engines (which remain unregulated), studies conducted at BOSMAL have presented some results from that engine type (e.g. [6], [10]), where modest reductions in both particle mass and number are normally observed in response to the addition of ethanol to gasoline), even if the response is sometimes hard to detect and non-monotonic. The statistical significance of the effect of ethanol on emissions from port fuel injected engines is often questionable – when Clairotte et al. [11] compared PM emissions from the E5 and E10 blends, the results were scarcely distinguishable. See [5] and references therein for recent data and further information and commentary.

Unregulated exhaust emissions

For the purposes of this discussion, "unregulated emissions" are any measurable exhaust emissions for which limits are not set in Euro 6 legislation. Such emissions are of interest for two main reasons: they provide additional information on the overall impact on air quality; they provide insights into the combustion and catalytic conversion processes. In the future, certain compounds which are currently unregulated may be added to automotive emissions legislation, thereby making them regulated compounds. Focussing on ethanol, emissions of formaldehyde, acetaldehyde and ethanol itself are often measured in studies examining the effect of ethanol blends. Due to the absence of ethanol in E0 petrol, emissions of ethanol from ethanol blends are always higher than from standard petrol, while for E85, which is mainly composed of ethanol, ethanol is the compound which makes up the largest proportion of the organic compounds emitted from the exhaust [1].

Ethanol emissions have been reported to increase linearly with increasing ethanol content [12], although some emission of ethanol has in fact been reported when running on E0 [13] – such a trend was also implied by the derived data presented in [6]. Similarly, as the main formation pathways for aldehydes (formaldehyde and acetaldehyde) involve partial oxidation of alcohol molecules (ethanol and methanol), emissions from E0 petrol are very low, thereby making emissions from higher ethanol blends much higher in comparison, even if the emission factors themselves are relatively low. However, excess emissions of formaldehyde may not be significant and there may be no real correlation between fuel ethanol content and formaldehyde emissions; Bielaczyc et al. [6] observed increases in engine out ('pre cat') formaldehyde, but no consistent increases in post cat formaldehyde were observed (see the 'extended studies' section below). Acetaldehyde, on the other hand, is almost universally found to increase with increasing ethanol content, particularly during and following a cold start [6]. A wide range of unregulated compounds, including ammonia, alkanes and aldehydes, nitrogen monoxide and nitrous oxide were measured in [6] – see Table 1 in the following section.

Extended studies: low ambient temperature and uncatalysed ('engine out') emissions

Low ambient temperature investigations have also been performed on non-FFVs using ethanol blends. Bielaczyc et al. [4] compared regulated emissions from tests performed at +22°C and at -7°C, reporting the relative change in emissions over the NEDC, as shown in Figure 5. The observed increases for emissions of HC were similar for E5, E10 and E25; E50 performed much worse, likely due to combustion difficulties related to fuel injection and the heat capacity of the fuel. CO emissions increased less for E10 and E25 than for E5, but again E50 performed poorly. No problematic trends were observed for relative NO_x emissions and relative CO_2 emissions appeared to vary little with the blend ethanol content.

Bielaczyc et al. ranked the test blends according to emissions performance and noted that the ranking was somewhat temperature-dependent. A statistical analysis [7] examined a complex matrix of results and revealed that when the ambient temperature is reduced and the fuel ethanol content is simultaneously increased, the only statistically significant change occurring in response to the convoluted variables is an increase in THC emissions, with CO and NO_x emissions statistically unaffected at the 95% confidence level.

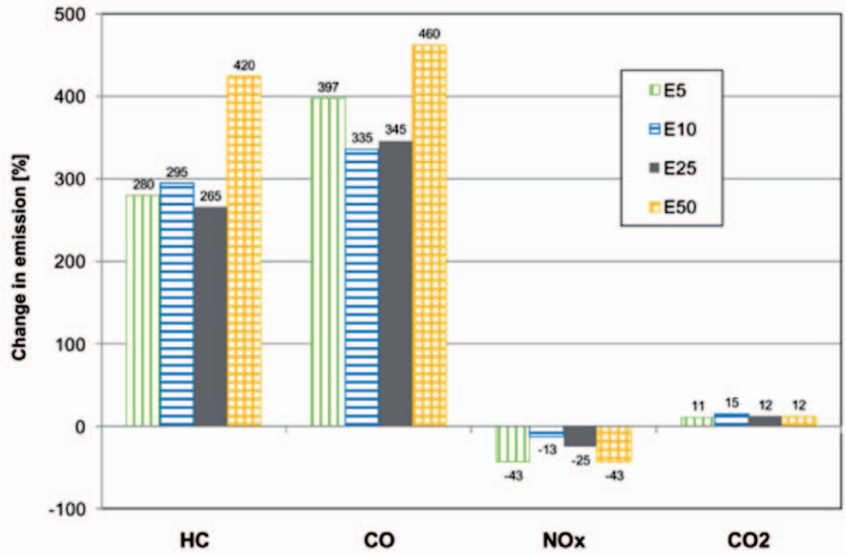

Figure 5. The relative change in regulated emissions over the NEDC for various petrol ethanol blends tested at 22°C and –7°C. (0% = emissions the same at both temperatures). Taken from [4]

Engine out emissions can be measured on an engine dynamometer, but a novel experimental method was employed in a study using a passenger car running on different ethanol blends was tested on a chassis dynamometer over the NEDC, measuring the concentrations of various pollutants before and after the catalytic converter using a Fourier transform infra-red analyser. Concentrations of certain compounds showed little or no response to the various fuel blends; others showed weak or non-linear, non-monotonic correlations; consistent, linear reductions in engine out concentrations of NO and several hydrocarbons were observed as ethanol content increased. Selected results are shown in Figures 6, 7 & 8 and all regressions deemed significant are summarized in Table 1.

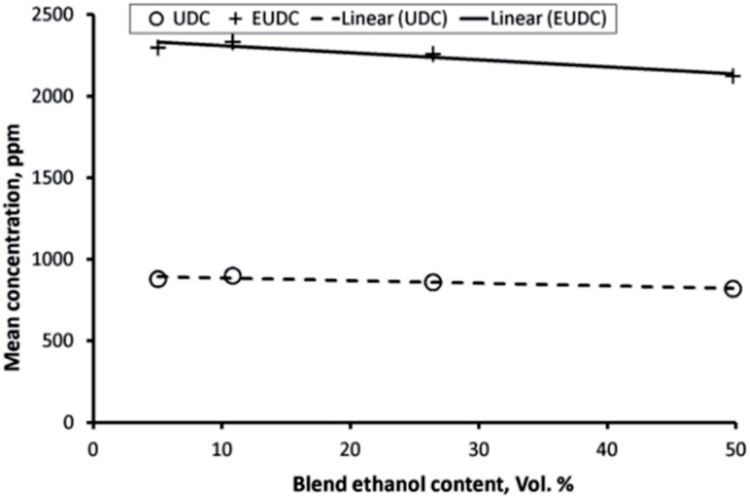

Figure 6. Pre cat NO concentrations as a function of blend ethanol content [6]

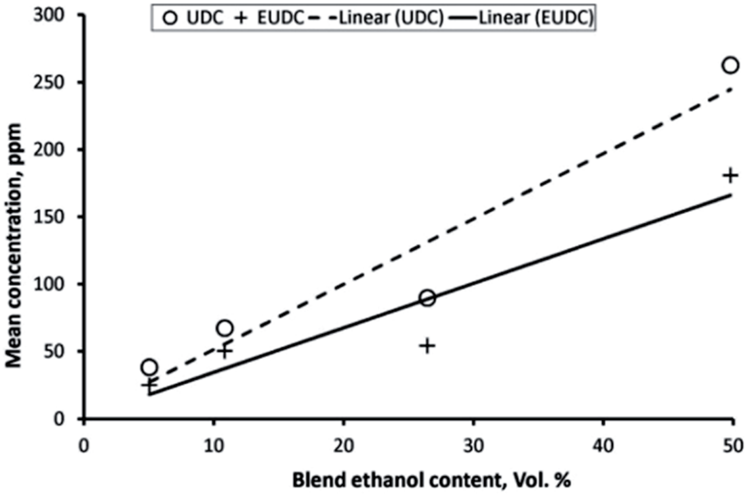

Figure 7. Pre cat ethanol concentrations as a function of blend ethanol content [6]

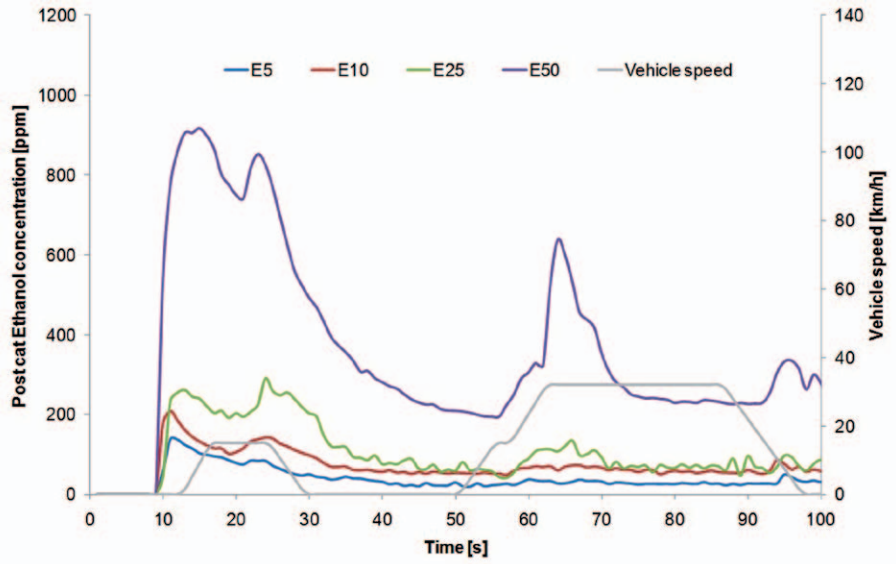

Figure 8. Pre cat ethanol concentrations for various blends over the first 100 seconds of the NEDC. Source: BOSMAL data – see [6] for commentary

Table 1. The results of a linear regression analysis conducted on mean concentrations of various gaseous pollutants from a passenger car over the NEDC, computed as a function of blend ethanol content, for blends E5-E50. The value of c (the y-intercept) can be taken as a proxy concentration for E0 fuel. NEDC phases: UDC=Urban Driving Cycle; EUDC=extra urban driving cycle. Taken from [6]

Compound	Sampling location	Phase	m (gradient)	c (y-intercept)	R^2
CO	Post cat	EUDC	-2.70	559	0.9644
NO	Pre cat	UDC	-1.59	902	0.8725
NO	Pre cat	EUDC	-4.36	2354	0.9058
NO	Post cat	EUDC	0.25	5.31	0.9413
NO_2	Pre cat	UDC	0.06	0.52	0.9970

Compound	Sampling location	Phase	m (gradient)	c (y-intercept)	R^2
NO_2	Pre cat	EUDC	0.05	0.66	0.9171
CH_4	Post cat	UDC	0.1256	21.226	0.9297
C_3H_8	Post cat	EUDC	-0.013	1.26	0.9899
C_6H_{14}	Pre cat	UDC	-2.12	232	0.9970
C_6H_{14}	Post cat	UDC	-0.18	28	0.8818
C_2H_2	Pre cat	UDC	-0.33	76	0.9403
C_2H_2	Pre cat	EUDC	-0.14	51	0.8478
C_7H_8	Pre cat	UDC	-0.97	128	0.9468
C_7H_8	Pre cat	EUDC	-0.80	101	0.8523
C_7H_8	Post cat	UDC	-0.15	15	0.9804
C_2H_6O	Pre cat	UDC	4.86	2.99	0.9247
C_2H_6O	Pre cat	EUDC	3.29	1.74	0.8880
HCOH	Pre cat	EUDC	3.30	1.76	0.8889
HCOH	Post cat	EUDC	-0.006	0.79	0.9721
CH_3CHO	Pre cat	UDC	0.31	38	0.9989
CH_3CHO	Pre cat	EUDC	0.29	31	0.9858
CH_3CHO	Post cat	UDC	0.11	3.57	0.9759

Summary and additional considerations

Despite the variable results obtained at BOSMAL and presented in many other studies in the literature, ethanol blends appear to have the potential to deliver benefits in terms of reduced HC and CO emissions. A sufficient number of studies have reported reductions in CO and THC (or at least NMHC) when running on blends up to E20–E25 to conclude that such emissions are lower overall. Similarly, the number of studies reporting increases in NO_x emissions leads to the conclusion that NO_x emissions do increase (though not under all conditions) – perhaps the best that can be hoped for is no significant increase in NO_x emissions. Small to substantial decreases in NO_x emissions have been reported, but these appear to be outweighed by studies reporting increases of various magnitudes. Increased emissions of acetaldehyde and ethanol appear to be an inherent disadvantage of using ethanol in SI engines, although current TWC aftertreatment systems fitted to production vehicles are generally not fully optimised for oxidation of such molecules. It is clear that the organic species present in the exhaust gas vary strongly with fuel ethanol content, which may require subtle changes to emissions testing and reporting of results, in order to give a clear picture of the actual compounds emitted. The terms 'THC' and 'hydrocarbons' cover a huge range of compounds, from the simplest – CH_4 – to massive aromatic structures. There are also currently some inconsistencies in the way the concentration of 'hydrocarbons' is quantified – see [11, 12, 14]; strictly speaking, ethanol and aldehydes are not hydrocarbons at all.

A recurring theme regarding exhaust emissions (in general, but particularly so when testing petrol-ethanol blends) is that of statistical significance. As exhaust emissions from modern vehicles are generally very low, changes in emissions that result from altering fuel chemistry moderately (e.g. moving from E10 to E20) can be hard to detect and suffer relatively low repeatability. In future this topic of statistical significance will have to be addressed in more detail. Given that the global potential for the introduction and expansion of petrol-ethanol blends as road transport fuels is vast, discussions over their environmental impact must be based on sound data, unclouded by statistical uncertainty.

Abbreviations and definitions

λ	Lambda
CH_4	Methane
CO	Carbon monoxide

CO_2	Carbon dioxide
DISI	Direct Injection Spark Ignition engine
E5	Fuel blend with 5% ethanol content
Ex	Fuel blend with x% ethanol content
EU	European Union
EUDC	Extra Urban Driving Cycle
FFV	Flex Fuel Vehicle
HC	Hydrocarbons; sometimes given as total hydrocarbons (THC)
NEDC	New European Driving cycle
NO	Nitrogen oxide
NO_x	Oxides of nitrogen
PM	Particulate Matter
PN	Particle Number
SI	Spark ignition
TWC	Three-way catalyst
UDC	Urban Driving Cycle

References

[1] Yanowitz, J. and McCormick, R. L.: (2009). *Effect of E85 on Tailpipe Emissions from Light-Duty Vehicles. J.* Air & Waste Manage. Assoc., 59, 172-182. DOI: 10.3155/1047-3289.59.2.172

[2] West, B. H., *et al.*: (2012). *Intermediate Ethanol Blends Catalyst Durability Program*. Oak Ridge National Laboratory report ORNL/TM-2011/234. Available online: http://info.ornl.gov/sites/publications/files/Pub31271.pdf

[3] Bielaczyc, P., Szczotka, A. and Woodburn, J.: (2011). *The Effect of Various Petrol-Ethanol Blends on Exhaust Emissions and Fuel Consumption of an Unmodified Light-Duty SI Vehicle*. SAE Technical Paper 2011-24-0177. DOI: 10.4271/2011-24-0177.

[4] Bielaczyc, P., Szczotka, A. and Woodburn, J.: (2012a). *A Study of Ethanol-Gasoline Blends' Influence on performance and Exhaust Emissions from a Light-Duty Gasoline Vehicle*. SAE Technical Paper 2012-01-1052. DOI: 10.4271/2012-01-1052.

[5] Bielaczyc, P., Szczotka, A., and Woodburn, J.: *Regulated Emissions, Unregulated Emissions and Fuel Consumption of Two Vehicles Tested on Various Petrol-Ethanol Blends*. SAE Technical Paper 2014-01-2824, 2014, DOI:10.4271/2014-01-2824.

[6] Bielaczyc, P., *et al.*: (2012). *An examination of the effect of ethanol–gasoline blends' physicochemical properties on emissions from a light-duty spark ignition engine*. Fuel Processing Technology, in press (2012). DOI: 10.1016/j.fuproc.2012.07.030.

[7] Coordinating Research Council, 2009a. *Effects of Vapor Pressure, Oxygen Content, and Temperature on CO Exhaust Emissions*. CRC report E-74-b. Available online: http://www.crcao.org/reports/recentstudies2009/E-74b/E-74b%20Revised%20 Final_Report_SR20090503.pdf

[8] Bielaczyc, P., Szczotka, A. and Woodburn, J.: (2012b). *Investigations on fuel ethanol content and ambient temperature on particle number and mass emissions from vehicles featuring direct injection gasoline engines*. Extended abstract and presentation, in: Proceedings of the 16th ETH Conference on Combustion Generated Nanoparticles, 24-27 June 2012, Zurich, Switzerland (CDROM), ISBN: 978-3-033-03556-0.

[9] Maricq, M. M., Szente, J. J. and Jahr, K.: (2012). *The Impact of Ethanol Fuel Blends on PM Emissions from a Light-Duty GDI Vehicle*. Aerosol Science and Technology, 46, 576-583. DOI: 10.1080/02786826.2011.648780.

[10] Dutcher, D. D., *et al.*: (2011). *Emissions from Ethanol-Gasoline Blends: A Single Particle Perspective*. Atmosphere, 2(2), 182-200. DOI:10.3390/atmos2020182. Available online: http://www.mdpi.com/2073-4433/2/2/182/pdf

[11] Clairotte, M., *et al.*: (2012). *Effects of low temperature on the cold start gaseous emissions from light duty vehicles fuelled by ethanol-blended gasoline*. Applied Energy, in press (2012). DOI: 10.1016/j.apenergy.2012.08.010.

[12] Kar, K., *et al.*: (2010). *Organic gas emissions from a stoichiometric direct injection spark ignition engine operating on ethanol/gasoline blends*. International Journal of Engine Research, 11, 499. DOI: 10.1243/14680874JER610.

[13] Knoll, K., *et al.*: (2009). *Effects of Mid-Level Ethanol Blends on Conventional Vehicle Emissions*. SAE Technical Paper 2009-01-2723. Available online (as NREL/ CP-540-46570): http://www.nrel.gov/docs/fy10osti/46570.pdf

[14] Sandström-Dahl, C.: (2009). *METEV – Measurement Technologies for Emissions from Ethanol Fuelled Vehicles*. AVL MTC report 9711 submitted to the International Energy Agency – Advanced Motor Fuels. Available online: http://www. iea-amf.vtt.fi/pdf/annex36_metev_final_report.pdf

Effect of alcohol blending on real driving emissions of particulate matter from ordinary gasoline automobile engines: A comparison of ethanol, n-butanol and isobutanol

Wpływ mieszanek alkoholowych na rzeczywistą emisję cząstek stałych zwykłych benzynowych silników samochodowych: porównanie etanolu, n-butanolu i izobutanolu

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Abstract

This paper summarizes the recent and ongoing work on real driving emissions of several automobiles with ordinary, non-flexible-fuel spark ignition engines, powered by alcohol-gasoline blends with higher concentrations of ethanol, n-butanol and isobutanol. On a Ford Focus automobile with a direct injection EcoBoost engine, powered by gasoline and its blends with 15% ethanol, 25% n-butanol and 25% isobutanol, particle size distribution were measured with an on-board fast mobility particle sizer along a 55 km route.

Particle emissions were moderately reduced by ethanol and considerably by both butanol blends. On a Škoda Fabia and Škoda Felicia cars with indirect injection engines, powered by blends with higher concentrations of ethanol, n-butanol and isobutanol, particle emissions measured by a miniature on-board system were examined over a 13 km route. Blends of 30% and 50% of butanol had no or slightly positive effect on particle emissions. Blends of 70% ethanol and 85% n-butanol and 85% isobutanol, used with an auxiliary engine control unit, had no or slightly positive effect on particle mass, and reduced total particle length (roughly corresponding to lung deposited surface area) by about one half.

Keywords: spark ignition engine, particle emissions, real driving emissions, oxygenated fuels, ethanol, butanol, portable on-board emissions monitoring systems, particle number

Introduction

This study evaluates the emissions performance of ordinary in-use gasoline engines when operated on higher concentrations of ethanol, n-butanol and isobutanol, with focus on real-world particulate matter emissions (real driving emissions).

Replacement of fossil automotive fuels with renewable, low carbon footprint, domestically produced fuels and reducing exhaust emissions of primarily particulate matter and secondarily nitrogen oxides are among the main challenges automobile engines are currently facing. A large variety of fuels have been examined, out of which several have obtained larger market penetration: natural gas in gaseous and liquid form, liquified petroleum gas, ethanol, and biodiesel. Of these, ethanol and biodiesel are produced from renewable resources, with ethanol being used primarily in spark ignition engines, and biodiesel virtually exclusively in compression ignition engines.

Ethanol is an oxygenated compound with 35% of oxygen by weight. For this reason, more ethanol (both by weight and by volume) is needed, compared to gasoline, to form a stoichiometric mixture with a given amount of air. Therefore, on any engine calibrated to run on gasoline, the quantity of the fuel delivered must be increased when running on ethanol. There are therefore two strategies to use ethanol: either blended in small concentrations (up to around 10%) with gasoline for general use, or in high concentrations in designated engines. The current practice in the Czech Republic, where E85 (spark ignition engine fuel containing 70-85% of ethanol) is widely available at filling stations, while the number of flexible fuel vehicles certified to run on this fuel is rather small, suggests that ethanol is used in higher concentrations in the existing vehicle fleet. Assuming that the fuel does not lead to adverse performance (otherwise it would not be used by the public), the remaining question is the effect of such practice on exhaust emissions. The effects observed during laboratory studies are reviewed in [1–3] and in previous works by the authors [4–6]. However, it has been known, that the emissions under realistic driving conditions are often higher than during standardized type-approval laboratory tests. Therefore, the question of the effects of higher concentrations of ethanol blends on real driving emissions was sought to be answered by real driving emissions tests.

Also, as ethanol is known to be hygroscopic and aggressive to many elastomers and other materials found in the fuel systems [7, 8]. For this reason, additional alcohols which could also be produced from biomass were considered. Two isomers of butanol, n-butanol (1-butanol) and isobutanol (2-methyl-propan-1-ol), have the potential to be commercially produced from biomass [9–12] at costs and fossil energy inputs comparable to ethanol [9]. Compared to ethanol, both n-butanol and iso-butanol have higher energy density, lower hygroscopicity, higher viscosity, better lubricity, lower vapor pressure [13], and are less aggressive towards many materials commonly used in vehicle fuel systems. Both isomers of butanol have been used in spark ignition engines, both port fuel injection [1–5, 14–19] and direct injection type [6, 20–22], with encouraging results, yet without a universal consistent conclusion as to the effect on the emissions.

In the recent past, the performance of butanol blends has been investigated by the authors on several engines, including throttle body injection, port injection and direct injection automobile gasoline engines, and several small carbureted engines used in garden equipment and an electric generator. Of these, three automobiles have been tested under real driving conditions with a portable on-board monitoring system, during which the emissions of particulate matter were also measured. These measurements are summarized in this paper.

Experimental

Portable on-board monitoring system

The vehicles were fitted with a portable, on-board exhaust emissions monitoring system designed by the first author [23, 24]. The system samples raw, undiluted exhaust gases via a 6 mm diameter stainless steel tube inserted into the tailpipe, and a 6 mm internal diameter, 5 m long conductive fuel line used as a sample line. The sample passes through a condensation bowl where condensate is trapped and periodically removed. The sample is then reheated to approximately 60°C by passing through a resistance-heated copper coil. Concentrations of nitrogen monoxide (NO), carbon monoxide (CO) and carbon dioxide (CO_2) were measured online with a pair of modified, optimized and tuned BAR-97 grade analyzers, utilizing non-dispersive infra-red analyzers (HC, CO, CO_2) and electrochemical cells (NO and NO_2). The response of the NDIR sensor used in this study to ethanol and to hydrocarbon mix during the operation on E85 has not been determined. Specifications for an analogous detector [25] show that the sensitivity to ethanol lies between the sensitivities of propane and hexane, both of which are commonly used to calibrate the automotive NDIR analyzer. Traditionally used flame ionization detector (FID) was not determined to be a reliable reference, as it has cross-sensitivity to oxygenated compounds, resulting in understatement of the concentration of oxygen-containing hydrocarbons [26]. Also, as the sample system is not heated, and portions of water vapor in the sample is removed by the condensate, it can be presumed that ethanol, which is water-soluble, is lost to condensate. Ethanol has been found to be one of the major constituents of organic species on ethanol-fueled vehicles [27]. The CO and CO_2 measurements using the NDIR method are rather straightforward and no adverse issues were anticipated. While the instrument measures both NO and NO_2 using electrochemical cells, only the NO measurement is sufficiently dynamic for transient tests, and was evaluated here quantitatively. The volumetric concentrations of total nitrogen oxides (NO_x) were assumed to be identical to those of NO in most cases during this study. This overall assumption has been verified by extensive comparison tests of the on-board system, and is also in agreement with analogous sensors being used, in many regions, in periodic emissions inspections of spark ignition vehicles nominally operating at stoichiometric ratio. This is also in agreement with general experience that for engines with no catalytic devices and for engines operating mostly at stoichiometric conditions, the concentrations of nitrogen dioxide (NO_2) are several percent of the total nitrogen oxides (NO_x); the only engines known to produce relatively high emissions of NO_2 are those equipped with a highly doped oxidation catalyst and operating lean (with excess air). This is also in agreement with the observed range of response of the NO_2 cell, based on which it is not apparent that larger quantities of NO_2 (tens of percent of total NO_x) were produced.

Concentrations of particulate matter were measured online with a forward scattering integrating nephelometer, which, for a given engine and a given setup, tends to provide output proportional to particle mass concentration [4, 23]. This measurement is believed to be possibly affected both by the low light scattering efficiency of smaller particles, and by the effects of fuel on the particle composition and morphology (mean size, fractal dimension…) and hence on the ratio of the light scattering efficiency to particle mass.

Concentrations of particulate matter expressed as total particle length, were measured with a modified industrial building smoke detector, equipped with a measuring ionization chamber, utilizing a small radioactive source (241Am, 30 kBq) to ionize the air. When voltage is applied to the electrodes in the chamber, a small ionization current flows through the chamber. Particles entering the chamber absorb the ions and decrease the ionization current. The detector was modified so that ionization current can be sensed directly and recorded by a data acquisition system. Laboratory comparison tests carried out on the engine exhaust by the first author [28] have shown that the system provides a response proportional to total particle length concentration (sum of the diameters of particles, expressed in length per unit of volume, i.e., $m.cm^{-3}$), that is, the sum of electric mobility diameters of all particles in a unit of volume.

On the DISI engine, where particulate emissions were anticipated to be the primary issue, particle size distributions and concentrations were measured online with a fast mobility particle sizer (EEPS, Model 3090, TSI), preceeded by a secondary dilution by a rotating disc diluter (MD-19, Matter Engineering) set to 180:1 dilution ratio; the diluter head was heated to 150°C.

On the throttle body and MPI engines, where particulate emissions were anticipated to be low, while unregulated gaseous compounds were of concern, measurements of gaseous emissions were also done with a prototype miniature portable FTIR (Fourier Transform Infra Red) analyzer with liquid nitrogen cooled MCT detector with a 6-meter path length cell running at 121°C and a resolution of 0.5 cm^{-1}.

DISI engine tests

A typical European small family car (C-segment production passenger car), 2013 Ford Focus station wagon, with downsized three-cylinder 1.0 liter turbocharged gasoline direct injection EcoBoost engine (parameters of the engine are given in Table 1), 6-speed manual transmission, tire size 205/55 R16, 1242 kg curb weight, was tested at the Czech Technical University in Prague on a 55 km route used for real driving emissions measurements. The vehicle was certified to Euro 6 standards, with rated fuel consumption of 5,8/4,2/4,8 l/100 km, rated CO_2 emmissions 114 g/km, designed to run on 95-octane (RON) gasoline (EN228). The vehicle mileage was 7962 km (4948 mi) at the beginning and 10 130 km (6296 mi) at the end of the study. The test route, overlaid on the map in Fig. 1, is located northwest of Prague in central region of Czech Republic with total altitude difference 165 m and includes approximately one third of urban, one third of suburban, and one third of freeway travel. The motorway part contains one single ascent of 75 m. The elevation profile of the route and typical speeds are given in Fig. 2. The speed in urban part is limited to 50 km/h, suburban to 90 km/h, motorway to 130 km/h. All runs were performed by the same driver in an attempt to compensate the influence of different driving styles of different drivers.

Non-oxygenated gasoline with a nominal research octane number of 95, meeting ČSN EN228 specifications, has been obtained at the local fueling station (EuroOil, Buštehrad, Hrebečská 695, 27343), and used as the baseline fuel for the testing. Commercially available E85 fuel, also obtained from a local fueling station (LPG-AUTO s.r.o., Michelská 4/11, Prague 14000) and analyzed to contain 70% of ethanol, was mixed with the base fuel to produce a blend containing 15% of ethanol by volume (E15). Technical grade n-butanol (Chemlogistic, Pardubice) and iso-butanol (Chemap, Dašice) were also mixed with the baseline fuel to obtain a blend of 25% of n-butanol with gasoline (nBu25) and a blend of 25% of isobutanol with gasoline (iBu25). The fuels were metered on mass basis using their actual (measured) densities into 20-liter (five-gallon) canisters and splash-blended.

Throttle body and port fuel injection engine tests

Two cars representative of significant share of cars with naturally aspirated spark ignition engines were used for experimental runs. Both cars are equipped with five gear manual transmission. For high alcohol share, an additional control unit for fuel injection pulse width increase was used. Additional unit producer instructions were followed, so for mixtures containing 85% by volume of butanol settings equivalent to concentration of ethanol up to 50% and for E85 settings for more than 50% ethanol mixture were applied. No other modifications of tested cars and their engines were carried out.

The first of the tested vehicles was a Škoda Felicia equipped with a four cylinder in-line single point fuel injection (SPI, or more accurately, throttle body injection – TBI) spark ignition engine manufactured in 1996 with mileage about 150 thousand km. This vehicle remains popular in the Czech Republic and represents a large share of the vehicle fleet despite obsolete air-fuel mixture technology (SPI). Selected parameters of this engine are listed in Table 1. This engine is equipped with a three way catalyst, utilizes an air to fuel ratio control circuit and is designed to meet emission standard Euro 2.

The second car, a Škoda Fabia, was chosen to represent a popularly used type of cars with naturally aspirated downsized engines. This car which has been manufactured in 2006, exhibits mileage about 150 thousands km and is propelled by a three cylinder port fuel injection (PFI) engine with selected parameters listed in Table 1. This engine is also equipped with a three way catalyst, utilizes an air to fuel ratio control circuit and is designed to meet emission standard Euro 4.

The base fuels were identical to the fuels for the DISI engine, however, pure E85 (71% ethanol) was used, and both isomers of butanol were blended with gasoline at 30%, 50% and 85% volume. For 85% butanol concentration a significant decrease of available torque made ordinary driving through the steep part of the testing route impossible for both cars, and an auxiliary control unit for fuel injection pulse width prolongation (Europecon Flex) was used for E85 and for 85% butanol blends.

Table 1. Selected parameters of the tested engines

Engine	Ford Ecoboost 10	Škoda 136B	Škoda 1.2 HTP (VW code BME)
Number of cylinders	3	4	3
Displacement [dm^3]	0.999	1.289	1.2
Bore [mm]	71.9	75.5	76.5
Stroke [mm]	82	72	86.9
Compression ratio [-]	10	10	10.5
Brake power [kW]	92 at 6000 rpm	50 at 5500 rpm	47 at 5400 rpm
Maximum torque [Nm]	170 Nm at 1400 – 4500 rpm 30 s overboost @ 200Nm 1400-4500 30s	100 at 3750 rpm	112 at 3000 rpm
Firing order		1 – 3 – 4 – 2	1 – 2 – 3

The local test route selected for this testing is a 13-km route featuring urban and hilly rural driving, typical for the region, and typical for the operation of this type of vehicle. The route and its elevation profile are given in Fig. 2. The route starts at the university campus. Traversing through a residential neighborhood in the first part, the road ascends 292 m through forest into a pass in Rudolfov (at 5 km), from where it descends along a creek (until 9.2 km), continuing through residential and mixed-use neighborhoods.

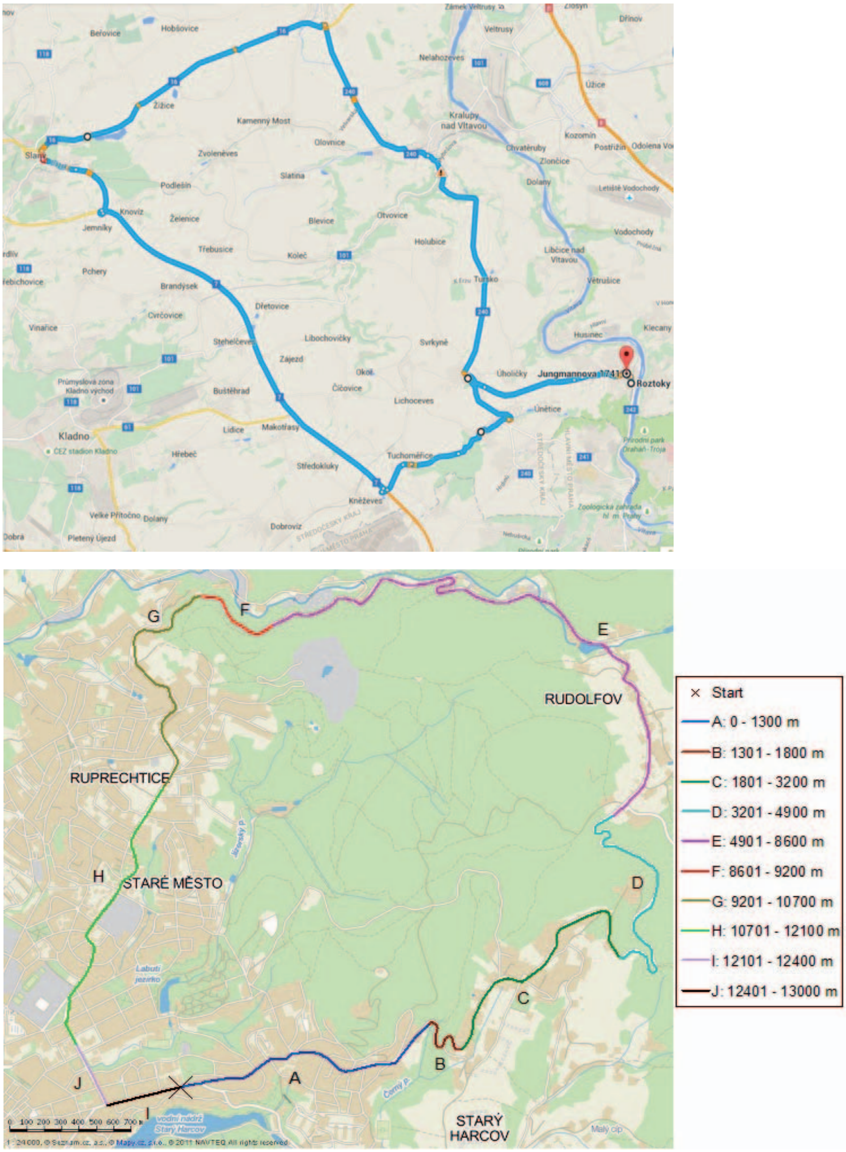

Figure 1. Test routes: Prague 55 km DISI route (left) and Liberec 14 km MPI route (right)

With a range of driving styles, the inclines and numerous curves on this route allow for the engine to be operated at points throughout its operating range. A conservative, leisurely driving style was practiced, as the most representative style for this type of vehicles, during all tests described here. On each fuel, typically five to six runs of the test cycle were made, with the first run considered a "preconditioning" run, with the expectation that of the remaining 4-5 runs, at least three, will produce valid data with a reasonable variance in total emissions per route among the runs.

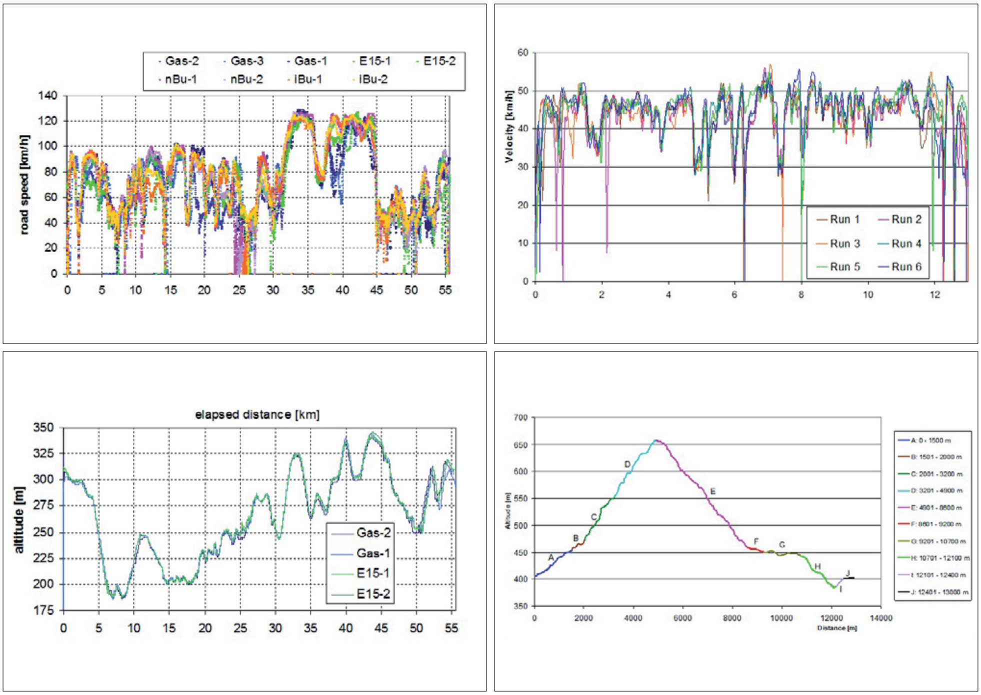

Figure 2. Speed (top) and elevation (bottom) profiles of the routes:
Prague (left) and Liberec (right)

Results and Discussion

The cumulative (left) and instantaneous (right) emissions of particulate matter expressed on mass (top) and number (bottom) basis for the DISI engine are plotted in Figure 3.

For the throttle body injection car, the cumulative and instantaneous particulate matter emissions expressed as particulate mass are shown in Figure 4 for each run on gasoline, E85 and blends of 85% n-butanol and isobutanol, and in Figure 5 for each run on blends containing 30% and 50% of butanol. The cumulative and instantaneous particulate matter emissions expressed as total particle length (a value rougly corresponding to the total surface of particles deposited in the lungs, or lung deposited surface area) are shown in Figure 6 for each run on gasoline, E85 and blends of 85% n-butanol and isobutanol, and in Figure 7 for each run on blends containing 30% and 50% of butanol. The particle emissions on the MPI engine were relatively low, however, strong effects of what appears to be lubricating oil consumption during engine motoring were observed. For this reason, data from the MPI engine are not presented, as they do not offer a meaningful comparison of fuels.

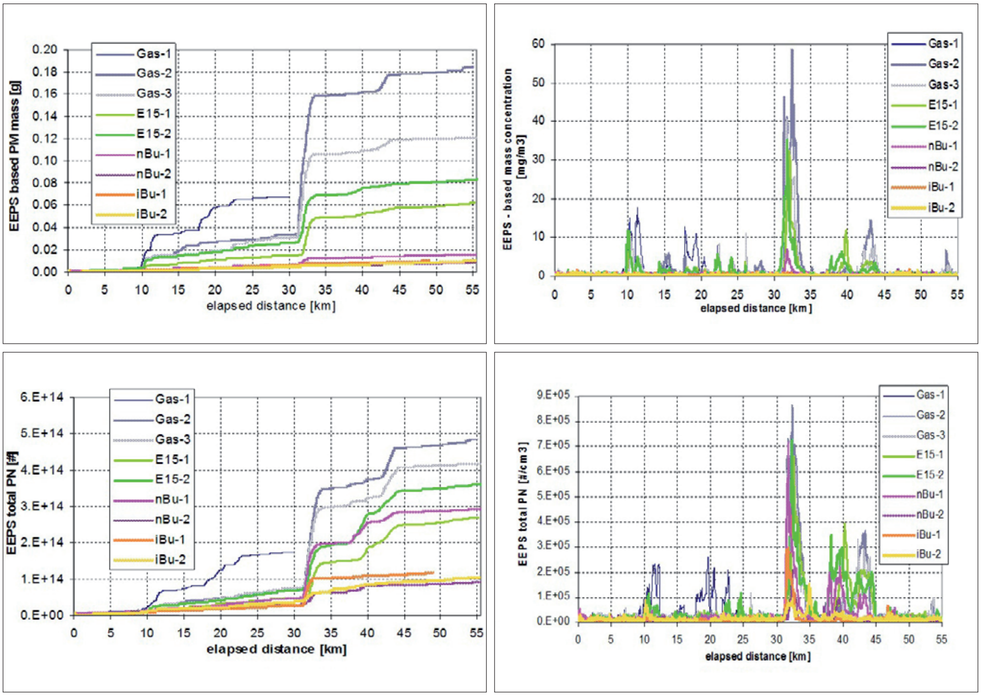

Figure 3. Cumulative (left) and instantaneous (right) emissions of particulate matter expressed on mass (top) and number (bottom) concentration basis for the DISI engine: comparison of non-oxygenated gasoline (Gas) and its blends with 15% ethanol (E15), 25% n-butanol (nBu25) and 25% isobutanol (iBu25)

For the DISI engine, the overall emissions over the test route, in the range of approximately 1×10^{12} – 8×10^{12} particles > 23 nm per km, correspond to the 2×10^{12} – 4×10^{12} particles per km range observed during the laboratory tests. The differences among the fuels are larger, and the general repeatability lower, compared to the laboratory tests (described in [6]). Furthermore, it is apparent that a large portion of total particle emissions from gasoline and E15 runs originates from high-power operation, notably acceleration on an uphill stretch of a freeway. The concentrations during such spikes are highest for gasoline, lower for E15, lower for nBu25, and lowest for iBu25. What appears to come out as the most potent take-home message is the observation that when we choose to blend either ethanol or butanol with gasoline to reach about 5% of oxygen by weight in the fuel, both n-butanol and iso-butanol, at 25% by volume in gasoline, appear to yield substantially higher reduction in particle mass and number emissions compared to 15% ethanol. There is no conclusive evidence as to which butanol isomer is better, leaving both n-butanol and iso-butanol as suitable candidates for consideration.

For the throttle body injection engine, particulate matter mass emissions were in the range of 2 to 2.5 mg/km. While some decrease was observed on all alcohol blends, and given the generally good test-to-test repeatability, they could be considered statistically significant, the method itself – light scattering – is a surrogate method for mass measurement, and it is the opinion of the authors that a 20% difference is too small to be reliably attributed to the fuel. Likewise, while a small reduciton in total particle length is apparent for 30% and 50% blends of both butanol isomers, such a difference is too small to be conclusively attributed to the fuel effects. The difference in particle length emissions for 85% blends of both n-butanol and isobutanol and for E85, all being approximately one half of gasoline values, are, however, substantial, and given the small variances among individual measurements, are statistically significant. It can therefore be concluded that

a) intermediate concentrations of 30% and 50% of butanol, used in unmodified engine, had slight or no positive effect on both particle mass and particle length emissions, and
b) that high concentrations of 85% butanol, as well as E85, when used with an auxiliary control unit, had slight or no positive effect on particle mass emissions, and reduced particle length emissions by approximately one half compared to gasoline.

The particle mass emissions for the DISI and TBI engine were comparable, in the range of one to several mg/km. This is consistent with the cumulative effects of DISI engine particulate matter emissions being considerably higher, and of emissions of newer cars being substantially smaller compared to older vehicles.

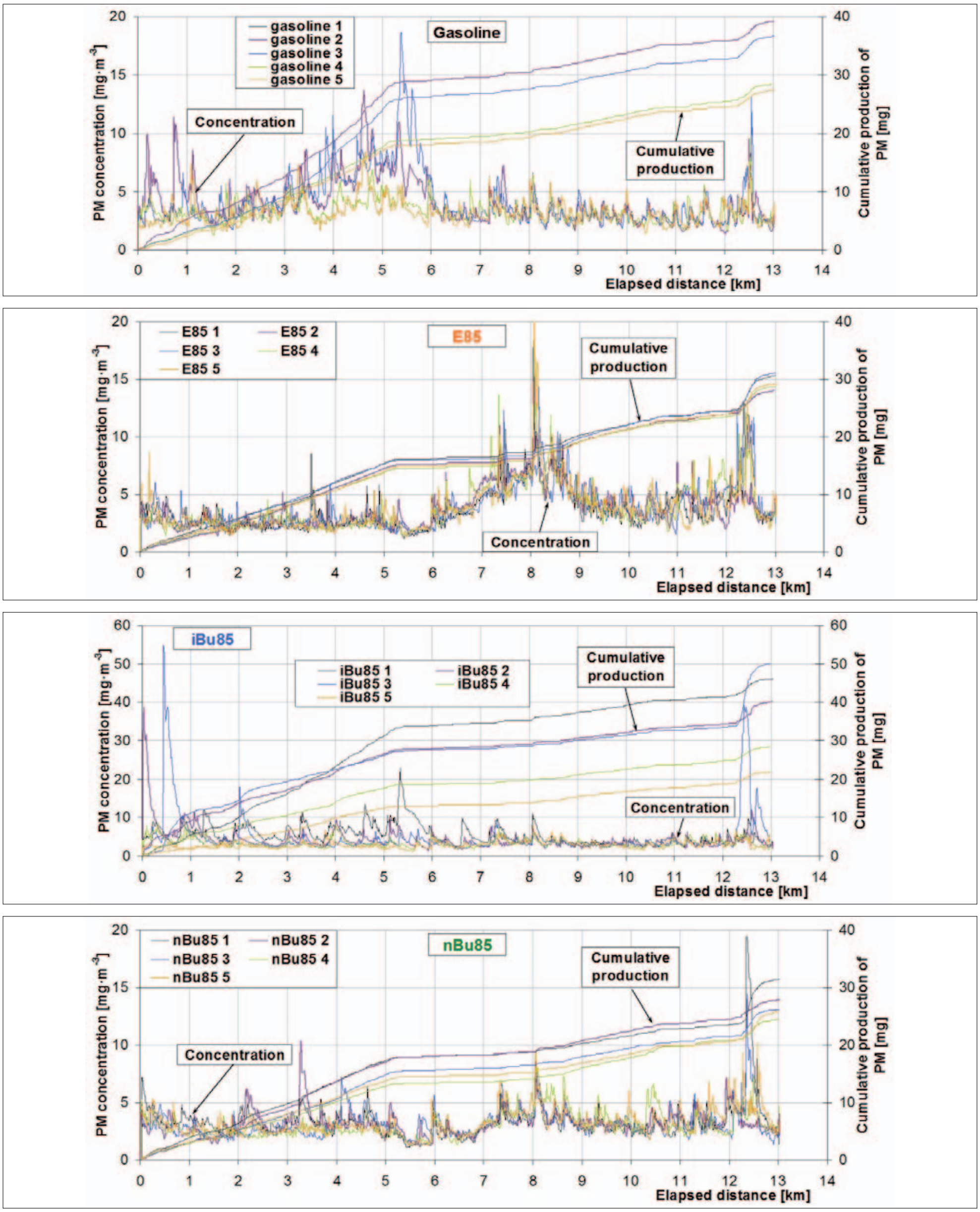

Figure 4. Instantaneous and cumulative particulate matter emissions measured by laser scattering expressed as particulate mass for (top to bottom) gasoline, E85 and blends of 85% n-butanol and isobutanol with gasoline

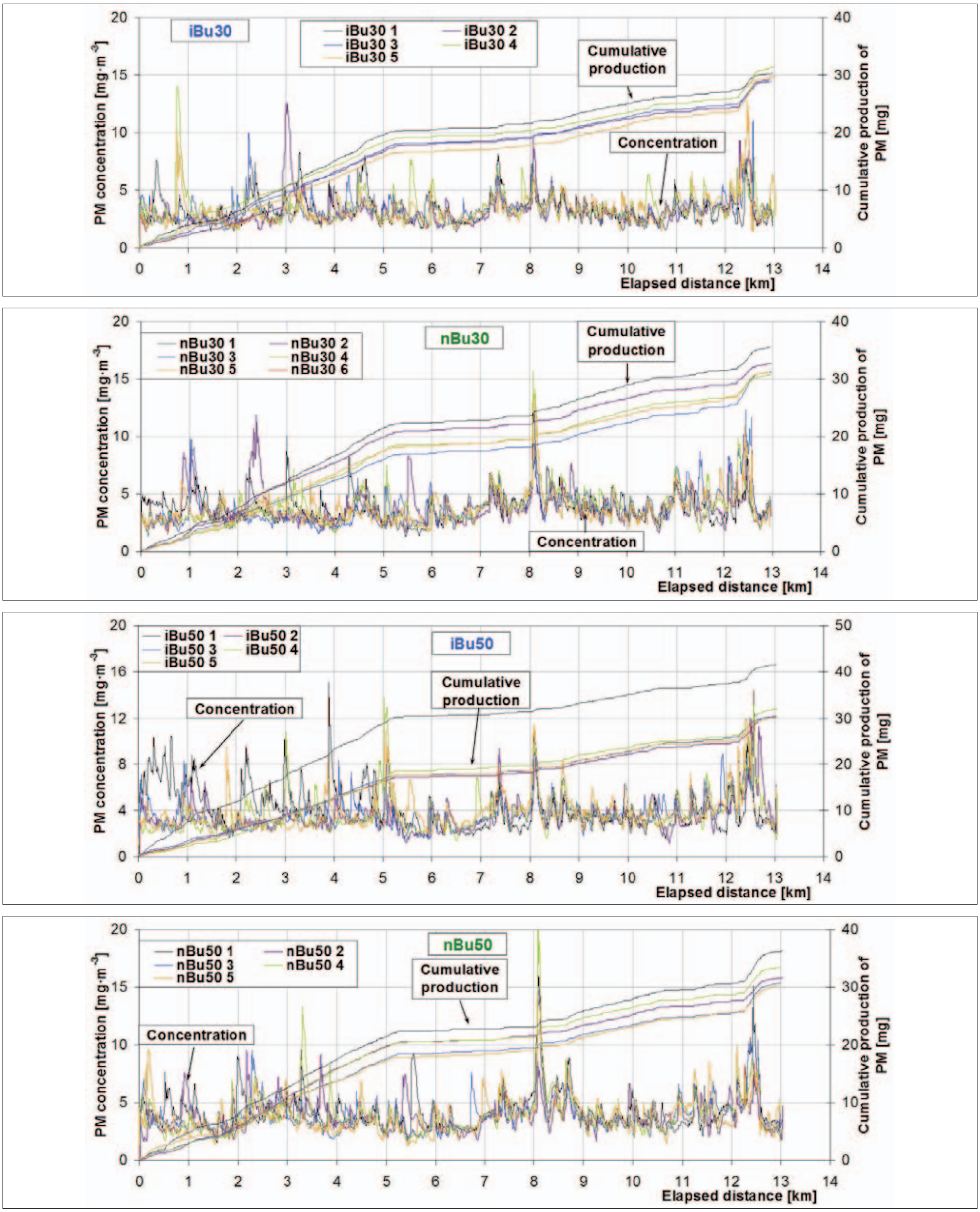

Figure 5. Instantaneous and cumulative particulate matter emissions measured by laser scattering expressed as particulate mass for (top to bottom) blends of 30% isobutanol, 30% n-butanol, 50% isobutanol and 50% n-butanol with gasoline

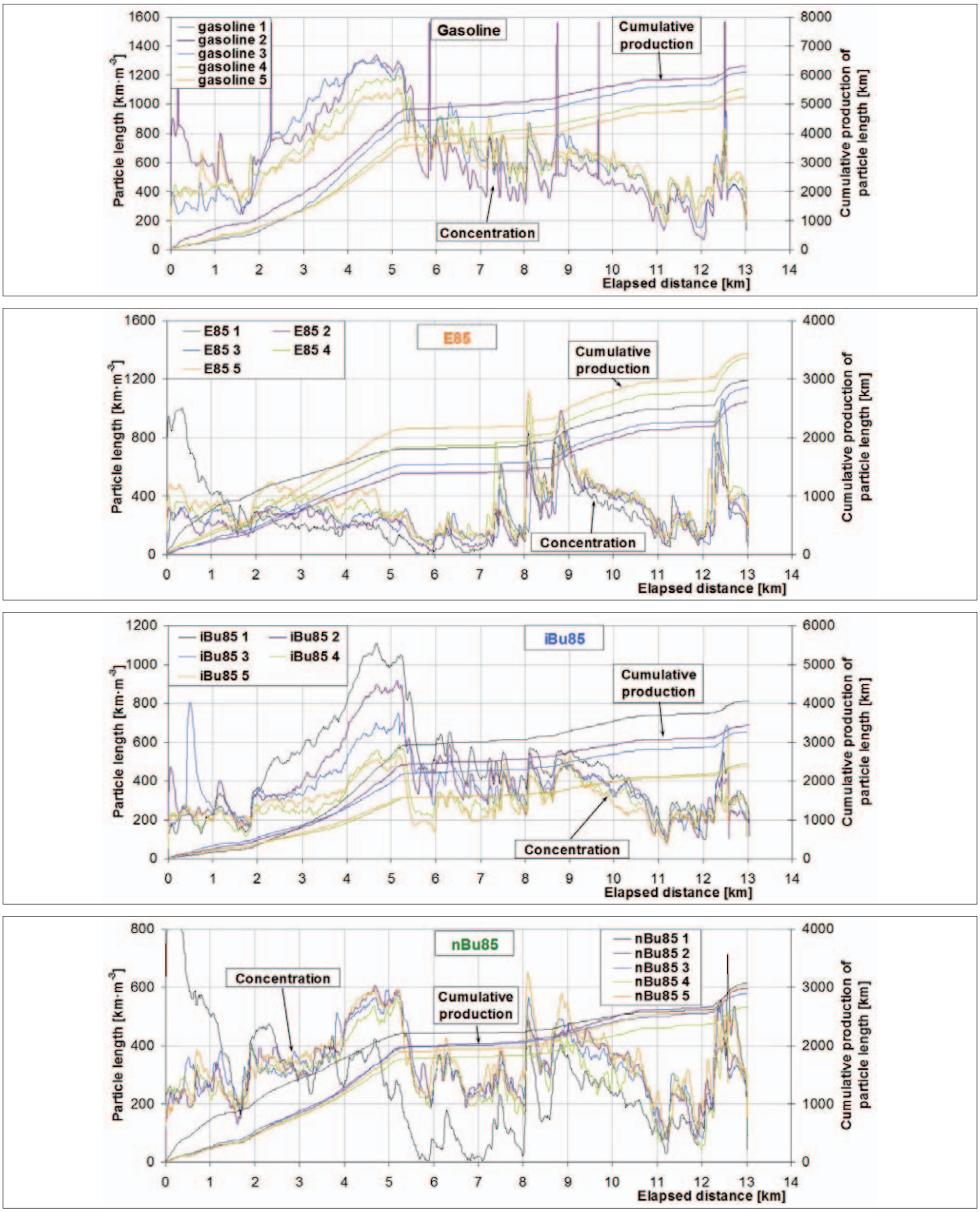

Figure 6. Instantaneous and cumulative particulate matter emissions measured by ionization chamber expressed as total particle length (a value corresponding to lung deposited surafce area) for (top to bottom) gasoline, E85 and blends of 85% n-butanol and isobutanol with gasoline

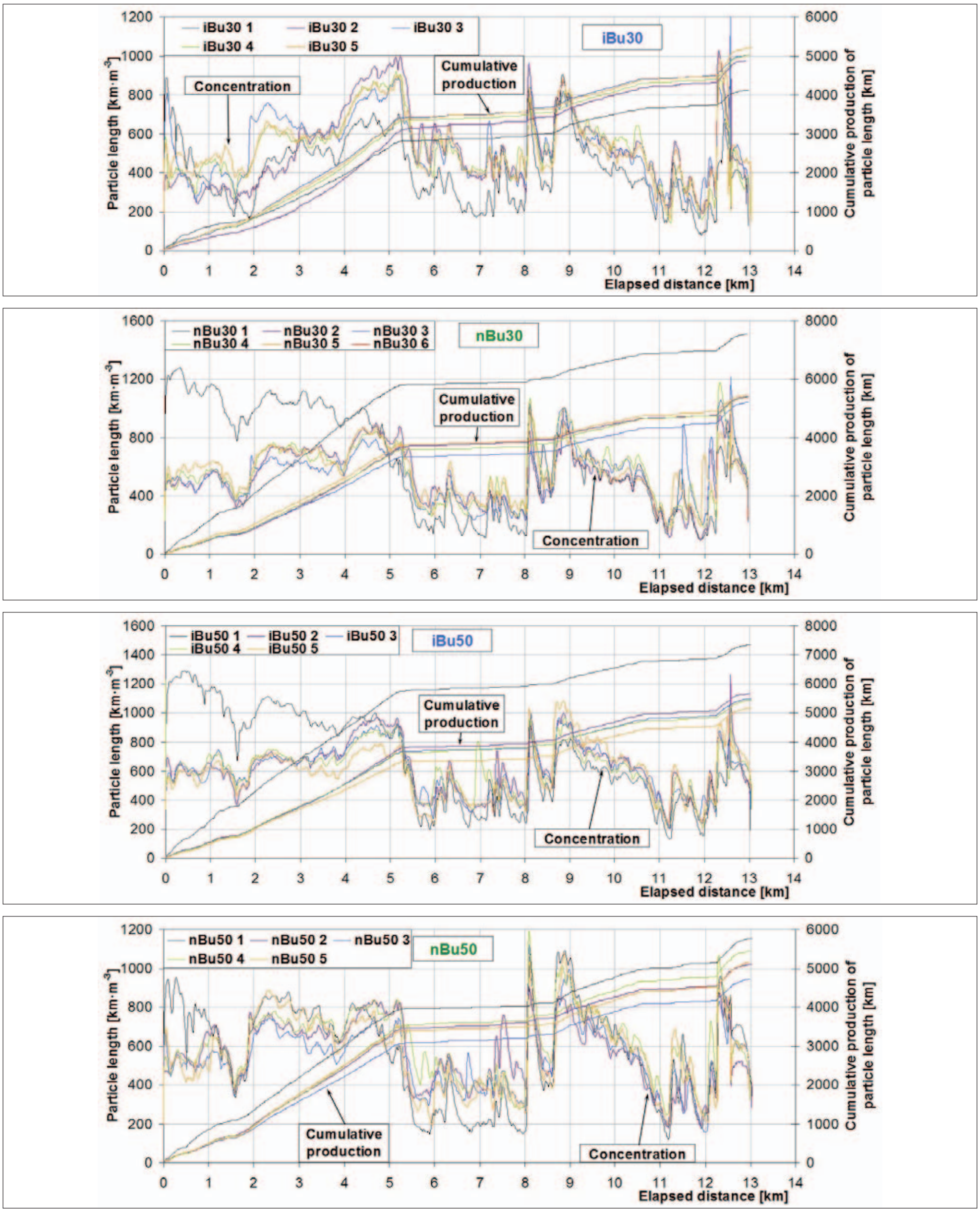

Figure 7. Instantaneous and cumulative particulate matter emissions measured by ionization chamber expressed as total particle length (a value corresponding to lung deposited surafce area) for (top to bottom) blends of 30% isobutanol, 30% n-butanol, 50% isobutanol and 50% n-butanol with gasoline

Acknowledgments

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References

[1] Karavalakis, G., Short, D., Vu, D., Villela, M. et al., *Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends*. Fuel 128: 410-421, 2014, doi: 10.1016/j.fuel.2014.03.016.

[2] Ratcliff, M.A., Luecke, J., Williams, A., Christensen, E. et al., *Impact of higher alcohols blended in gasoline on light-duty vehicle exhaust emissions*. Environ. Sci. Technol. 47(23), 13865-13872, 2013, doi:10.1021/es402793p.

[3] Stansfield, P., Bisordi, A., OudeNijeweme, D., Williams, J. et al., *The Performance of a Modern Vehicle on a Variety of Alcohol-Gasoline Fuel Blends*. SAE Int. J. Fuels Lubr. 5(2):2012, doi:10.4271/2012-01-1272.

[4] Vojtisek-Lom, M., Pechout, M. and Mazac, M., *Real-World On-Road Exhaust Emissions from an Ordinary Gasoline Car Operated on E85 and on Butanol-Gasoline Blend*. SAE Technical Paper 2013-24-0102, 2013, doi:10.4271/2013-24-0102.

[5] Pechout, M., Dittrich, A., Mazac, M., and Vojtisek-Lom, M., *Real Driving Emissions of Two Older Ordinary Cars Operated on High-Concentration Blends of N--Butanol and ISO-Butanol with Gasoline*. SAE Technical Paper 2015-24-2488, 2015, doi:10.4271/2015-24-2488.

[6] Vojtisek-Lom, M., Beranek, V., Stolcpartova, J., Pechout, M. et al., *Effects of n-Butanol and Isobutanol on Particulate Matter Emissions from a Euro 6 Direct-injection Spark Ignition Engine During Laboratory and on-Road Tests*. SAE Int. J. Engines 8(5):2015, doi:10.4271/2015-24-2513.

[7] Jones, B., Mead, G., Steevens, P., 2008: *The Effects of E20 on Plastic Automotive Fuel System Components*. Online at https://www.mda.state.mn.us/news/publications/renewable/ethanol/e20onplastics.pdf.

[8] Bailey, B.: *Performance of Ethanol as a Transportation Fuel*. In: Handbook on Bioethanol: Production and Utilization. Edited by C. E. Wyman. Online at http://infohouse.p2ric.org/ref/36/35015.pdf

[9] Tao, L., Tan, E.C.D., McCormick, R.L., Zhang, M.et al., *Technoeconomic analysis and life-cycle assessment of cellulosic iso-butanol and comparison with cellulosic ethanol and n-butanol*. Biofuels Bioprod. Biorefin. 8(1): 30-48, 2014, doi:10.1002/bbb.1431.

[10] Xue, C., Zhao, X.Q., Liu, C.G., Chen, L.J. and Bai F.W., *Prospective and development of butanol as an advanced biofuel*. Biotechnol Adv. 31(8): 1575-84, 2013, doi:10.1016/j.biotechadv.2013.08.004.

[11] Cascone, R., *Biobutanol: a replacement for bioethanol?*. Chem. Eng. Prog. 104(4)" S4–S9, 2008.

[12] Patakova, P., Maxa, D., Rychtera, M., Linhova, L. et al., *Perspectives of biobutanol production and use*. In Biofuel`s engineering process technology, ed. Bernandes M.A.D.S., 243-266, 2011, InTech, Rijeka, Croatia, doi:10.5772/961.

[13] Andersen, V.F., Anderson, J.E., Wallington, T.J., Mueller, S.A. et al., *Vapor Pressures of Alcohol-Gasoline Blends*. Energ. Fuel. 24(6): 3647-3654, 2010, doi:10.1021/ef100254w.

[14] Szwaja, S. and Naber, J.D., *Combustion of n-butanol in a spark-ignition SI engine*. Fuel, 89(7): 1573-1582, 2010, doi:10.1016/j.fuel.2009.08.043.

[15] Dernotte, J., Mounaim-Rousselle, C., Halter, F. and Seers, P., *Evaluation of butanol-gasoline blends in a port fuel injection, spark-ignition engine*. Oil Gas Sci. Technol. – Rev. IFP 65(2): 345–351, 2010, doi:10.2516/ogst/2009034.

[16] Gu, X., Huang, Z., Cai, J., Gong, J. and Lee, Ch., *Emission characteristics of a spark-ignition engine fuelled with gasoline-n-butanol blends in combination with EGR*. Fuel 93(1): 611-617, 2012, doi:10.1016/j.fuel.2011.11.040.

[17] Wigg, B., Coverdill, R., Lee, C., and Kyritsis, D., *Emissions Characteristics of Neat Butanol Fuel Using a Port Fuel-Injected, Spark-Ignition Engine*. SAE Technical Paper 2011-01-0902, 2011, doi:10.4271/2011-01-0902.

[18] Merola, S., Tornatore, C., Valentino, G., Marchitto, L. et al., *Optical Investigation of the Effect on the Combustion Process of Butanol-Gasoline Blend in a PFI SI Boosted Engine*. SAE Technical Paper 2011-24-0057, 2011, doi:10.4271/2011-24-0057.

[19] Tornatore C., Marchitto L., Valentino G., Corcione F.E. et al., *Optical diagnostics of the combustion process in a PFI SI boosted engine fueled with butanol-gasoline blend*. Energy 45(1): 277-287, 2012, doi:10.1016/j.energy.2012.03.006.

[20] Karavalakis, G., Short, D., Vu, D., Russell, R.L. et al., *The impact of ethanol and iso--butanol blends on gaseous and particulate emissions from two passenger cars equipped with spray-guided and wall-guided direct injection SI (spark ignition) engines*. Energy. in print: 2015, doi:10.1016/j.energy.2015.01.023.

[21] Wallner, T. and Frazee, R., *Study of Regulated and NonRegulated Emissions from Combustion of Gasoline, Alcohol Fuels and their Blends in a DI-SI Engine*." SAE Technical Paper 2010-01-1571, 2010, doi:10.4271/2010-01-1571.

[22] Thewes, M., Müther, M., Brassat, A., Pischinger, S. et al., *Analysis of the Effect of Bio--Fuels on the Combustion in a Downsized DI SI Engine*. SAE Int. J. Fuels Lubr. 5(1):274-288, 2012, doi:10.4271/2011-01-1991.

[23] Vojtisek-Lom M., Fenkl M., Dufek M., Mareš, J., *Off-cycle, real-world emissions of modern light-duty diesel vehicles*. SAE Technical Paper 2009-24-0148, 2009, DOI: 10.4271/2009-24-0148.

[24] Vojtisek-Lom, M., Cobb, J.T., *On-road light-duty vehicle emission measurements using a novel inexpensive on-board portable system*. Presented at the 8th CRC On--road vehicle emissions workshop, San Diego, CA, April 20-22, 1998.

[25] Documentation to the CGS500-IR NDIR Gas Sensor, Monicon. Online at http://www.monicon.com/Images/MoniconCGS500.pdf

[26] Holm, T., *Aspects of the mechanism of the flame ionization detector*. Journal of Chromatography A, 842 (1999) 221–227.

[27] Yanowitz J., McCormick R.L., *Effect of E85 on Tailpipe Emissions from Light-Duty Vehicles*., J. Air & Waste Manage. Assoc., 59, 2009, 172-182, DOI:10.3155/1047-3289.59.2.172.

[28] Vojtíšek-Lom, M., *Total Diesel Exhaust Particulate Length Measurements Using a Modified Household Smoke Alarm Ionization Chamber*. J. Air & Waste Manage. Assoc., 61, 2011, 126-134, DOI: 10.3155/1047-3289.61.2.126.

Influence of ethanol on genotoxic emissions of a GDI vehicle

Wpływ etanolu na genotoksyczną emisję pojazdu z silnikiem GDI

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Abstract

Alcohol-based fuels are promising substitutes for petrol-based fuels to be used in internal combustion engines. Blending of ethanol with gasoline increases the oxygen content of the fuel, allowing a more complete combustion and hence reducing the emissions of several pollutants, but it is not clear if emissions of genotoxic compounds and therefore, the genotoxic potential of an exhaust are also reduced. The gasoline direct injection technology is quickly replacing traditional port fuel injection technologies due to enhanced fuel efficiency and lower CO_2 emissions. However, substantial emissions of soot-like particles have been reported in literature. In this study we compared emissions of a Euro-5 GDI vehicle

(1.6 L) when operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) under transient conditions and study the effects on particle and emissions of polycyclic aromatic hydrocarbons, including those reported to be genotoxic.

Introduction

The substantial contribution of petrol-based fuels to traffic-related CO_2 emission appeals for an urgent development of low carbon fuels. Alcohol fuels exhibit high potential in this respect. The use of ethanol in gasoline is well known but its interest has recently increased due to the new ways of ethanol production from biomass or other feedstocks. The production of ethanol from biomass is promoted in several countries, like United States, Brazil or Sweden. According to the U.S. Department of Energy, 95% of U.S. gasoline typically contains 10% of ethanol (E10). Other blends are also available (E15 and E85), but require flexible fuel vehicles. The oxygen content of gasoline is increased with the addition of ethanol. This increase promotes a more complete combustion of fuel and therefore reduces emissions of several pollutants like hydrocarbons and CO, but the effects on other non-regulated pollutants are uncertain. The polycyclic aromatic hydrocarbons (PAHs), which are commonly present in combustion processes [1, 2] are important pollutants especially those PAHs, considered as human carcinogens. In general, PAHs are products of incomplete combustion of fossil fuels and organic matter. They are also formed in internal combustion engines [3]. Conesa et al [4] showed the importance of the chemical composition of inherent materials and the presence of oxygen in the formation of these compounds. It is well known that PAH emissions from mobile sources depend on several parameters like fuel type, vehicle technology, capacity of engine, operating conditions and whether the vehicle engine and the catalyst, if present, have been warmed up or not. Several PAHs and nitro-PAHs have been identified as genotoxic compounds. The World Health Organization (WHO) classifies carcinogenic substances according to five groups. Benzo(a)pyrene is classified as group 1 being carcinogenic to humans. After up-take, this PAH is transformed in cells into an active metabolite which can interact with DNA causing mutations which eventually lead to cancer. PAHs 1, 9–12, 15, 16 and 20 (Figure 1) represent group 2A carcinogens, probably carcinogenic to humans and PAH 14 is a group 2B carcinogen possibly carcinogenic to humans.

Increased attention is given to nitro-PAHs, due to higher mutagenic (2×10^5 times) and carcinogenic (10 times) properties of certain nitro-PAHs compared to respective parent

PAHs. Furthermore, nitro-PAHs can be a significant fraction of the direct-acting mutagenic compounds present in vehicle exhausts [5, 6] and extracts of ambient air particles [7].

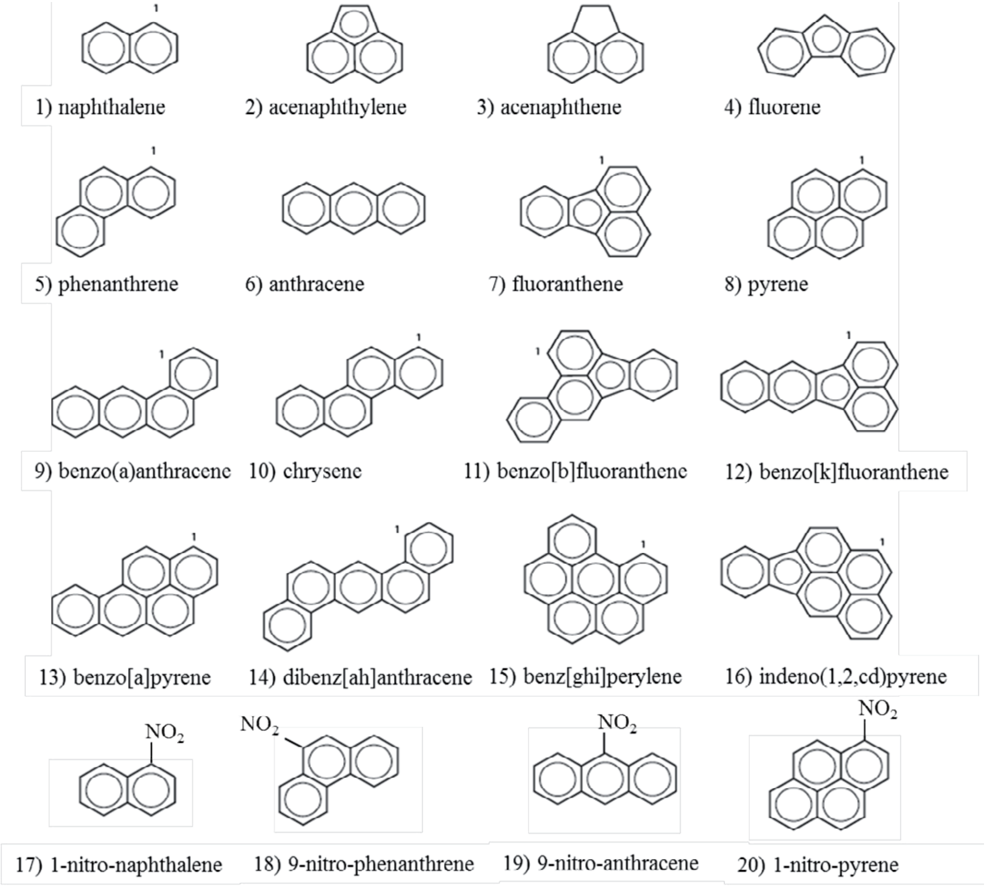

Figure 1. Chemical structures of the PAHs and nitro-PAHs analysed

The use of ethanol in gasoline direct injection vehicles (GDI) has recently been acquiring interest. These vehicles have been introduced into the market, promising enhanced fuel efficiencies and hence lower carbon dioxide emissions in comparison with the traditional port fuel injection vehicles (PFI). However, an important drawback of the GDI technology is the increase in particle emissions. The fuel, once injected, has less time to properly mix with the incoming air before the ignition. The stratified charging that direct injection produces allows richer mixtures near the spark plug and injector, and leaner mixtures further away from the spark plug and injector. One drawback of this is that the combustion process forms numerous particles of soot similar to those of untreated diesel exhaust. Previous studies have reported that GDI vehicles under lean conditions released 6×10^{12} particles/km, exceeding those of diesel vehicles equipped with filters by orders of magnitude [8]. Ulrich et al. [9] showed that particle number emissions of GDI vehicles in two standardized cycles exceeded the current Euro 5 limit of 6×10^{11} particles/km.

Experimental

Test cycle and fuels

A Euro 5 flex fuel GDI vehicle (Volvo V60) with a 1.6 L engine was used as a reference vehicle. All tests were performed at the chassis dynamometer of the University of Applied Science of Bern (UASB, Nidau). The world harmonized light vehicle test cycle (Worldwide Light-duty Test Cycle – WLTC) was used (Figure 2) which includes parts of urban (26 km/h), extra-urban (45 km/h), highway (61 km/h) and motorway (94 km/h) driving. The cycles were investigated under cold start and hot engine/catalyst conditions.

A batch of commercial gasoline was used as reference fuel (RON 95, Class D/D1 according to SN EN 228) and blended with ethanol (see Table 1). Two ethanol/gasoline blends with a 10% (E10) and 85% (E85) of ethanol were used.

Table 1. Characteristics of the fuels used

	Gasoline	E10	E85	Ethanol
Density (g/cm^3 at 15°C)	0.737	0.742	0.781	0.789
Stoichiometric air/fuel ratio	14.6	14.0	9.8	9.0

	Gasoline	E10	E85	Ethanol
Lower calorific value (MJ/kg)	43.0	41.3	28.9	26.8
Boiling point (°C)	30–200	-	-	78.5
Octane number	95	-	-	110
Latent heat of evaporation (kJ/kg)	420	-	-	900
Oxygen content (% m/m)	<5	-	-	34.8

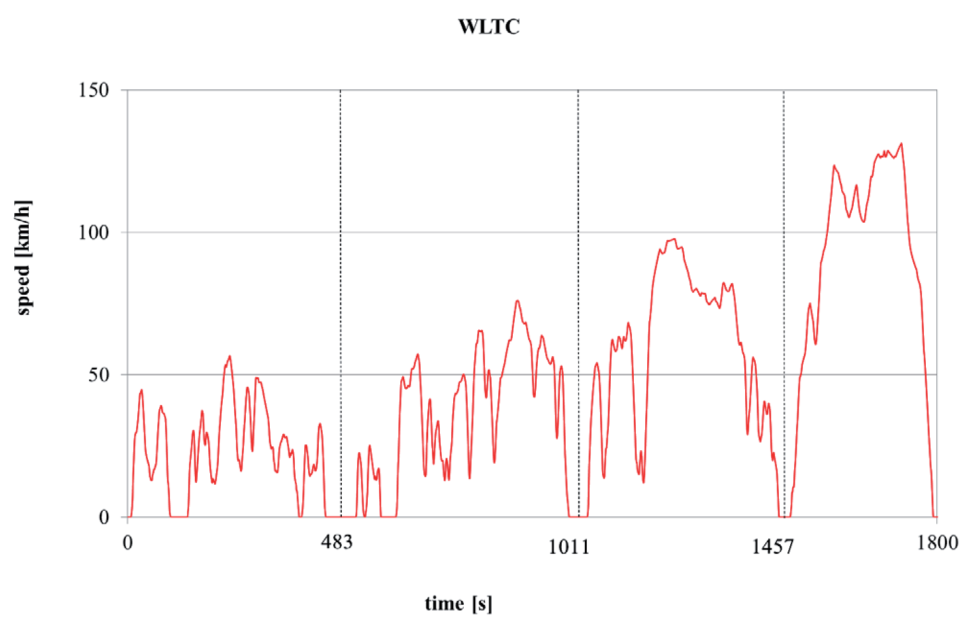

Figure 2. WLTC cycle used for tests under cold start and hot engine/catalyst conditions

Exhaust sampling, work-up and chemical analysis

Diluted exhaust has been sampled from a constant volume sampling (CVS) tunnel. Aliquots of the diluted exhausts are collected in all-glass sampling devices, including filter, condenser, and adsorber units (XAD2) according to the filter/condenser method described in the European standard EN-1948-1 [10]. This allows quantitative sampling of PAHs and nitro-PAHs in combined samples which included particle-bound, liquid and gaseous compounds. An approximated scheme of the set-up is explained elsewhere [6].

All solvents were analytical grade and purchased from Merck (Darmstadt, Germany) or Biosolve (Valkenswaard, The Netherlands). Prior to sampling, the glass apparatus was cleaned and heated to 450°C over night. Aliquots of $^{13}C_6$-naphthalene, $^{13}C_6$-phenanthrene and $^{13}C_3$-pyrene were placed on a quartz swab and given to the condensate separator prior to each sampling. These compounds were used to calculate the losses during sampling and work-up.

The combined sample was extracted in a Soxhlet apparatus with dichloromethane. An aliquot of a mixture of those 16 perdeuterated PAHs (CIL, Andover, MA, USA) given in Figure 1, was added to the samples as quantification standards. Furthermore, aliquots of a mixture containing D_7-1-nitronaphthalene, D_9-9-nitrophenanthrene, (both from Chiron, Trondheim, Norway) and D_9-1-nitropyrene and D_{11}-6-nitrochrysene (CIL, Andover, MA, USA) were added as quantification standards for nitro-PAHs. The extraction was followed by a multistep cleanup procedure with silica which allowed the fractionation of PAHs and nitro-PAHs. Analysis of PAHs and nitro-PAHs was performed by gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on 30 m and 15 m capillary columns (Restek, Bellefonte, USA) for PAHs and nitro-PAHs, respectively. Detection and identification was achieved by high resolution mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron ionization mode (GC/EI-HRMS).

Quantification of PAHs was performed with the internal standard method. Five concentrations of standard solutions containing the deuterated compounds and the 16 PAHs (Supelco, Bellefonte, USA) were analyzed to determine respective calibration curves. In addition, a mixture of 25 nitro-PAHs and the four deuterated nitro-PAH standards was used to determine respective response factor for these compounds.

For compounds identified by mass spectrometry but not present in a labelled form in the standard solution, a quantification was performed on the basis of the relative response factor of the PAH, alkyl-PAH or nitro-PAH with those standards having the closest retention time in the chromatogram.

Results and discussion

In this paper we discuss the results for selective PAHs and nitro-PAHs and compare them with particle number emissions. In Figure 3 the effect of ethanol blending on the emissions of some PAHs and PN is shown. The four PAHs displayed in this figure are representatives of the 16 PAHs analyzed, from naphthalene, the most volatile PAH with a boiling point of 218°C to benzo(a)pyrene, a class 1 carcinogen with a boiling point of 495°C. PAH concentrations are reported in undiluted exhaust in ng/Nm^3 and particle number emissions in particles/km.

All the16 PAH shown in Figure 1 were detected in E0 samples, whereas some of the higher molecular mass PAHs were not found in E10 and E85 samples.

A clear decreasing trend on PAH and particle emissions can be observed when comparing E0, E10 and E85 data, most pronounced in the hot start WLTC cycle (Figure 3). The trends seem to be more pronounced for four- and five-ring PAHs than for two- and three-ring PAHs. In other words fuel effects are stronger, with increased ring number and decreased volatility of the compound.

The results obtained under cold start conditions differ to a same degree (Figure 3, blue bars) from those for hot engine/catalyst conditions (red bars). In general, the PAH concentrations show a downward trend under hot start conditions, with E85 concentration being the lowest, except for naphthalene which is slightly higher than that obtained for E10. As an example, the concentration of BaP which was 157 ng/Nm^3 for E0 is reduced to 30 and 17 ng/Nm^3 when gasoline is blended with 10% and 85% ethanol, respectively. This means a reduction of BaP emissions of 81% for E10 and almost 90% when using E85 fuel. Average reductions of 78% and 84% were obtained for other PAHs with E10 and E85, respectively.

Under cold start conditions, the observed trends are less consistent. Overall, decreasing trends are observed when comparing ethanol blends (E10 and E85) with gasoline (E0). This trend is also found for the PN emissions. It seems like, as the number of rings increases in PAHs, the trends become more unsteady under cold start conditions. There are examples where the concentration decreases from E0 to E10 and the opposite occurs for others. However, it is clear that in most cases, emissions of PAHs and PN are higher under cold start conditions and decrease with higher ethanol levels. This is in accordance with the literature [11, 12]. Overall, one can conclude that blending ethanol with gasoline decreases both PAH and PN emissions under cold and hot start conditions.

PAHs are ubiquitous air pollutants and as such are also found in dilution air. However, concentrations in examined exhausts exceeded those of the dilution air in most cases and emissions under cold start conditions mostly exceeded those from a hot engine/catalyst.

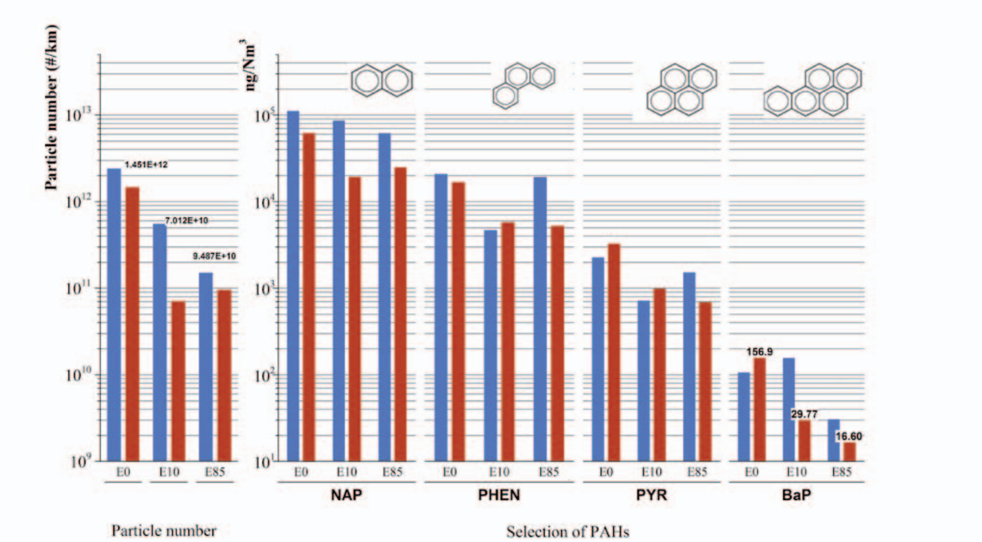

Figure 3. Effects of ethanol blending on the particle number (PN) and PAH emissions. Gasoline (E0) and gasoline/ethanol blends (E10 and E85) were tested under cold (blue) and hot start conditions (red) in the WLTC cycle. The abbreviations used are: NAP (naphthalene), PHEN (phenanthrene), PYR (Pyrene) and BaP (Benzo(a)pyrene). Respective structures are also given

Regarding the particles, a substantial decrease is observed with the use of E10 and E85 fuels. A decrease of 95% is observed with respect to PN when E10 is used and a reduction of 94% was obtained for E85.

Observing these results, it can be concluded that both, PN and PAH emissions, decrease when gasoline is blended with ethanol.

Data on PAH and PN emissions on GDI vehicles are scarce. Similarly, a decrease of PAH and PN emissions was reported for direct injection spark ignition vehicles with E10 [13]. Storey et al. [14] also found a decrease of PN emissions of GDI vehicles driven under transient cycles when using E10.

Figure 4 shows a selection of some nitro-PAHs which resulted in the highest exhaust concentrations. As reported before [6], nitro-PAHs are constituents of non-filtered and filtered diesel exhausts and are also found in GDI vehicle exhaust as it is shown here. Exhaust concentrations varied from 1 to 650 ng/Nm^3 as shown in Figure 4. The levels found for nitro-PAHs ranged from one to two orders of magnitude higher than those detected in ambient air. To this extent, nitro-PAH ambient air levels reported in literature varied substantially. While Li et al. [15] measured concentrations ranging from 1.1 ± 1.1 ng/m^3 others [16] reported values from 0.03 to 3.00 ng/m^3.

Overall, it seems that the use of ethanol is also reducing nitro-PAH emissions, as it happens for the PAHs. Note that hot start emissions are higher in most samples. A similar phenomenon was observed for nitro-PAHs detected in diesel exhaust with and without filter [5]. In the reported study, nitro-PAH concentrations in filtered diesel exhaust were higher in some cases, due to nitration processes in the filter, but lower for others due to better efficiency conversion in the filter.

Conclusions

The use of gasoline blended with ethanol produced a substantial reduction of genotoxic PAH nitro-PAH and particle number emissions of a EURO-5 GDI vehicle. The use of only 10% of ethanol is sufficient to reduce PN by 95% and PAHs in the range of 78–84%. Nevertheless, these results should be confirmed with further experiments and the use of other alcohol-based fuels.

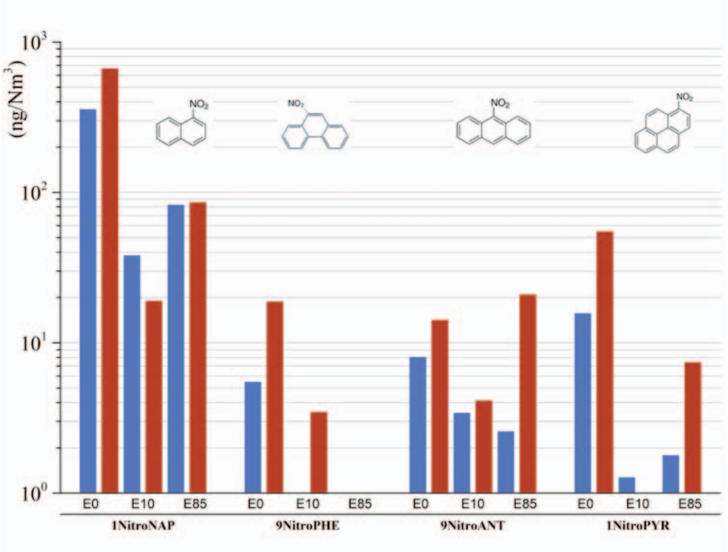

Figure 4. Effect of ethanol blending on selected nitro-PAH emissions. Gasoline (E0) and ethanol blends (E10 and E85) were tested under cold (blue) and hot start conditions (red) in the WLTC cycle. Those bars not appearing are non-detected

References

[1] Srogi, K., *Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review.* Environmental Chemistry Letters, 2007. 5(4): p. 169-195.

[2] Tobiszewski, M. and J. Namieśnik, *PAH diagnostic ratios for the identification of pollution emission sources.* Environmental Pollution, 2012. 162(0): p. 110-119.

[3] Alasdair H. Neilson, J.A., *PAHs and related compounds: Chemistry*. Vol. Part I. The handbook of environmental chemistry. 1998, Berlin: Springer-Verlag.

[4] Conesa, J.A., et al., *Comparison between emissions from the pyrolysis and combustion of different wastes.* Journal of Analytical and Applied Pyrolysis, 2009. 84(1): p. 95-102.

[5] Heeb, N.V., et al., *Secondary effects of catalytic diesel particulate filters: Conversion of PAHs versus formation of Nitro-PAHs.* Environmental Science & Technology, 2008. 42(10): p. 3773-3779.

[6] Heeb, N.V., et al., *Impact of Low- and High-Oxidation Diesel Particulate Filters on Genotoxic Exhaust Constituents.* Environmental Science & Technology, 2010. 44(3): p. 1078-1084.

[7] Bamford, H.A., et al., *Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials.* Chemosphere, 2003. 50(5): p. 575-587.

[8] Mohr, M., A.-M. Forss, and U. Lehmann, *Particle Emissions from Diesel Passenger Cars Equipped with a Particle Trap in Comparison to Other Technologies.* Environmental Science & Technology, 2006. 40(7): p. 2375-2383.

[9] A. Ulrich, A.W., A. Hess, N. Heeb, L. Emmenegger, J. Czerwinski, M. Kasper, J. Mooney, A. Mayer, *particle and metal emissions of diesel and gasoline engines. Are particle filters appropiate measures?*, in *16th Conference on Combustion Generated Nanoparticles*. 2012: Zürich.

[10] European Committee for Standardization, *Stationary source emissions – determination of mass concentration of PCDDs/PCDFs and dioxin-like PCBs – part I: sampling of PCDDs/PCDFs*. 1996: Brussels.

[11] Chang, H.-L., et al., *Gasoline Cold Start Concept (gCSC™) Technology for Low Temperature Emission Control.* SAE Int. J. Fuels Lubr., 2014. 7(2): p. 480-488.

[12] Ni, P., X. Wang, and S. Wei, *Effects of intake air temperature on SI engine emissions during a cold start.* International Journal of Sustainable Energy, 2011. 33(2): p. 243-250.

[13] Aakko-Saksa, P.T., L. Rantanen-Kolehmainen, and E. Skyttä, *Ethanol, Isobutanol, and Biohydrocarbons as Gasoline Components in Relation to Gaseous*

Emissions and Particulate Matter. Environmental Science & Technology, 2014. 48(17): p. 10489-10496.

[14] Storey, J.M.E., et al., *Exhaust Particle Characterization for Lean and Stoichiometric DI Vehicles Operating on Ethanol-Gasoline Blends*. 2012, SAE International.

[15] Li, W., et al., *Concentrations and origins of nitro-polycyclic aromatic hydrocarbons and oxy-polycyclic aromatic hydrocarbons in ambient air in urban and rural areas in northern China.* Environmental Pollution, 2015. 197: p. 156-164.

[16] Dimashki, M., S. Harrad, and R.M. Harrison, *Measurements of nitro-PAH in the atmospheres of two cities.* Atmospheric Environment, 2000. 34(15): p. 2459-2469.

Valorization of n-butanol as gasoline replacement in a DISI engine and the effect of injection phasing

Waloryzacja alkoholu butylowego jako zamiennika benzyny w silniku o zapłonie iskrowym z bezpośrednim wtryskiem oraz efekt zmian faz wtrysku na emisję spalin

Simona Silvia Merola*, Adrian Irimescu, Gerardo Valentino – Istituto Motori CNR, Napoli, Italy;
Ramón Fernando Colmenares-Quintero – Research Group TERMOMEC, Universidad Cooperativa de Colombia, Medellín, Colombia;
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Abstract

Alcohols represent a viable replacement for gasoline, with the advantages of providing improved energy security as well as reduced environmental impact. Compared to ethanol, which holds the majority of the alternative fuels market share in transportation, n-butanol features higher energy density and better compatibility with existing fuel systems designed for gasoline. Given this background, the present study investigated the use of pure n-butanol fuelling of a wall guided direct injection spark ignition (DISI) engine with optical accessibility through the piston crown. Different injection timings were considered, and variations of soot emissions were evaluated based on smoke measurements. Besides thermodynamic investigations through the analysis in-cylinder pressure traces, flame chemiluminescence was applied for a more detailed view of the chemical processes during combustion. All conditions were benchmarked to gasoline fuelling, thus giving comprehensive information on the effect of fuel properties. It was found that the change in injection timing, even by a relatively reduced crank angle, had a significant effect on the smoke at the exhaust, for both fuel types. Early fuel delivery resulted in high soot emissions, while late injection had the opposite effect. No soot-nitrogen oxides trade-off point, specific for diesel power units, could be identified, but the optimum injection strategy resulted in high engine output and low particulate emissions. The alcohol featured increased sensitivity not only to changes in the start of injection, but also showed the potential for very low smoke. The investigations further emphasize the importance of air-fuel mixture formation and also identified ways to minimize the environmental impact of DISI engines through the development of optimized control strategies.

Keywords: spark ignition engine, wall guided direct injection, gasoline, n-butanol, flame emission

1. Introduction

Environmental regulations, energy security, diversity and global warming, are just some of the factors that have encouraged the search for partial or total substitutes for fossil fuels. Among the alternatives, fuels derived from renewable resources such as alcohols are being considered for automotive applications. Currently, ethanol is the alternative more used for fuel replacement in spark ignition engines; in fact, it is widely used as an alternative fuel in countries such as United States, Brazil, China, etc. However, ethanol is corrosive to aluminium or polymer components which are present in the existing pipelines, injection systems and fuel tanks. Therefore, to use ethanol in the actual combustion engines, some engine components should be modified [1, 2].

On the other hand, butanol is a very competitive fuel for use in internal combustion engines. It has higher heating value, lower volatility, and it is less hygroscopic and corrosive than ethanol. However, its main disadvantage is the low production volumes, which makes it less cost-competitive with ethanol and gasoline. It is expected that cost effective production of butanol will be reached in the foreseeable future [1–3]. Because of butanol's potential as a fuel, some studies have been presented in the last years in which both compression and spark ignition engines were fuelled with pure butanol or butanol-fossil fuel blends [4–7].

Tornatore et al. [8] studied engine performance at different spark timings and fuel injection phasing with a 40% butanol-gasoline blend in a port fuel injection (PFI) spark ignition engine. Their results showed similar engine performance compared to that obtained in the same conditions using pure gasoline. Gu et al. [9] in a similar study, investigated emissions and performance at different exhaust gas recirculations (EGR) and spark timings with butanol-gasoline blends (0-100%vol butanol). Reductions in specific NO_x emissions were found for blends and pure butanol compared with gasoline. However, as the butanol content increased, the engine performance decreased. Deng et al. [3,10] reported higher knocking resistance at higher spark timing advances using 30 and 35%vol butanol/gasoline blends in a spark ignition engine. Sing et al. [5] evaluated the behaviour of a spark ignition (SI) engine using butanol-gasoline blends (butanol vol.<75%). Without hardware modification, fuel blends showed similar performance and emissions to those obtained using gasoline. Similar results were found by Irimescu et al. [11] in an optical accessible DISI engine fuelled with butanol at part load operation. The authors also reported NO_x and soot reduction when the engine was fuelled with butanol compared to those obtained with gasoline.

Merola et al. [12] studied the combustion performance of 20% butanol addition to gasoline in an optical accessible engine. Data were taken at 2000 rpm with boosting and wide open throttle. In a study at low load, Aleiferis et al. [13] investigated the flame development at stoichiometric and lean conditions with ethanol, butanol, iso-octane and methane. Experiments were carried out with engine velocity at 1500 rpm and intake pressure at 0.5 bar. Their results showed more cyclic stability for alcohols regarding changes in fuelling. Karavalakis et al. [14] studied ethanol and iso-butanol blends (Alcohol vol< 32%) in two passenger cars equipped with DISI engines. Higher ethanol and butanol blends showed reductions in particulate matter (PM) and soot mass emissions.

In summary, results for pure butanol and various blends showed that both engine performance and emissions could be similar to those obtained using gasoline. Therefore, butanol results in a promising bio-fuel to reach low smoke emissions, with reduced changes in the engine performance. In order to optimize engine operation with butanol as gasoline replacement several engine settings require adjustment. To this end, the present work studied the effects of spark timing and fuel injection strategies on the performance and smoke emissions of a DISI engine fuelled with butanol (both parameters can be modified electronically in the commercial engines). The main goal was to achieve lower smoke emissions without performance limitations when butanol is used as gasoline replacement.

2. Methodology

2.1. Experimental setup

Experiments were carried out on an optically accessible single cylinder DISI engine (Figure 1). It was equipped with the cylinder head of a commercial gasoline engine with similar geometrical specifications (bore, stroke and compression ratio). The cylinder head was equipped with four valves per cylinder and a centrally located spark plug; the injector was side coupled and had 6 holes oriented for directing the spray towards the piston crown (wall guided system). Further details on the engine are given in Table 1.

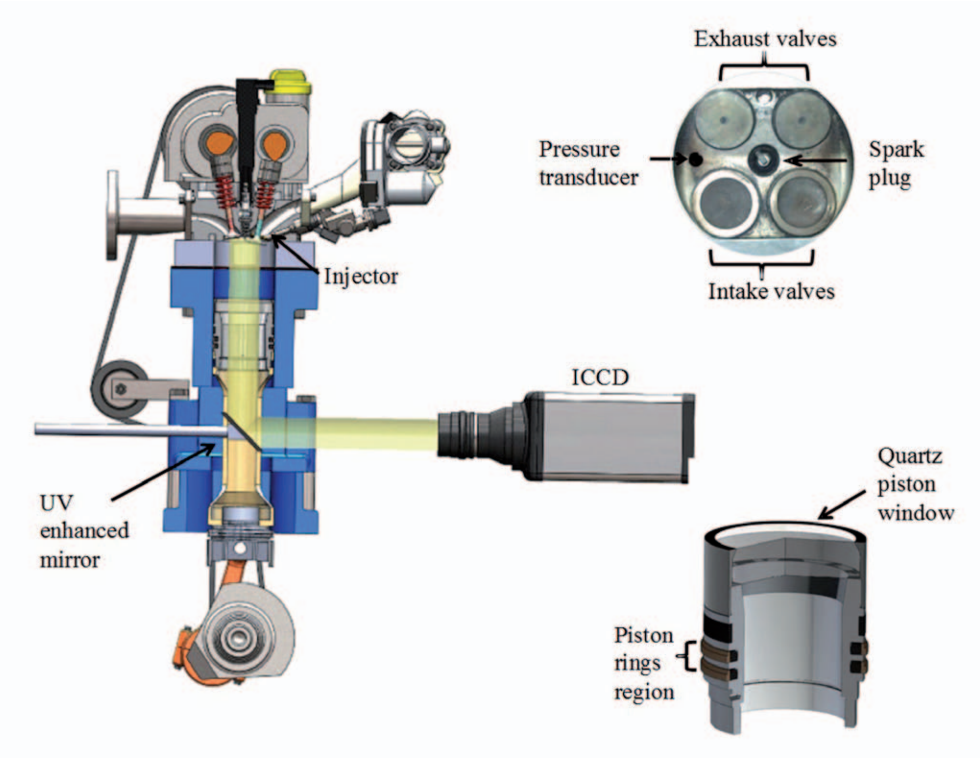

Figure 1.Representation of the experimental setup

Table 1.Engine characteristics

Parameter	Value
Displacement	399 cm^3
Stroke	81.3 mm
Bore	79 mm
Connecting rod	143 mm
Compression ratio	10:1
Number of valves	4
Exhaust valve open (EVO)	153 CAD aTDC
Exhaust valve close (EVC)	360 CAD aTDC
Inlet valve open (IVO)	357 CAD aTDC
Inlet valve close (IVC)	144 CAD bTDC

In-cylinder pressure signals were detected with an accuracy of ±1% using a non-cooled piezo-electric transducer (AVL GH12D). Pressure was recorded with a resolution of 0.2 CAD (crank angle degree) through an optical encoder. Two hundred pressure curves were acquired in each experimental condition at steady state operation. Smoke emissions were determined with an accuracy of ±3% using an AVL 415S smoke meter.

Intake air temperature and ambient pressure were close to 300 K and 1 atm, respectively. Fuel injection pressure was set at 100 bar. Coolant temperature was maintained within the range of ±2 K around 330 K using a temperature control system coupled to the engine cooling circuit. All the trials were carried out at 2000 rpm and with air/fuel ratio close to stoichiometric condition ($\lambda \approx 1$); the duration of injection (DOI) was set at 43 CAD for all butanol test conditions, while this was reduced to 36 CAD when the engine was fuelled with gasoline (baseline fuel). This change in the DOI was made in order to compensate the differences in chemical and physical properties of both fuels (Table 2). The spark timing and start of injection were selected around the optimum condition for gasoline; 15 CAD before the top dead centre (bTDC) for spark advance (SA) and 300 CAD bTDC for start of injection (SOI). The experimental conditions are shown in Table 3. Unless otherwise specified, all start of injection and spark timing values are given in CAD bTDC at the end of compression.

Table 2. Fuel properties. Adapted from [15]

Fuel type	n-Butanol	Gasoline
Chemical formula	C_4H_9OH	C_4-C_{12}
Stoichiometric air/fuel ratio	11.2	14.7
Density (kg/m^3)	810	736
Lower heating value (MJ/kg)	33	42.9
Latent heat of vaporization (kJ/kg)	716	380-500

Table 3. Experimental conditions

Parameter	Values
Spark timing (CAD bTDC)	5, 10, 15, 20, 25
Start of injection (CAD bTDC)	260, 300, 340

2.2. Thermodynamic analysis

Using in-cylinder pressure data it was possible to calculate net heat release and indicated mean effective pressure (IMEP), among other thermodynamic parameters. Combustion diagnostic was performed using a simplified approach based on the first law of thermodynamics applied to the engine combustion chamber. (see Eq.(1)) [16].

$$\frac{dQ}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta} \qquad (1)$$

where Q is the heat release measured in J, in-cylinder pressure p in Pa, V is the cylinder volume in m^3, and the ratio of specific heats γ was chosen as equal to 1.35 [16].

Bulk gas temperature (T) was evaluated for the time interval between IVC and EVO (see Eq. (2)).

$$T(\theta) = \frac{T_{IVC}}{p_{IVC} V_{IVC}} p(\theta) V(\theta) \qquad (2)$$

where charge temperature T_{IVC} at intake valve closure was chosen as 300 K.

3. Results and discussion

The effect of butanol on engine performance was evaluated using different spark timings and start of injection strategies. Results for butanol were compared with those obtained for gasoline at spark advance (SA) 15 CAD and SOI 300 CAD bTDC. According to the results of this investigation, engine performance was always lower for butanol than for gasoline (Figure 2). However, it should be noted that the lowest difference was around 0.2 bar (≈3%) and was reached at SOI 300 CAD bTDC and SA 20 CAD (similar configuration to that used with gasoline). The highest IMEP values for butanol were measured at SOI 300, followed by SOI 340 and SOI 260 CAD bTDC. In this last condition, the lowest performance could be related to the low air velocity during the injection phase, which affects the mixing process between air and fuel.

Figure 2 also shows that the maximum brake torque (MBT) point was more advanced for the alcohol (i.e. 20 CAD bTDC) compared to gasoline, but differences were reduced in a ±5 CAD range around the 15 CAD bTDC setting.

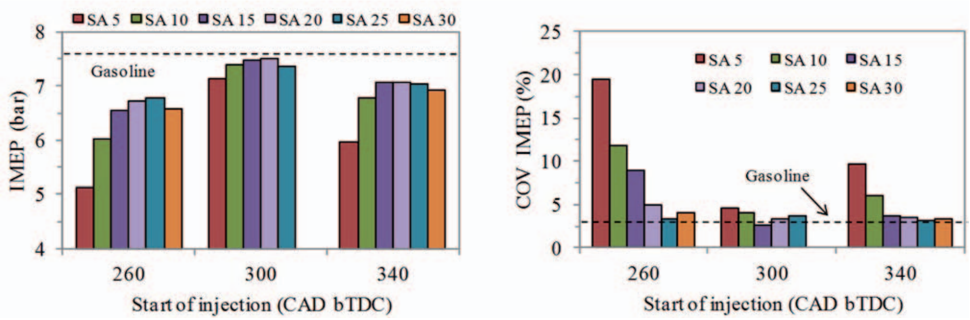

Figure 2. Indicated mean effective pressure (left) and coefficient of variance of IMEP (right)

Engine stability was evaluated through the coefficient of variation (COV) of the IMEP; this parameter was found to be around the 5% threshold, accepted as a limit for commercial engines for most of the injection-spark timing range. The SOI 260 condition featured the highest COV values. These results could be related to the mixture homogeneity between air and butanol which is affected by fuel vaporization spray impingement on the combustion chamber wall, among others. Roughly the same conclusion can be drawn after examining the values of peak pressure, as well as its cycle-to-cycle variation (Figure 3).

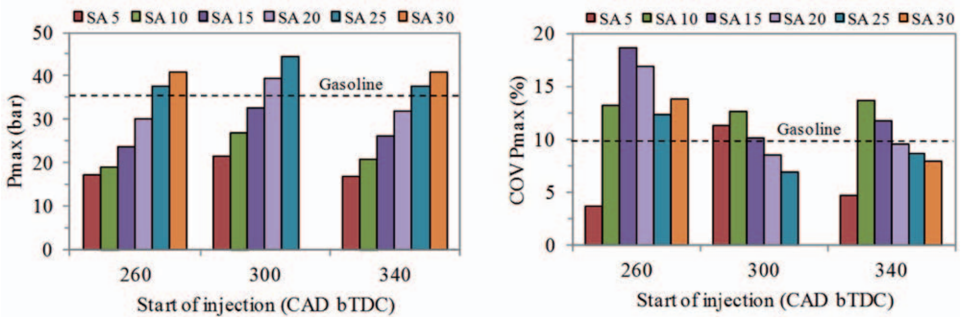

Figure 3. Peak pressure (left) and coefficient of variance of peak pressure (right)

As it was aforementioned, the highest IMEP values were measured using spark advance between 10-25 CAD. Therefore, in order to analyse the points with potential to achieve high performance with low emissions, the following discussion about emissions were focused on the SA interval between 10-25 CAD. Figure 4 shows the effect of spark and injection timing on engine pollutant emissions. CO concentrations were comparable for the two fuels, and within the expected range for stoichiometric operation. Unburned hydrocarbons (HC) generally featured lower values for the alcohol compared to the reference case with gasoline fuelling; for the SOI 260 setting, much higher HC concentrations were recorded, which can be attributed to the different distribution of the mixture inside the combustion chamber and the mechanism of slow oxidation within the top-land region. NO_x emissions were reduced when using butanol compared to gasoline. The difference found between the two fuels can be directly related to the thermal effect [16, 17].

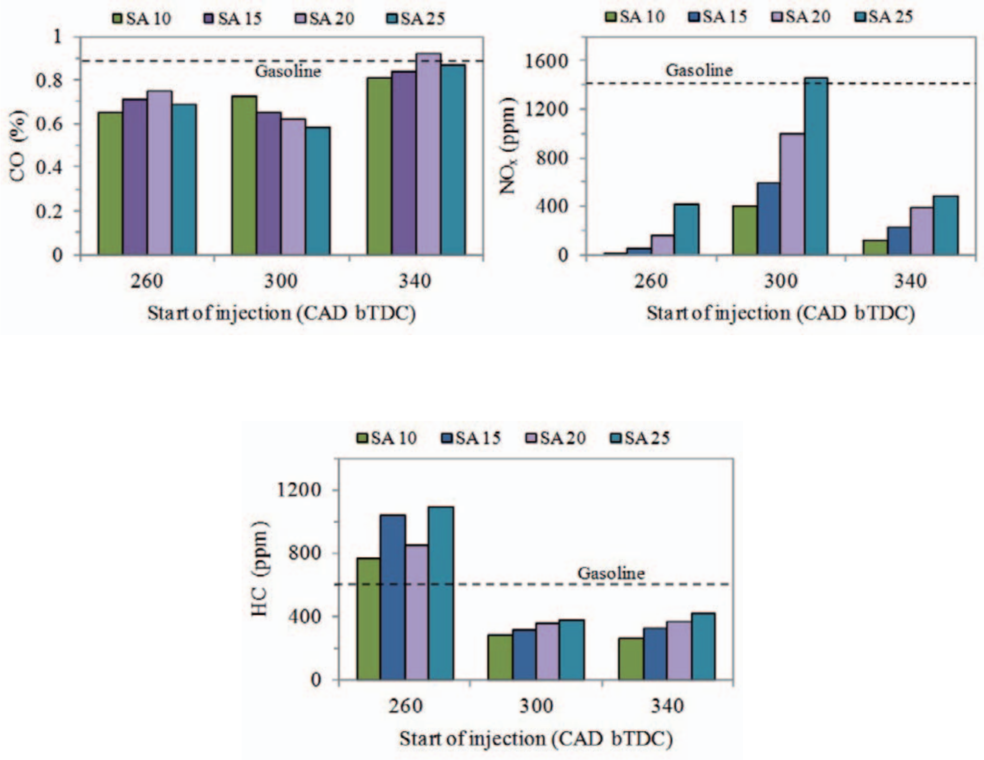

Figure 4. Pollutant emissions for butanol and the reference case of SOI 300, SA 15 for gasoline

A more detailed analysis of the in-cylinder pressure traces was performed for the optimum setting of SOI 300 CAD bTDC and SA 15 CAD bTDC. As an overall trend, peak pressure was higher for gasoline than for butanol, most likely due to the lower evaporative rates achieved by butanol promoted by its high latent heat of evaporation compared with gasoline (Table 2). After the fuel injection phase, complete butanol evaporation would reduce the temperature of a stoichiometric fuel/air mixture by about 50°C, while this reduction would be only 18°C for gasoline, as can be found using the relations given in [16]. These temperature drops are accompanied by a decrease in fuel saturation pressure. Therefore, it is possible that the fuel reached saturation conditions, which would result in fuel droplets after the injection phase and lower mixture homogeneity for butanol.

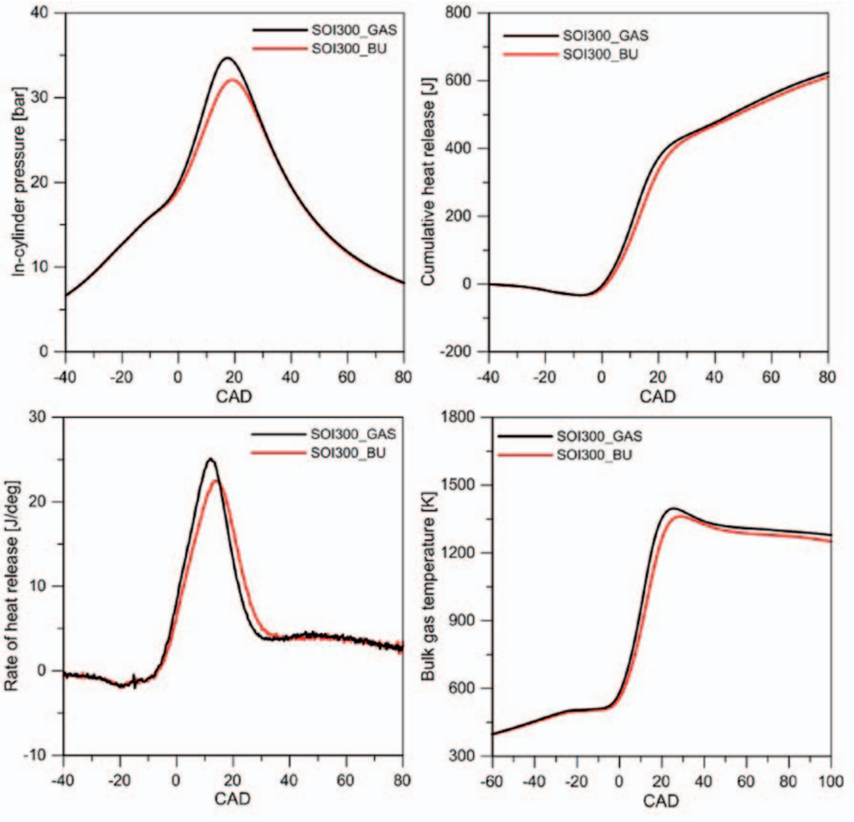

Figure 5.Combustion performance comparison between gasoline and butanol (SOI_300 CAD bTDC; SA_15 CAD bTDC)

According to the analysis of the rate of heat release, gasoline develops faster combustion during the first phase, while comparable values for the final part could also be related to mixture homogeneity differences between both fuels. The maximum burning velocity for fuels are usually obtained close to the stoichiometric conditions, therefore fuel rich or lean zones inside the combustion chamber reduce the flame propagation velocities as could have happened when butanol was tested. On the other hand, the bulk gas temperature decreased slightly when butanol was used with respect to gasoline. This reduction is related to lower in-cylinder pressure and explains the observed variation in NO_x emissions, especially when considering the exponential relation between gas temperature and formation rates for this pollutant species.

In order to better understand the effect of the butanol fuelling, optical investigations were performed. Specifically, digital imaging and natural emission spectroscopy both in the UV-visible wavelength range were applied for both fuels. UV-visible imaging was performed to follow the flame front propagation from spark ignition to the late combustion phase. Figure 6 (with ASOS for after start of spark) presents a selection of images detected fixing the SOI at 300 CAD bTDC and the spark timing at 15 CAD bTDC for butanol and gasoline. The flame kernel was resolvable around 5 CAD after the spark discharge, due to the very high luminosity of spark induced plasma that can be well appreciated at 2 CAD bTDC.

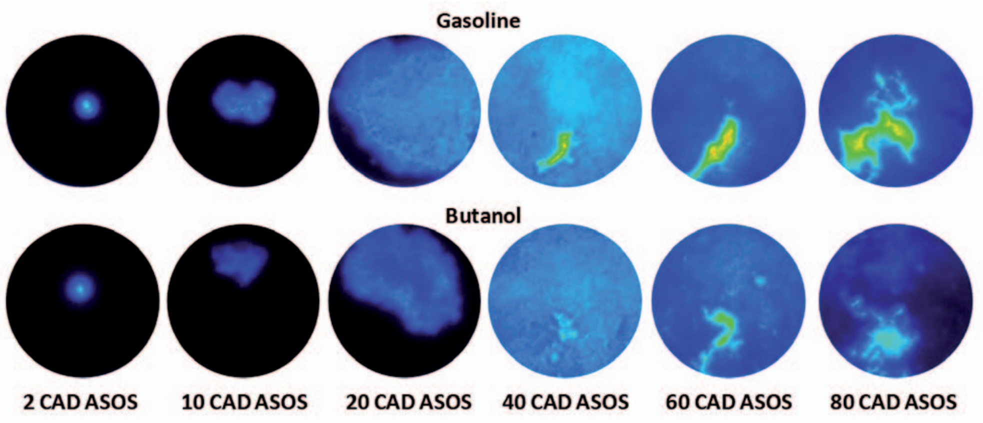

Figure 6. Flame front propagation detected fixing the SOI at 300 CAD bTDC and the spark timing at 15 CAD bTDC for butanol and gasoline

After ignition, the flame evolved from kernel phase (10 CAD ASOS) towards the combustion chamber walls with a small asymmetry in the flame outline. A distortion from the circular shape was evident for both conditions around 20 CAD ASOS. The flame progressed with different velocity towards the intake and exhaust valves, due to the combined effects of local temperature and air-fuel ratio gradients [18]. Moreover, the burned gas area in these early combustion stages resulted larger and less distorted for gasoline compared tobutanol. The effect was in agreement with the lower evaporation rate of butanol previously discussed. The burning of fuel deposits on the piston surface induced fuel rich zones that slowed down the flame front propagation inducing flame shape distortion [19].

Regarding the chemical species that featured the combustion process, Figure 7 shows the typical flame emission spectra measured at different CADs after the spark timing (ASOS) for butanol and gasoline. The spectra were obtained fixing the SOI at 300 CAD bTDC and the spark timing at 15 CAD bTDC. The acquisition location is identified by a small square in the flame image on the bottom of the figure. In agreement with literature [12, 18], the early combustion stage (until to 20 CAD ASOS) was characterized by OH and CH superimposed to HCO broadband contribution [20], [21]. In this phase, OH radicals participated to the initiation of combustion, being key species for breaking C–H bonds in hydrocarbon fuels. At 10 CAD ASOS, OH emission band at 309 nm appeared together with the 282 nm band for gasoline flame emission. This confirmed the higher gas temperature of the fuel combustion already in the early combustion phase. Successively, CH, HCO and formaldehyde evolved through the interaction with the oxygen compounds to form CO_2. At 20 CAD ASOS, the excited CO_2 was detected. CO_2 was featured by a broad band emission extended from approximately 300 nm to 500 nm with a peak around 400 nm [22].

From 20 to 40 CAD ASOS, the emission spectra evolved in intensity with a similar spectral behaviour. Then a continuous signal, increasing with the wavelength, appeared. This was due to the emission of soot precursors formed as a consequence of the diffusion flames due to the fuel deposits burning [11, 12, 23]. In the late combustion phase the soot signal increased becoming more intense for gasoline than for butanol.

The fuelling effect on the soot formation and oxidation was better appreciated through the evolution of the luminous emissions in two regions of interest (ROIs) corresponding to half of the combustion chamber. As shown in Figure 8 (left), the diffusion flames were still significant at 100 CAD ASOS and always more intense for gasoline. This confirmed that the fuel deposits flames persisted well after the normal combustion. This reached the highest luminosity around 40 CAD ASOS for both the fuels and then decreased faster than the fuel burning flame (Figure 8, right). The evolution of the UV-visible spatially integrated signal demonstrated the effect of butanol in the reduction of soot emissions; these results agree with the soot concentrations measured by smokemeter at the exhaust (Figure 9). In particular, butanol fuelling permitted to maintain the smoke emissions lower than gasoline; higher values were measured only for advanced injection timing. Smoke emissions increased advancing the spark timing. This resulted in higher peak pressure and also more mass of unburned fuel trapped in the crevices. The highest smoke emissions could be related to the rate of Arrhenius-dependent particulate matter nucleation which is a function of the in-cylinder pressure and bulk gas temperature [24, 25].

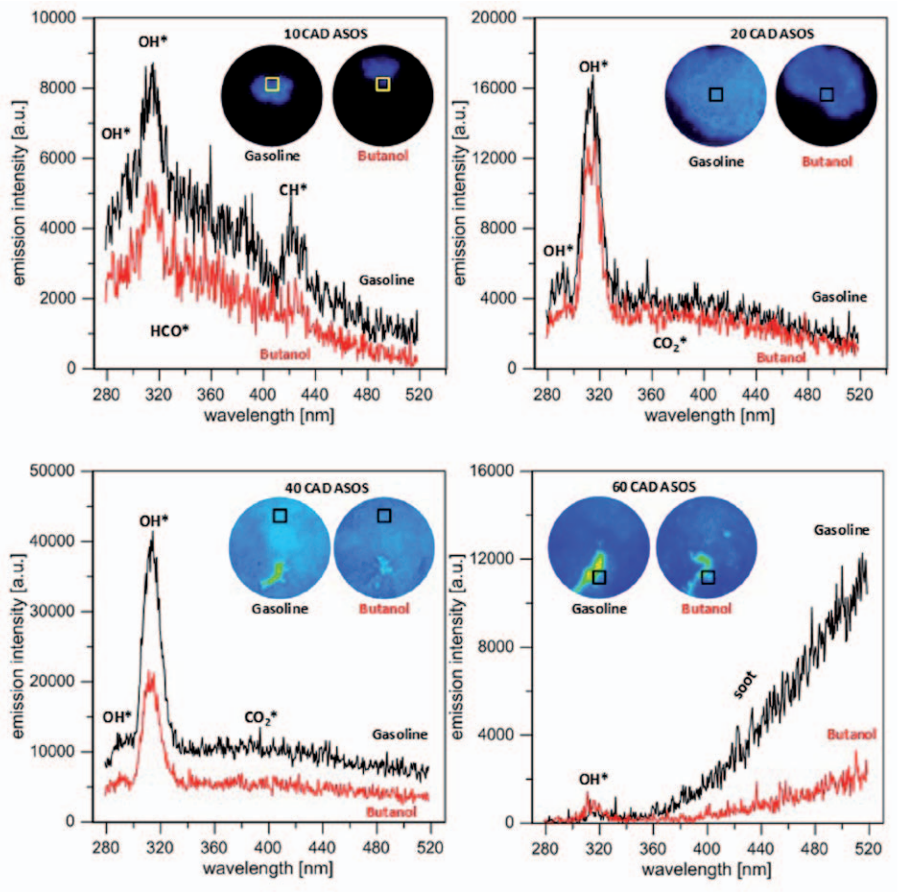

Figure 7. UV-visible emission spectra detected at different CADs after the spark timing (ASOS) for butanol and gasoline (SOI 300 CAD bTDC, spark timing 15 CAD bTDC); the acquisition location is identified by a small square in the flame image

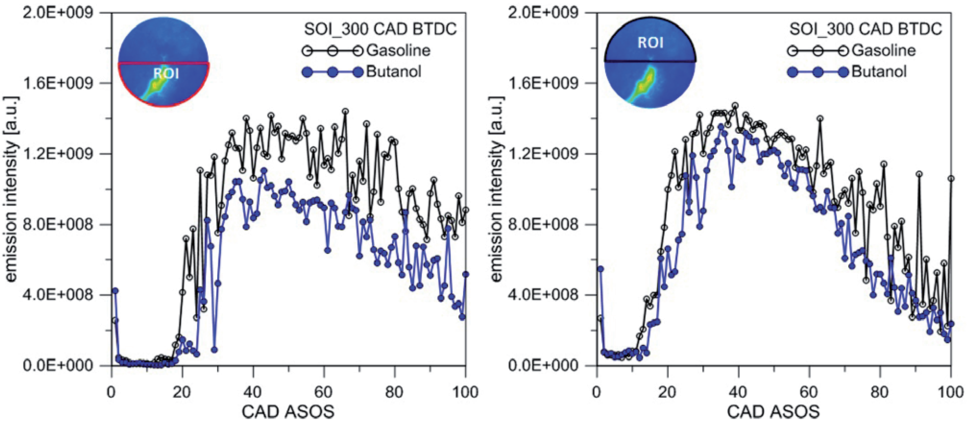

Figure 8. Spatially integrated luminous emissions evaluated in two regions of interest (ROI) corresponding to half combustion chamber

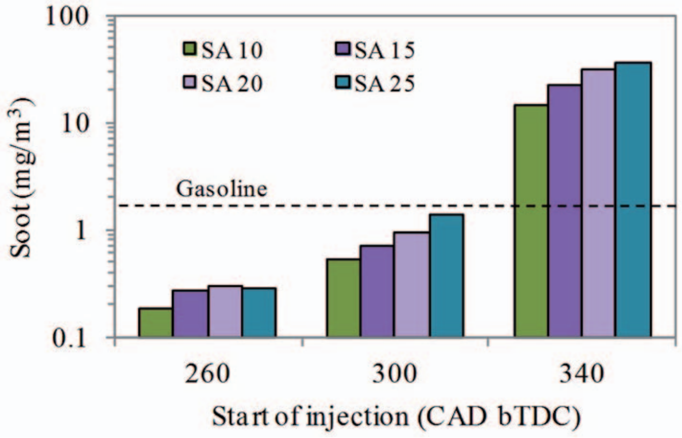

Figure 9. Soot concentration measured at the exhaust at different SOI settings

Conclusions

The possibility of replacing gasoline with n-butanol was investigated in a DISI engine. Apart from thermodynamic data, optical measurements gave improved insight into the formation of soot. The effect of injection phasing was investigated through in-cylinder pressure measurements and UV-visible flame visualization in a wall guided DISI engine. Within the range of three different injection strategies, significant differences were recorded depending on fuel type. Overall engine performance was lower for butanol compared to gasoline in the reference condition. This was determined by poor fuel evaporation and uneven distribution inside the combustion chamber of the alcohol. Despite this, an optimal butanol injection strategy was identified (SOI_300 CAD bTDC; SA_15 CAD bTDC) that allowed to improve NO_x, HC, CO emission without penalty in terms of combustion efficiency. Optical data demonstrated that different charge distributions were obtained when changing the fuel. Diffusive flames due to fuel deposits burning were detected in the region between the injector and the intake valves – that persisted in the late combustion phase and resulted more intense for gasoline. This could be correlated to differences in liquid properties and the fact that gasoline is a multi-component fuel, as well as chemical kinetics. These results agree with lower soot concentrations measured for the optimal butanol fuelling setting. As a general conclusion, gasoline could be replaced with n-butanol with minimal changes in engine performance.

References

[1] C. Jin, M. Yao, H. Liu, C.F.F. Lee, J. Ji, Progress in the production and application of n-butanol as a biofuel, Renew. Sustain. Energy Rev. 15 (2011) 4080–4106. doi:10.1016/j.rser.2011.06.001.

[2] Z. Zhang, T. Wang, M. Jia, Q. Wei, X. Meng, G. Shu, Combustion and particle number emissions of a direct injection spark ignition engine operating on ethanol/gasoline and n-butanol/gasoline blends with exhaust gas recirculation, Fuel. 130 (2014) 177–188. doi:10.1016/j.fuel.2014.04.052.B.

[3] B. Deng, J. Yang, D. Zhang, R. Feng, J. Fu, J. Liu, et al., The challenges and strategies of butanol application in conventional engines: The sensitivity study of ignition and valve timing, Appl. Energy. 108 (2013) 248–260. doi:10.1016/j.apenergy.2013.03.018.

[4] A. Elfasakhany, Experimental investigation on SI engine using gasoline and a hybrid iso-butanol/gasoline fuel, Energy Convers. Manag. 95 (2015) 398–405. doi:10.1016/j.enconman.2015.02.022.

[5] S.B. Singh, A. Dhar, A.K. Agarwal, Technical feasibility study of butanol-gasoline blends for powering medium-duty transportation spark ignition engine., Renew. Energy. 76 (2015) 706–716. doi:10.1016/j.renene.2014.11.095.

[6] A.F. López, M. Cadrazco, A.F. Agudelo, L. a. Corredor, J. a. Vélez, J.R. Agudelo, Impact of n-butanol and hydrous ethanol fumigation on the performance and pollu-

tant emissions of an automotive diesel engine, Fuel. 153 (2015) 483–491. doi:10.1016/j.fuel.2015.03.022.

[7] B. He, M. Liu, H. Zhao, Comparison of combustion characteristics of n-butanol/ethanol – gasoline blends in a HCCI engine, Energy Convers. Manag. 95 (2015) 101–109. doi:10.1016/j.enconman.2015.02.019.

[8] C. Tornatore, L. Marchitto, G. Valentino, F. Esposito Corcione, S.S. Merola, Optical diagnostics of the combustion process in a PFI SI boosted engine fueled with butanol-gasoline blend, Energy. 45 (2012) 277–287. doi:10.1016/j.energy.2012.03.006.

[9] X. Gu, Z. Huang, J. Cai, J. Gong, X. Wu, C.F. Lee, Emission characteristics of a spark-ignition engine fuelled with gasoline-n-butanol blends in combination with EGR, Fuel. 93 (2012) 611–617. doi:10.1016/j.fuel.2011.11.040.

[10] B. Deng, J. Fu, D. Zhang, J. Yang, R. Feng, J. Liu, et al., The heat release analysis of bio-butanol/gasoline blends on a high speed SI (spark ignition) engine, Energy. 60 (2013) 230–241. doi:10.1016/j.energy.2013.07.055.

[11] A. Irimescu, L. Marchitto, S.S. Merola, C. Tornatore, G. Valentino, Combustion process investigations in an optically accessible DISI engine fuelled with n-butanol during part load operation, Renew. Energy. 77 (2015) 363–376. doi:10.1016/j.renene.2014.12.029.

[12] S.S. Merola, G. Valentino, C. Tornatore, L. Marchitto, In-cylinder spectroscopic measurements of knocking combustion in a SI engine fuelled with butanol-gasoline blend, Energy. 62 (2013) 150–161. doi:10.1016/j.energy.2013.05.056.

[13] P.G. Aleiferis, J. Serras-Pereira, D. Richardson, Characterisation of flame development with ethanol, butanol, iso-octane, gasoline and methane in a direct-injection spark-ignition engine, Fuel. 109 (2013) 256–278. doi:10.1016/j.fuel.2012.12.088.

[14] G. Karavalakis, D. Short, D. Vu, R.L. Russell, A. Asa-Awuku, H. Jung, et al., The impact of ethanol and iso-butanol blends on gaseous and particulate emissions from two passenger cars equipped with spray-guided and wall-guided direct injection SI (spark ignition) engines, Energy. 82 (2015) 168–179. doi:10.1016/j.energy.2015.01.023.

[15] X. Zhang, C. Tang, H. Yu, Q. Li, J. Gong, Z. Huang, Laminar Flame Characteristics of iso -Octane/ n -Butanol Blend–Air Mixtures at Elevated Temperatures, Energy & Fuels. 27 (2013) 2327–2335. doi:10.1021/ef4001743.

[16] J.B. Heywood, Internal Combustion Engine Fundamentals, McGraw-Hill, 1988.

[17] F.N. Alasfour, NO_x Emission from a spark ignition engine using 30% Iso-butanol–gasoline blend: Part 1—Preheating inlet air, Appl. Therm. Eng. 18 (1998) 245–256. doi:10.1016/S1359-4311(97)00081-1.

[18] S.S. Merola, A. Irimescu, C. Tornatore, L. Marchitto, G. Valentino, Split Injection in a DISI Engine Fuelled with Butanol and Gasoline Analyzed through Integrated Methodologies, SAE Int. J. Engines 8(2015) 474–494, doi:10.4271/2015-01-0748.

[19] M.R. Gold, C. Arcoumanis, J.H. Whitelaw, J. Gaade, S. Wallace, Mixture preparation strategies in an optical four-valve port-injected gasoline engine, Int. J. Engine Res. 1(2000), 41–56.

[20] A.G. Gaydon. The spectroscopy of flames (1957). London: Chapman and Hall.

[21] S.D., Peyerimhoff, R.J., Buenker, W.E., Kammer, H., Hsu, Calculation of the electronic spectrum of formaldehyde, Chemical Physics Letters, 8:1 (1971) 129-135, http://dx.doi.org/10.1016/0009-2614(71)80596-1.

[22] J.M., Samaniego, F.N., Egolfopoulos, and C.T. Bowman, CO_2* chemiluminescence in premixed flames, Combustion Science and Technology, 109, 1:6, (1995) 183–203.

[23] B. S., Haynes, H. G., Wagner, Soot formation. Progress in Energy and Combustion Science, 7, 4 (1981) 229-273.

[24] D. Kayes, S. Hochgreb, Mechanisms of particulate matter formation in spark-ignition engines. 1. Effects of engine operating conditions, Environ. Sci. Technol. 33 (1999) 3957–3967.

[25] Z. Hu, N. Ladommatos, Reduction of Unburnt Hydrocarbon Emissions from Spark Ignition Engines Using In-Cylinder Catalysts. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering 210 (1996) 123-129,

Blends of ethanol, n-butanol and isobutanol with 5% oxygen in ordinary engines: Effects on exhaust emissions over the Artemis cycle

Mieszanki etanolu, n-butanolu i izobutanolu z 5% zawartością tlenu w zwykłych silnikach: wpływ na emisję w cyklu Artemis

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Abstract

In the EU, alcohol fuels are used mostly in the form of ethanol, sold either as E85, or mixed in less than 10% concentrations into gasoline for the general fleet. This work examines the effects of extending the ethanol share to 15%. Additionally, considering the high hygroscopicity and corrosivity of ethanol, two isomers of butanol, n-butanol and isobutanol, were blended with gasoline at 25% by volume, all blends corresponding to approximately 5% oxygen by weight. These four fuels were examined in two typical spark ingition automobile engines, a Ford Focus car with a Euro 6 EcoBoost direct injection (DISI) engine, and a Skoda Fabia car with a Euro 5 multipoint injection (MPI) engine. Both cars were tested on chassis dynamometer using the Artemis driving cycle. There were no measurable effects on the emissions of hydrocarbon and carbon monoxide. The alcohol fuels increased the emissions of nitrogen oxides on the MPI engine. On the DISI engine over the Artemis cycle, the number of emitted solid particles and the emissions of elemental carbon and polyaromatic hydrocarbons were reduced relative to gasoline, by about one half for both butanol isomers, while ethanol did not yield observable effects. Particle emissions of the MPI engine were generally smaller. The results suggest that both n-butanol and isobutanol are viable fuels, which could be considered as an alternative to ethanol.

Keywords: spark ignition engine, direct injection, particle emissions, particle number, particle size distribution, oxygenated fuels, ethanol, butanol

Introduction

This study evaluates the effects of three alcohols, ethanol and two isomers of butanol, on exhaust emissions from ordinary cars when blended with gasoline at a ratio corresponding to approximately 5% of oxygen by weight.

With rising concerns about petroleum being imported, at a great cost to the society, from politically problematic regions, concerns about energy security, self-sufficiency, sustainability, and concerns about climate, and with internal combustion engines powered by hydrocarbon fuels dominating the transportation sector, drop-in replacement fuels for the general vehicle fleet are being sought. To date, ethanol has been the most widely used alternative fuel for spark ignition (gasoline) engines, both in concentrated form (E85, with 70-85% of ethanol), and in low concentration blends in general use gasoline. Ethanol has its drawbacks: it is hygroscopic, it is aggressive to many materials used in older vehicles, and its high oxygen content (35% by weight) effectively limits the blending ratio (on most vehicles to approximately 15-20%) should no changes be made to the fuel metering.

Butanol is a four-carbon alcohol present in four isomers: n-butanol (1-butanol); secbutanol (2-butanol); isobutanol (2-methyl-1-propanol) and tertiary butanol (2-methyl-2-propanol). Of these, n-butanol and iso-butanol can be readily produced from biomass [1-4] and have been used in automobile spark ignition engines [5-13]. In comparison to ethanol both butanol isomers have higher energy density, lower hygroscopicity, higher viscosity, better lubricity, lower vapor pressure [14] and are less aggressive towards many materials commonly used in vehicle fuel systems. Operation of port fuel injection (MPI) engines on butanol has been associated with worsened cold startability [14], worsened atomization of fuel [15-16], shorter duration of both early and main combustion stages [7-9], higher heat release rates [17], lower cycle-to-cycle variability [7], better combustion stability [8-9], increased emissions of hydrocarbons (HC) [10-11] and lower emissions of particulate matter (PM) [13, 17, 18]. There does not appear to be a consensus as to the effect of butanol on nitrogen oxide (NO_x) emissions [9-11, 13] relative to gasoline.

Differences between the two isomers were observed, without offering a clear advantage of one over another. Both n-butanol and isobutanol can be produced from biomass at comparable costs [1] and both have the potential to reduce PM emissions. However there are differences in their production pathways and properties. N-butanol has lower embedded fossil fuel energy [1], isobutanol has higher octane number [19], flame speed and exhaust emissions [19,21]. These performance and emissions differences are not well quantified, as most studies focus only on either one of the isomers, ([19, 21, 22] give reports on both isomers in MPI engines, [23] on both isomers in DISI engines). Isobutanol, compared to n-butanol, yielded lower NO_x emissions [19], higher emissions of butyraldehyde [20], comparable [20] or higher [21] emissions of formaldehyde, comparable emissions of acetaldehyde [20,21] and higher emissions of acetone [21]. N-butanol exhibited higher emissions of formaldehyde and acetaldehyde [21].

Blending of either isomer into gasoline increases the fuels octane rating [24]. Problematic cold starts and diluted oil caused by insufficiently atomized and thus condensated fuel, were observed on direct injection (DISI) engines running on n-butanol [12]. Combusting of n-butanol in DISI engine at part load, produces favourable emissions with improvement in smoke opacity in comparison to gasoline [25, 26]. The usage of isobutanol-gasoline blends in different spray guided DISI engines, results in reduced emissions, particularly decreased PM and particle number (PN) emissions [5, 20]. While n-butanol has been combusted in research DISI engines [25, 26], most of the studies on production engines [5, 11, 20] were done with isobutanol and U.S. engines.

In this study, the effects of both isomers of butanol have been examined on two vehicles representative of the gasoline vehicle fleet. Non-oxygenated gasoline and E15, mixture of 15% ethanol with gasoline, have been used as reference fuels. E15 was chosen with the possibility to compare the results with U.S. tests, and represents, in the opinion of the authors, a reasonable blend. While the general gasoline in the Czech Republic contains only around 5-6% of ethanol, higher concentrations are often used by the public by mixing commercially sold E85 with gasoline and using such intermediate blends in the general vehicle fleet [18, 27, 28]. For blending butanol, a concentration of 25% of either n-butanol or isobutanol has been selected as being, on the fuel elemental composition basis, notably the oxygen content, closest to E15.

The focus of the study was on exhaust emissions, and of these, on particulate matter. Ultrafine particles emitted by internal combustion engines are very small, on the order of units to hundreds of nanometers in diameter, with most particles falling into the nanoparticle (< 100 nm diameter) range. Such small particles exhibit a high efficiency of deposition in human lung alveoli [27], have the ability to penetrate through the cell membrane and into the bloodstream, and contain a complex mixture known to contribute to many ailments [30], and representing a substantially higher risk than the "general" urban particulate matter [31, 32].

Experimental

Two gasoline vehicles, one with direct injection and one with port fuel injection engine, were chosen:

1) A 2013 Ford Focus Station wagon with a 1.0-liter EcoBoost 10 liquid cooled inline three-cylinder spark ignition engine EcoBoost 1,0, forced induction by exhaust turbocharger with charged air intercooler air to air type, swept volume 999 cm^3, bore × stroke 71,9 × 82 mm, compression ratio 10.0:1, power 92 kW @ 6000 min^{-1}, torque 170 Nm @ 1400 – 4500 min^{-1}, 30 s overboost 200 Nm @ 1400 – 4500 min^{-1}, curb weight 1242 kg, tire 205/55 R16, Euro6, mileage 7862 km, fuel consumption 5,8/4,2/4,8 l/100km, emmisions 114g CO_2/km.
2) A 2011 Skoda Fabia 1.4 16V, 5MT, liquid cooled inline four-cylinder naturally aspirated spark ignition engine EA111, model Volkswagen CGGB, MPI, swept volume 1390 cm^3, bore × stroke 76,5 × 75,6 mm, compression ratio 10,5:1, power 63 kW @ 5000 min^{-1}, torque 132 Nm @ 3800 min^{-1}, kerb weight 1104 kg, tyre 205/55 R16, Euro5, mileage 600 km, fuel consumption 8,6/5,3/6,5 l.100 km^{-1}, emissions 129 g $CO_2.km^{-1}$.

Basic fuel was BA95 (RON, ČSN 228) without biopart additives (provided by petrol station EuroOil, Hrebečská 695, Buštěhrad, 27343). E85 obtained from (LPG-AUTO s.r.o., Michelská 4/11, Prague 14000), (analyzed to have 70% volume of ethanol) was mixed with basic fuel to produce a blend containing 15% volume of ethanol – **E15**. Analogical blends were produced containing 25% volume of technical grade n-butanol-(Chemlogistic, Pardubice), fuel denoted as **nBu25**, and iso-butanol (Chemap, Dašice), denoted as **iBu25**. The fuels were metered on mass basis using their actual (measured) densities into 20-liter canisters and splash-blended. The vehicle fuel tank was emptied, new fuel added, and a minimum of one WLTP cycle was run to allow for the engine control unit to adapt to the new fuel.

Tests were performed at test facility in VTP Roztoky on a four-wheel chassis dynamometer MAHA AIP-ECDM 48L-4mot. As a basic driving cycle the Common Artemis Driving Cycle (motorway variant 130 km.h^{-1}), created to represent driving ways in Europe [31-32]. The vehicle was filled with the tested fuel and driven along a WLTP (World Harmonized Light Vehicle Test Procedure) cycle for engine control unit adaptation and preconditioning. The following day, the following tests were run: WLTP with cold start, WLTP with hot start, and four repeats of the Artemis cycle. The results for the Artemis cycle represent the average of the four test runs.

The exhaust was routed into a fullflow dilution tunnel with a constant volume sampler (CVS) operating at 10.8 m^3.min^{-1}. The diluted exhaust was sampled with the following instrumentation for online measurements:

- a traditional set of instruments (HC – heated flame ionization detector, CO and CO_2 – non-dispersive infra-red analyzers, NO_x – chemiluminescence analyzer),
- two FTIR analyzers (a prototype instrument with a 6-meter path length cell running at 121°C and Nicolet Antaris IGS with a 5-meter cell running at 165°C, both equipped with ZnSe windows and liquid nitrogen cooled MCT detector and both running at a resolution of 0.5 cm^{-1}),
- counter of non-volatile particles with a diameter greater than 23 nm per Particle Measurement Programme (PMP) requirements (denoted as particle number (PN) emissions per PMP),
- fast mobility particle sizer (EEPS, Model 3090, TSI), preceeded by a secondary dilution, by a rotating disc diluter (MD-19, Matter Engineering) set to 180:1 dilution ratio; the diluter head was heated to 150°C

Diluted exhaust was further sampled on

- 47 mm diameter filters: glass fiber, Teflon-coated filters (Pall TX40HI20-WW); pure quartz filters (Whatman QMA); and PTFE membrane (Pall Teflo) filters, all at 50 liters per minute (lpm) sampling rate,
- 150 mm diameter quartz fiber (Whatman QM-A) filters for organic compounds analysis at 500 lpm sampling rate,
- 8” × 10” (203 × 254 mm) Teflon-coated glass fiber filters (Pall TX40HI20-WW), at 67.8 m^3.h^{-1} (1130 lpm) sampling rate, for subsequent off-line chemical analyses and toxicological assays.

The sample from the high volume sampler was returned to the CVS; the sum of the remaining flows not returned to the CVS was added to the CVS nominal flow and the emissions calculations were done with the corrected flow.

Results and Discussion

The summary results for the test for hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and for total particle mass (PM) are shown in Figure 1. The results from the direct injection (DISI) engine are always shown on the left, and the results for the port fuel injection (MPI) engine on the right. For the DISI vehicle, error bars represent the standard deviation among the four runs of the Artemis cycle. For the MPI vehicle, the repeatability was generally poor, was not quantified, and the data are given for qualitative comparison only. The effects of the fuel on HC and CO are, for both vehicles, not significant. The effect of the fuel on NO_x was not significant for DISI, while all alchol fuels have increased NO_x emissions on the MPI vehicle. Both butanol isomers, but not E15, have reduced PM on the DISI vehicle, while there were no consistent and significant effects of the fuels on the MPI vehicle.

The emissions of the number of solid particles per Particle Measurement Programme (PN-PMP) and the emissions of the number of all particles (without excluding the volatile fraction) and of particles with a diameter larger than 23 nm are shown in Figure 2. The results from the direct injection (DISI) engine are always shown on the left, and the results for the port fuel injection (MPI) engine on the right. For the DISI vehicle, error bars represent the standard deviation among the four runs of the Artemis cycle. For the MPI vehicle, the repeatability was generally poor, was not quantified, and the data are given for qualitative comparison only. On the DISI vehicle, both butanol isomers have decreased the solid PN emissions by about one half, while there was no difference between gasoline and E15. This difference is smaller, and variances increase, if volatile particles are included (EEPS > 23 nm), and ceases to be readily observable when all particles are considered. In the last case, the variability increases dramatically notably during the motorway cycle, where it is believed that the relatively low dilution ratio has induced nucleation of very small (~ 10 nm) particles. On the MPI vehicle, E15 seemed to substantially increase particle number emissions, which were otherwise generally low. Also, on the MPI vehicle, PMP data are missing for iBu25 due to a measurement device error.

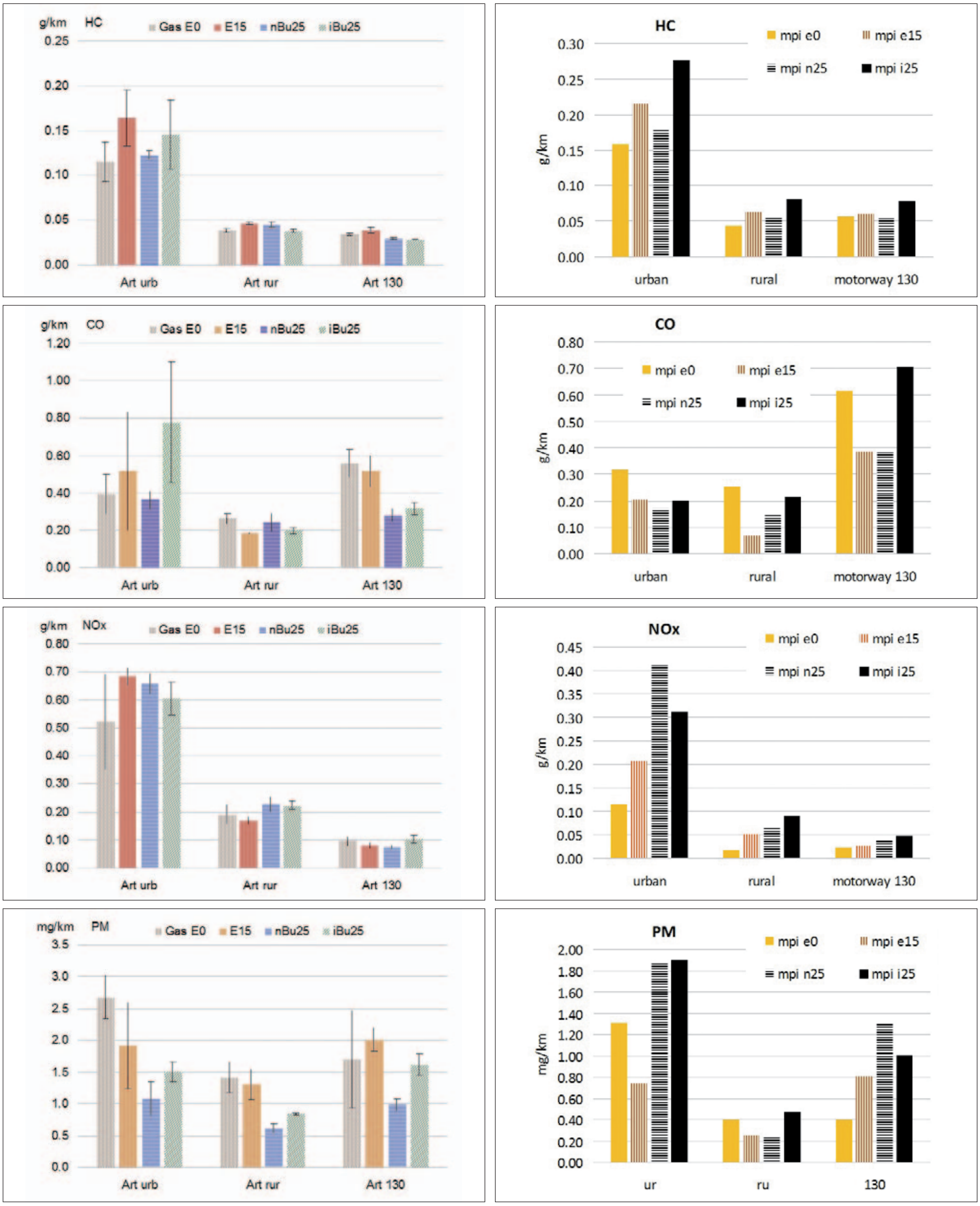

Figure 1. Mean emissions over urban, rural and motorway (130 km/h) parts of the Artemis driving cycle for direct injection (left) and port injection (right) vehicles – comparison of gasoline (E0), 15% ethanol (E15), 25% n-butanol (nBu25) and 25% isobutanol (iBu25): top to bottom: hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and particulate matter mass (PM)

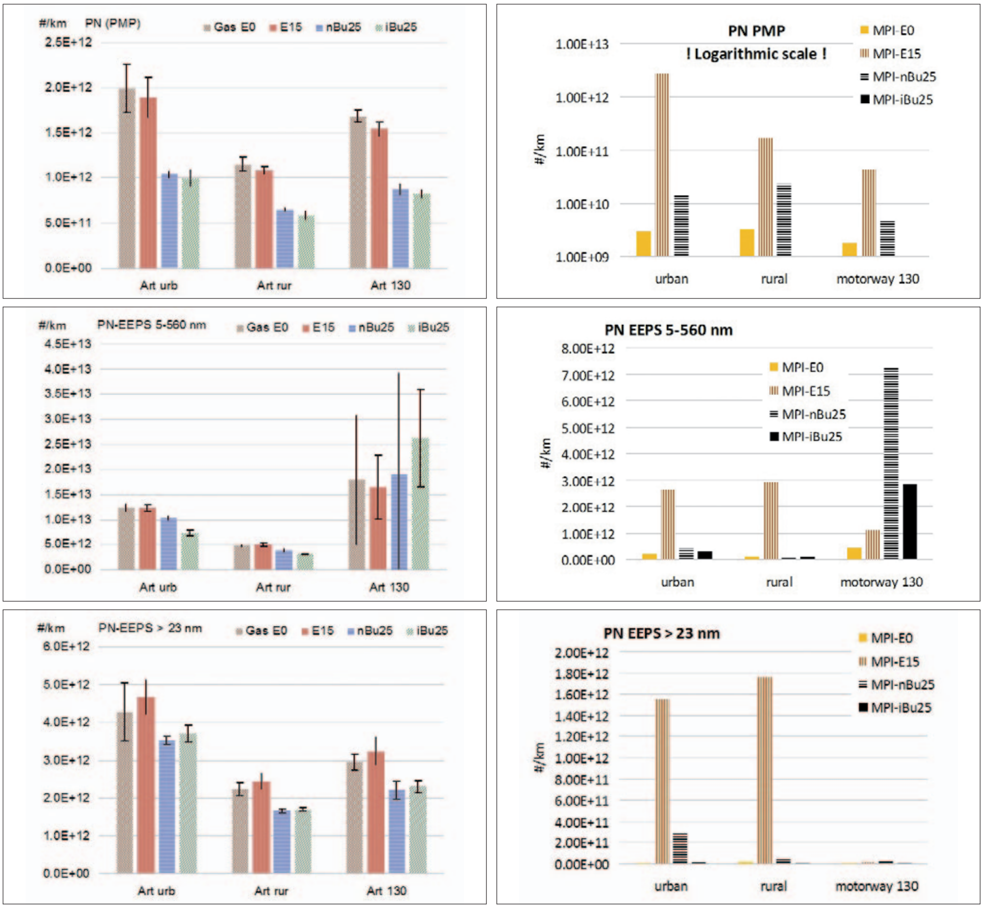

Figure 2. Mean particle number emissions (expressed as total particles per km) over urban, rural and motorway (130 km/h) parts of the Artemis driving cycle for direct injection (left) and port injection (right) vehicles – comparison of gasoline (E0), 15% ethanol (E15), 25% n-butanol (nBu25) and 25% isobutanol (iBu25): top to bottom: solid particle number per Particle Measurement Programme (PMP), total particle count from size distributions, total count of particles > 23 nm from size distributions (PMP data for iBu25 not shown due to measurement error)

The emissions of the elemental and total carbon and of polyaromatic hydrocarbons (PAH) are plotted in Figure 3 for the WLTP cycle with cold and hot start and for the Artemis cycle. The PAH evaluated include fluorene, phenantrene, anthracene, pyrene, benzo(a)

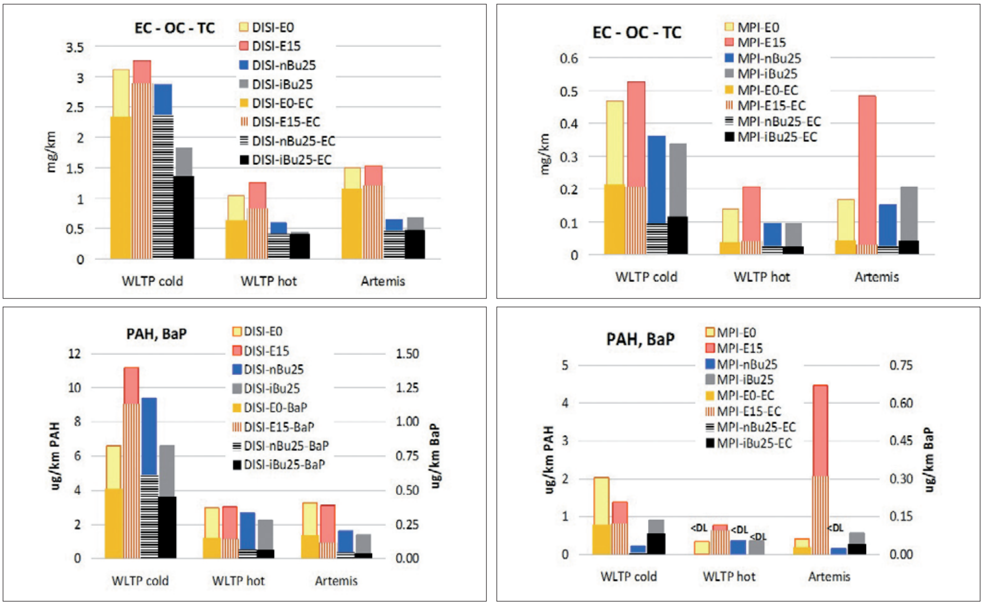

Figure 3. Mean emissions over WLTP cycle run with cold and hot start, and over the Artemis driving cycle for direct injection (left) and port injection (right) vehicles – comparison of gasoline (E0), 15% ethanol (E15), 25% n-butanol (nBu25) and 25% isobutanol (iBu25): elemental and organic carbon (top) and polyaromatic hydrocarbons (fluorene, phenantrene, anthracene, pyrene, benzo(a)anthracene, chrysene, triphenylene, benz(b+j+k)fluoranthenes, benzo(e)pyrene, benzo(a) pyrene, indeno(123cd)pyrene, dibenzo(ah) antracene, benzo(ghi) perylene)

anthracene, chrysene, triphenylene, benz(b+j+k)fluoranthenes, benzo(e)pyrene, benzo(a) pyrene, indeno(123cd)pyrene, dibenzo(ah) antracene, and benzo(ghi) perylene. The results from the direct injection (DISI) engine are shown on the left, and the results for the port fuel injection (MPI) engine on the right. As each data point in the graph represents a single analysis, no statistical evaluation is given. It is apparent that on the DISI engine, the carbonaceous part of the particulate matter was primarily elemental carbon, and that relative to gasoline, E15 has slightly increased, and both butanol isomers substantially decreased, both elemental and total carbon. On the MPI engine, organic carbon (semi-volatile compounds) have prevailed over elemental carbon, and relative to gasoline, there was an increase (small, but larger than for DISI) associated with E15, and a decrease (smaller than for DISI) associated with both butanol blends. On the DISI engine, emissions of PAH, and also of benzo(a)pyrene (BaP) which was plotted separately, were reduced by about one half for both butanol isomers over the Artemis cycle, with no measurable differences between E15 and gasoline without alcohols. A similar effect can be observed for the WLTP hot cycle, while generally worse results for alcohols are observed during the WLTP with the cold start. The PAH emissions for the MPI engine were generally lower, with only larger value observed during the Artemis driving cycle on E15. This larger value could have been caused by contamination of the dilution tunnel during unexpected shutdown of the tunnel flow during the preceding test.

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References

[1] Tao, L., Tan, E.C.D., McCormick, R.L., Zhang, M. et al., *Technoeconomic analysis and life-cycle assessment of cellulosic iso-butanol and comparison with cellulosic ethanol and n-butanol*. Biofuels Bioprod. Biorefin. 8(1): 30-48, 2014, doi:10.1002/bbb.1431.

[2] Xue, C., Zhao, X.Q., Liu, C.G., Chen, L.J. and Bai F.W., *Prospective and development of butanol as an advanced biofuel*. Biotechnol Adv. 31(8): 1575-84, 2013, doi:10.1016/j.biotechadv.2013.08.004.

[3] Cascone, R., *Biobutanol: a replacement for bioethanol?*. Chem. Eng. Prog. 104(4)" S4–S9, 2008.

[4] Patakova, P., Maxa, D., Rychtera, M., Linhova, L. et al., *Perspectives of biobutanol production and use*, in Biofuel`s engineering process technology, ed. Bernandes M.A.D.S., 243-266, 2011, InTech, Rijeka, Croatia, doi:10.5772/961.

[5] Karavalakis, G., Short, D., Vu, D., Russell, R.L. et al., *The impact of ethanol and iso-butanol blends on gaseous and particulate emissions from two passenger cars equipped with spray-guided and wall-guided direct injection SI (spark ignition) engines*. Energy. in print: 2015, doi:10.1016/j.energy.2015.01.023.

[6] Stansfield, P., Bisordi, A., OudeNijeweme, D., Williams, J. et al., *The Performance of a Modern Vehicle on a Variety of Alcohol-Gasoline Fuel Blends* SAE Int. J. Fuels Lubr. 5(2): 813-822, 2012, doi:10.4271/2012-01-1272.

[7] Szwaja, S., Naber, J.D. *Combustion of n-butanol in a spark-ignition SI engine*. Fuel, 89(7): 1573-1582, 2010, doi:10.1016/j.fuel.2009.08.043.

[8] Dernotte, J., Mounaim-Rousselle, C., Halter, F., Seers, P., *Evaluation of butanol-gasoline blends in a port fuel injection, spark-ignition engine*. Oil Gas Sci. Technol. – Rev. IFP 65(2): 345–351, 2010, doi:10.2516/ogst/2009034.

[9] Gu, X., Huang, Z., Cai, J., Gong, J., Lee, Ch., *Emission characteristics of a spark-ignition engine fuelled with gasoline-n-butanol blends in combination with EGR*. Fuel 93(1): 611-617, 2012, doi:10.1016/j.fuel.2011.11.040.

[10] Wigg, B., Coverdill, R., Lee, C., and Kyritsis, D., *Emissions Characteristics of Neat Butanol Fuel Using a Port Fuel-Injected, Spark-Ignition Engine*. SAE Technical Paper 2011-01-0902, 2011, doi:10.4271/2011-01-0902.

[11] Wallner, T., Frazee, R., *Study of Regulated and NonRegulated Emissions from Combustion of Gasoline, Alcohol Fuels and their Blends in a DI-SI Engine*. SAE Technical Paper 2010-01-1571, 2010, doi:10.4271/2010-01-1571.

[12] Thewes, M., Müther, M., Brassat, A., Pischinger, S. et al., *Analysis of the Effect of Bio-Fuels on the Combustion in a Downsized DI SI Engine*." SAE Int. J. Fuels Lubr. 5(1):274-288, 2012, doi:10.4271/2011-01-1991

[13] Pechout, M., Dittrich, A., and Vojtisek-Lom, M., *Operation of an Ordinary PFI Engine on n-butanol and Iso-butanol and Their Blends with Gasoline*. SAE Technical Paper 2014-01-2618, 2014, doi:10.4271/2014-01-2618.

[14] Andersen, V.F., Anderson, J.E., Wallington, T.J., Mueller, S.A. et al., *Vapor Pressures of Alcohol-Gasoline Blends*. Energ. Fuel. 24(6): 3647-3654, 2010, doi:10.1021/ef100254w.

[15] Aleiferis P.G., van Romunde Z.R., *An analysis of spray development with iso-octane, n-pentane, gasoline, ethanol and n-butanol from a multi-hole injector under hot fuel conditions*. Fuel 105: 143-168, 2013, doi:10.1016/j.fuel.2012.07.044.

[16] Merola, S., Tornatore, C., Valentino, G., Marchitto, L. et al., *Optical Investigation of the Effect on the Combustion Process of Butanol-Gasoline Blend in a PFI SI Boosted Engine*. SAE Technical Paper 2011-24-0057, 2011, doi:10.4271/2011-24-0057.

[17] Tornatore, C., Marchitto, L., Valentino, G., Corcione, F.E. et al., *Optical diagnostics of the combustion process in a PFI SI boosted engine fueled with butanol-gasoline blend*. Energy 45(1): 277-287, 2012, doi:10.1016/j.energy.2012.03.006.

[18] Vojtisek-Lom, M., Pechout, M., Mazac, M., *Real-World On-Road Exhaust Emissions from an Ordinary Gasoline Car Operated on E85 and on Butanol-Gasoline Blend*. SAE Technical Paper 2013-24-0102, 2013, doi:10.4271/2013-24-0102.

[19] Regalbuto, C., Pennisi, M., Wigg, B., Kyritsis, D., *Experimental Investigation of Butanol Isomer Combustion in Spark Ignition Engines*. SAE Technical Paper 2012-01-1271, 2012, doi:10.4271/2012-01-1271.

[20] Karavalakis, G., Short, D., Vu, D., Villela, M. et al., *Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends*. Fuel 128: 410-421, 2014, doi: 10.1016/j.fuel.2014.03.016.

[21] Ratcliff, M.A., Luecke, J., Williams, A., Christensen, E. et al., *Impact of higher alcohols blended in gasoline on light-duty vehicle exhaust emissions*. Environ. Sci. Technol. 47(23), 13865-13872, 2013, doi:10.1021/es402793p.

[22] Pechout, M., Dittrich, A., Mazac, M., Vojtisek-Lom, M., *Real Driving Emissions of Two Older Ordinary Cars Operated on High-Concentration Blends of N-Butanol and ISO-Butanol with Gasoline*. SAE Technical Paper 2015-24-2488, 2015, doi:10.4271/2015-24-2488.

[23] Vojtisek-Lom, M., Beranek, V., Stolcpartova, J., Pechout, M. et al., „Effects of n-Butanol and Isobutanol on Particulate Matter Emissions from a Euro 6 Direct-injection Spark Ignition Engine During Laboratory and on-Road Tests," SAE Int. J. Engines 8(5):2015, doi:10.4271/2015-24-2513.

[24] Christensen, E., Yanowitz, J., Ratcliff, M., McCormick, R.L., *Renewable oxygenate blending effects on gasoline properties*. Energ. Fuel. 25(10), 4723-4733, 2011, doi:10.1021/ef2010089.

[25] Tornatore, C., Irimescu, A., Marchitto, L., Merola, S.S., Valentino G., *Combustion Process Analysis in a DISI Engine Fuelled with N-Butanol through UV-VIS Emission Spectroscopy*. IJET 7(3): 242-248, 2015, doi:10.7763/IJET.2015.V7.799.

[26] Irimescu, A., Marchitto, L., Merola, S.S., Tornatore, C., Valentino, G., *Combustion process investigations in an optically accessible DISI engine fuelled with n-butanol during part load operation*. Renew. Energ. 77, 363-376, 2015, doi:10.1016/j.renene.2014.12.029.

[27] Pechout, M., Trnka, M., Novotny, M., Vojtisek, M., *Adaptation of Small Spark Ignition Engine to Alcohol Fuels*. Listy Cukrovarnicke a Reparske, 130(7-8): 262-267. 2014.

[28] Polcar, A., Cupera, J., Sedlak, P., *Exhaust emissions of spark-ignition engine fuelled by E85*. Listy Cukrovarnicke a Reparske, 130(4): 149-153, 2014.

[29] Gerde, P., Muggenburg, B.A., Lundborg, M., Dahl, A.R., *The rapid alveolar absorption of diesel soot-adsorbed benzo(a)pyrene: bioavailability, metabolism and dosimetry of an inhaled particle-borne carcinogen.* Carcinogenesis 22, 2001, 741-749.

[30] Krzyzanowski M., Kuna-Dibbert B., Schneider J., eds., *Health Effects of Transport-Related Air Pollution*. Copenhagen: World Health Organization; 2005..

[31] Künzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., Filliger, P., Herry, M., Horak, F., Puybonnieux-Texier, V., Quénel, P., Schneider, J., Seethaler, R., Vergnaud, J.-C., Sommer, H.,. *Public-health impact of outdoor and traffic-related air pollution: a European assessment*. The Lancet 356, 892000, 5-901.

[32] Janssen, N.A.H. et al., *Black Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared with PM10 and PM2.5*. Environ Health Perspect. 2011 December; 119(12): 1691–1699. www.ncbi.nlm.nih.gov/pmc/articles/PMC3261976/

[33] United Nations Economic Commission for Europe (UNECE) Working Group 29, materials online at https://www2.unece.org/wiki/pages/viewpage.action?pageId=2523179 and http://www.unece.org/trans/main/welcwp29.html

[34] Andre, M., *The ARTEMIS European driving cycles for measuring car pollutant emissions*. Sci. Total Environt, 334-335:73-84, 2004, doi:10.1016/j.scitotenv.2004.04.070.

Spray Combustion Investigation through Optical Techniques in a Prototype Compression Ignition Engine fuelled with n-Butanol-Diesel Blends

Optyczne techniki badania spalania rozpylonej strugi paliwa w prototypowym silniku z ZS zasilanym mieszankami oleju napędowego z n-butanolem

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Abstract

The increasing energy demand from emerging countries and the simultaneous fossil oil shortage promote the use of alternative fuels. Even if gasoline and diesel continue to dominate automotive market, the use of non-conventional fuels such as biodiesel or alcohols is growing. Exhaust emissions and performance of compression ignition engines fuelled with diesel-alcohol fuel blends have been widely investigated. On the other hand, a deeper understanding of in-cylinder combustion is necessary as the different chemical physical properties of alcohols, such as oxygen content, volatility and cetane number affect the ignition, combustion mechanism and the pollutants formation.

This work reports results of cycle resolved visualization and UV-visible optical imaging, carried out in an optically accessible compression ignition engine. Two different blends of diesel and n-butanol were tested: 20% and 40% of n-butanol by volume. The effect of n-butanol concentration on flame lift-off length and soot formation was investigated. Exhaust Gas Recirculation (O_2 at intake 17%) was used for further reducing the local temperature peak. The combined effect of EGR and high oxygen content of n-butanol/diesel blends induced a simultaneous reduction of both NO_x and soot emission. The correlation of optical measurements with thermodynamic and exhaust emission analysis allowed to emphasize the role of n-butanol oxygen content in the soot oxidation process.

Keywords: Diesel Engine, n-butanol, PPCI, UV-Visible imaging, Soot, NO_x

Introduction

In order to meet increasingly rigid emission guidelines, the scientific community interested in Diesel engines is working on the development of advanced injection equipment, complex exhaust gas after treatment systems and new combustion modes, etc. In recent years, some new combustion mechanisms have been investigated such as HCCI (Homogeneous Charge Compression Ignition) and PPCI (Partially Premixed Compression Ignition).

For HCCI combustion, the fuel–air mixture is homogeneously premixed before the start of combustion initiated by autoignition: the temperature is reduced by homogeneous lean combustion, allowing low smoke and NO_X engine out emissions. The main challenge of HCCI is to control ignition timing, which influences the power and efficiency. The phenomenon of auto-ignition leads to the main combustion control which is affected by a few factors [1, 2]: fuel auto-ignition chemistry and thermodynamic properties, combustion duration, wall temperatures, concentration of reacting species, residual rate, degree of mixture homogeneity, intake temperature, compression ratio, amount of EGR, engine speed, engine temperature, convective heat transfer to the engine, and other engine parameters [3].

In PPCI combustion, the total amount of fuel is delivered before the start of combustion in order to have better premixing of air and fuel, resulting in a great reduction in NO_X and smoke emissions. Meanwhile, it can effectively combine the ignition timing with injection timing to ensure better control of the combustion process, so it has attracted more and more researchers' attention [4]. PCCI is not fully homogeneous, but it uses injection timing and EGR to greatly increase the controllability of combustion phasing and the rate of combustion.

In recent times, several fuels have been tested in compression ignition engines to explore the potential of reducing pollutants emissions, while maintaining high thermal efficiency. Alcoholic fuels show high volatility and resistance to auto-ignition: they appear advantageous in fuel–air mixing processes due to their long ignition delay and fast evaporation process [5]. As a clean and renewable biofuel, n-butanol has many superior properties compared with other alcohols, such as good miscibility in diesel, low cetane number and high volatility, which make it an attractive alternative or blending component to diesel fuel to achieve PPCI. Butanol has been widely investigated as a diesel additive on conventional diesel engine in recent years. As reported in the scientific literature, compared to diesel fuel, the blend with 40% n-butanol by volume in diesel leads to a longer ignition delay, faster burning rate but higher emissions. EGR can be used to reduce this pollutant [6]. The addition of n-butanol to diesel fuel can improve combustion stability and decrease soot and CO emissions while it results in higher NO_x emissions [7]. n-Butanol-diesel blends can dramatically reduce engine soot emissions in steady and transient operation [8]. These blends were also investigated in LTC (low temperature combustion) diesel engines [9, 10, 11]: they exhibit longer ignition delay, higher thermal efficiencies and under LTC mode, they can significantly reduce engine-out NO_x emissions and smoke, without significantly compromising engine performance.

This paper reports the characterization of spray combustion for n -butanol – diesel blends (20% and 40%) in an optically accessible high swirl compression ignition engine equipped with a common rail multi-jets injection system. A double stage injection strategy with EGR of 50% was tested in order to study the attained PPCI regime. Thermodynamic analysis and exhaust pollutant measurements were performed simultaneously to UV-visible digital imaging and cycle resolved visualization. Moreover, 2D chemiluminescence was detected through flame emission filtering at 310 and 690 nm to follow the OH and soot evolution.

Experimental Set-up and Test Condition

A single cylinder 2-stroke compression ignition engine was used for the experiments. Figure 1 shows a sketch of the engine and of the combustion chamber. An external high swirl optically accessible combustion bowl (ϕ=50 mm; L=30 mm), equipped with a high pressure common rail injection system, is connected to the main cylinder through a tangential duct. A compressed air flow is forced into the bowl as the piston approaches Top

Dead Centre (TDC). As a result, a counter clockwise swirl flow is obtained, reproducing a fluid dynamic environment, similar to a real direct injection diesel engine, with the rotation axis coincident to the symmetry axis of the chamber. Further details concerning the engine specifications are reported in table 1.

The injector is mounted within the combustion bowl, with its axis coincident to the chamber axis. The fuel is sprayed within the swirling air motion and the combustion process mainly develops within the chamber. After TDC, as the piston moves downward, the flow reverses its motion and hot gases flow through the tangential duct to the cylinder and finally to exhaust ports.

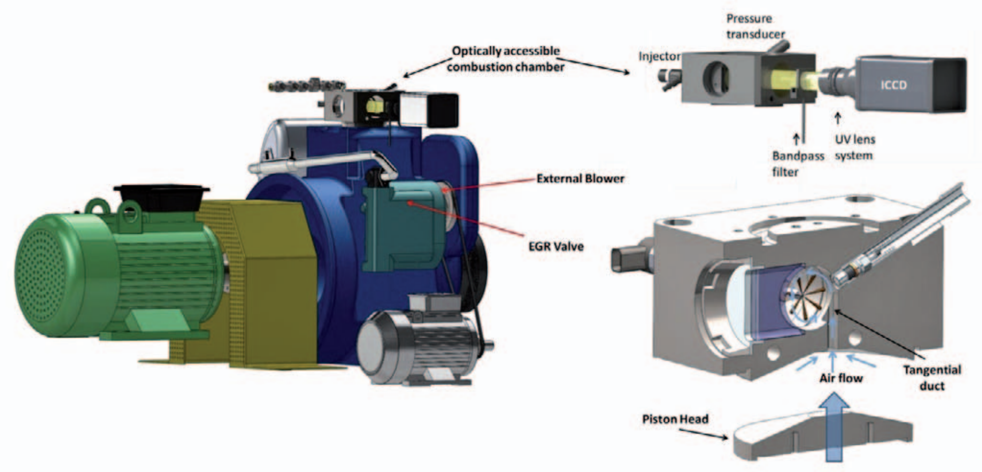

Figure 1. Sketch of the optically accessible engine (left) and cross section of the optically accessible combustion chamber (right)

The combustion chamber provides two optical accesses. The first one is circular (ϕ=50 mm) and it is placed in front of the injector, used to collect images. The second one, with a rectangular shape (size of 10 × 50 mm), is mounted on a side of the chamber, at 90° with respect to the bowl axis and it is used for the laser illumination input. The injection equipment includes a common rail system with a solenoid controlled injector located on the opposite side of the circular optical access. The nozzle is a micro-sac 7 hole, 0.136 mm diameter, 148° spray angle nozzle. An external roots blower provides intake air pressure of 0.107 MPa, with peak pressure within the combustion chamber of 4.3 MPa under motored conditions.

Table 1. Engine specifications

single cylinder CI engine	
Cylindrical Bowl (mm×mm)	50×30
Bore (mm)	150
Stroke (mm)	170
Connecting Rod (mm)	360
Compression ratio	10.1:1
Air supply	Roots blower
Abs. intake air pressure (MPa)	0.107
Bosch Injector nozzle	7/0.136/148°

A crank angle encoder signal synchronized the cameras acquisitions and the engine, through a delay unit. The AVL Indimodul recorded the TTL signal to monitor optical acquisitions, the current signal from injector solenoid and the in-cylinder pressure trace. Results of the in-cylinder pressure were computed averaging 300 consecutive engine cycles. Exhaust gaseous emissions were acquired by the AVL DiGas 4000 analyzer for NO_x (1 ppm resolution), smoke was measured by a part flow opacimeter (AVL Opacimeter 439). The opacity was correlated to the particulate mass concentration through an empirical formula [12]. Two different volume fractions of n-butanol and diesel fuel were tested: 20%v and 40%v of n-butanol (BU20 and BU40, respectively). The main characteristics of tested fuels are reported in [13]. The injection time was adjusted to achieve the same energy content as diesel (935 J/str) for all the investigated blends. The injection pressure was fixed at 80 MPa. The start of injection was swept from 14 to 2 cad BTDC with a step of 3 Crank Angle Degrees (CAD). Two different levels of O_2 at intake were tested: 21 and 17%.

The spray combustion process was recorded through the quartz window using two different cameras. A CMOS camera (Phantom 1611) for cycle resolved acquisitions and an intensified CCD camera (PiMAX 3) for 2D chemiluminescence. The Phantom camera was equipped with a 1280×800 pixels sensor with 28×28 μm pixel size, 12-bit pixel digitization; it was coupled with 105 mm focus lens, allowing to characterize the whole combustion cycle. A ROI of 768×768 pixel was set in order to increase the frame speed up to 25000 fps corresponding to an acquisition interval of 40 μs, (0.12 CAD@500rpm). 2D chemiluminescence measurements were performed through the PiMAX 3 camera. It was featured by a 1024×1024 pixels sensor with 13×13 μm pixel size, 16-bit pixel digitization and 1MHz sustained repetition. The ICCD was equipped with a 78 mm focal length lens (Nikkor) and employed in full-chip configuration. The set-up allowed a resolution of 83 μm per pixel. In addition to the broadband acquisition that exploits the high quantum efficiency of the ICCD in the spectral range 250-700 nm, two 50×50mm band-pass filters (Asahi Spectra Inc.) were used to selectively record flame emissions at 310 nm and 690 nm.

The high transmission (65%) and small width (10 nm FWHM) of the UV filter permitted to select the OH emission, due to the A-X transition without interference of other radiative species [14][15][16]. Since the soot luminosity is characterized by a continuous broadband spectrum similar to the Planck black body curve [14][17][18], 690nm band-pass filtering allowed to separate the soot emission by the other excited species contribution, that emitted in the visible wavelength range as CH and C_2.

ICCD sequential and repetitive gating modes were used. Sequential acquisition collected one frame per cycle with fixed gate width, but variable delay with respect to the trigger (i.e. raising edge of the injection signal). Repetitive mode detected one frame per cycle with fixed gate width and delay with respect to the trigger. For both acquisition modes, optical investigations were carried out on 100 consecutive engine cycles. In the sequential acquisitions, data were recorded at an interval of 133.3 μs (0.4 CAD). Without spectral filtering, the camera would be overexposed due to the flame luminosity. Thus, ICCD exposure time was fixed at 16.66 μs (0.05 CAD). Chemiluminescence investigations were performed by setting the exposure time at 66.66 μs (0.2 CAD). In order to obtain quantitative information from the combustion visualization, "ad hoc" image processing was developed through Vision Assistant 2011 of National Instruments [19]. More details regarding the methodology are reported in [13].

Results and discussions

First measurements investigated the effect of the injection timing and intake oxygen level on the performance and exhaust emissions. The pressure trace average of 300 cycles is shown in Figure 2 for net diesel and BU40, without (left) and with 50% EGR (right). The lower Cetane Number (CN) of BU40 slightly delayed the start of combustion (SOC) at all investigated starts of injection, with an increase in peak pressure. By introducing the

EGR, the SOC was further delayed and the pressure peak of the diesel fuel was higher than BU40 at the most delayed SOIs. In fact, as shown in Figure 2, for 2 CAD BTDC SOI, the SOC occurred after the TDC, during the expansion stroke. As a consequence, an increase in the induction period results in lower combustion temperature and pressure.

Further details can be found in Figure 3, reporting the in-cylinder pressure peak for all the investigated fuels, injection times and EGR levels. The maximum pressure peak of ~5.6 MPa was recorded at ~1.0 CAD BTDC, at the most advanced start of injection (14 CAD BTDC) for BU40. The peak also turned out to be the most advanced when compared to the other test cases. The minimum peak of ~ 4.8 MPa located at 4.4 CAD ATDC was found for the most delayed injection strategy (2 CAD BTDC). In fact, considering the late start of injection, close to TDC, the combustion almost occurs during the expansion stroke.

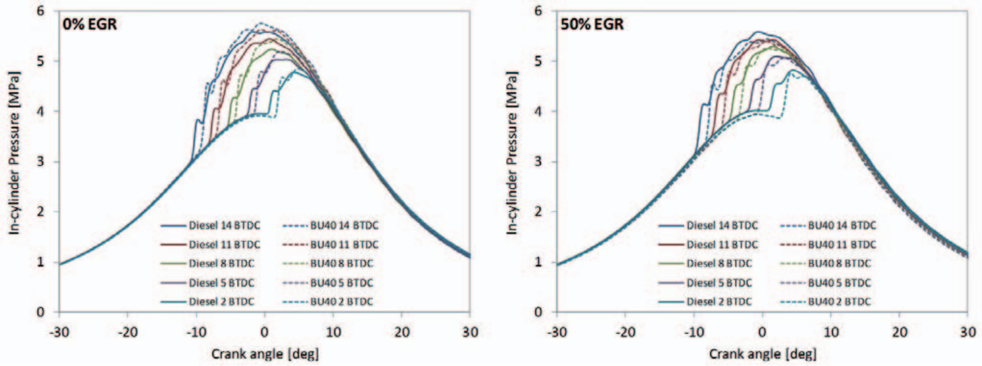

Figure 2. Combustion pressure for diesel fuel and BU40 at different starts of injection, without (left) and with EGR (right)

A deeper understanding of the effect of n-butanol concentration on the combustion mechanisms can be achieved considering the ID as obtained by pressure traces. The ID was defined as the difference between the electronic SOI and the SOC occurrence, estimated as the relative maximum of the first derivative of pressure signal.

Figure 4 shows the measured ID as a function of the start of injection, for all the tested fuels and intake oxygen concentrations. A red dot line was overlapped to the plot, representing the effective end of injection. As expected the higher resistance to autoignition of n-butanol extended the induction period as a function of its volume fraction. As a consequence, for BU40 a Partially Premixed Combustion was obtained, independently of the SOI. Reversely, the diesel fuel is completely injected before the end of injection just at the most advanced SOI. By introducing the EGR (figure 4, right) the ID increased of about 1 CAD for all investigated conditions and PPCI conditions were obtained even with Diesel and BU20.

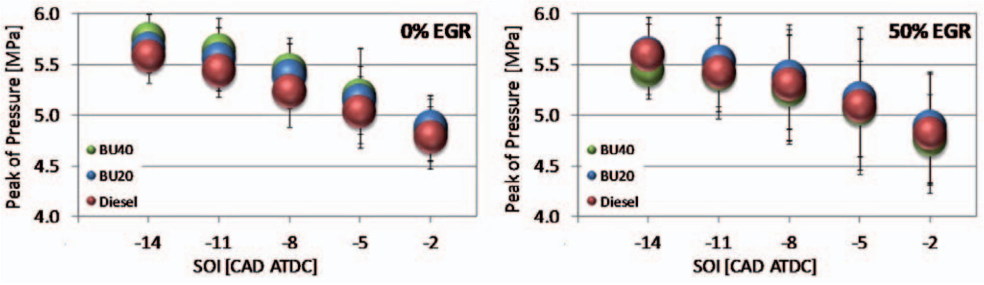

Figure 3. Peak pressure at different starts of injection without (left) and with EGR (right).

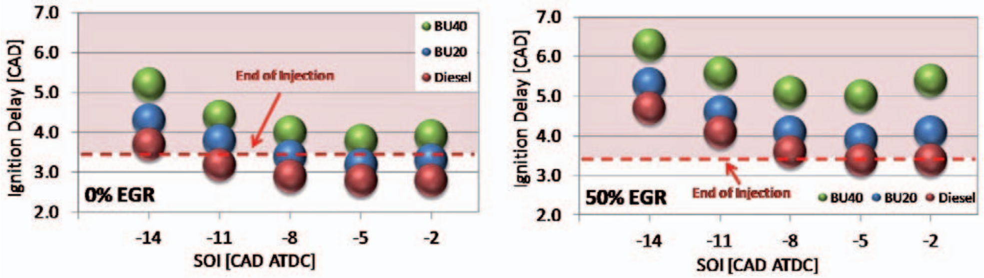

Figure 4. Ignition delay at different starts of injection without (left) and with EGR (right)

The lower CN of n-butanol, together with its higher volatility and molecule oxygen content, clearly affected the exhaust emission. The NO_x-Soot trade-off for all the investigated blends and injection timings is shown in Figure 5. High NO_x levels were measured at advanced start of injection, with an asymptotic decreasing trend versus the SOI down to values below 100 ppm. On the contrary, the soot concentration ranged from about 3 mg/m^3 at 14 CAD BTDC SOI to 70 mg/m^3 at 2 CAD BTDC SOI.

As expected the n-butanol use resulted in a consistent lowering of soot emissions. The lower cetane number of BU20 and BU40, extending the ignition delay, gave more time for mixing and reduced the locally rich fuel/air mixture regions that are directly related to the soot production. In addition, the higher volatility of the blends promoted the dispersion of fuel vapour within the combustion chamber, further enhancing the mixture preparation.

The reduction in oxygen content induced a drop of in-cylinder temperature with a strong reduction in NO$_x$. On the other hand, the lower oxygen concentration and lower temperature favoured soot formation and worsened soot oxidation, especially at the most delayed SOI. However, n-butanol-diesel reduced the soot emission up to seven times compared to net diesel, without significant increase in NO$_x$.

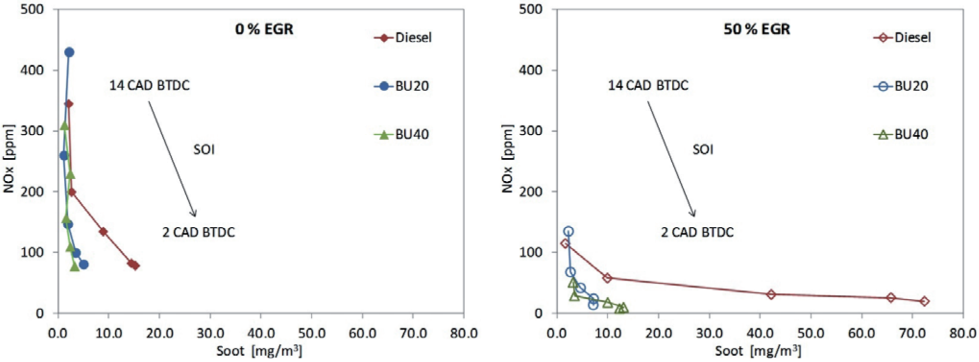

Figure 5. NO$_x$-soot trade off for all the fuels at different starts of injection without (left) and with EGR (right)

The best compromise between NO$_x$ and Soot emission was obtained for the central SOI. At this injection condition (8 CAD BTDC) both n-butanol concentration and EGR were effective and induced an overall reduction of trade-off curve. For this reason it was set as representative for optical investigations. Figure 6 shows the diesel combustion evolution, with 21% O$_2$ at intake, as recorded by the cycle resolved CMOS camera, with an acquisition interval of 0.12 CAD. The combustion started far from the nozzle, at 5 CAD BTDC, when the energizing current to the injector solenoid was interrupted. However the needle was still lifted and the injection was not complete, as demonstrated by the presence of compact fuel jets behind the flame.

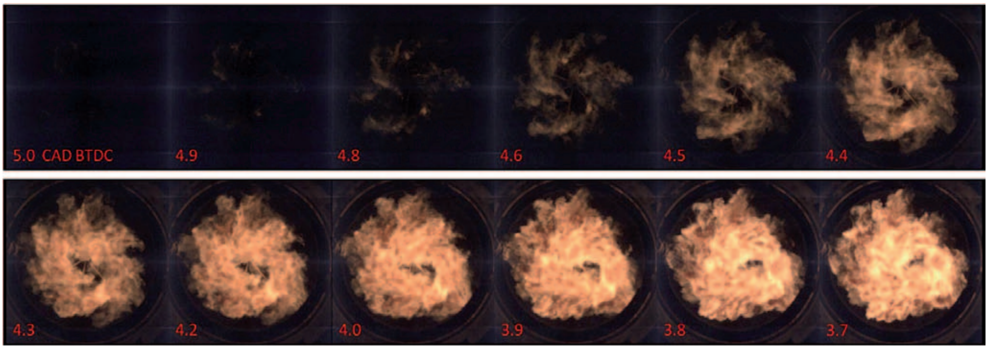

Figure 6. Selected images of cycle resolved sequence of diesel combustion without EGR

With the introduction of the EGR the in-cylinder temperature was lowered and the SOC was delayed by about 0.5 CAD (figure 7). Even if the injection was complete for this test case, the induction time was not enough to obtain a complete air-fuel mixing and the jets shape was still evident.

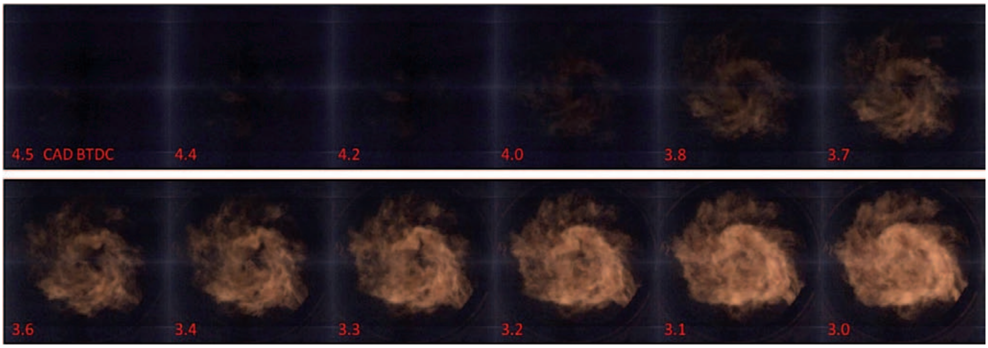

Figure 7. Selected images of a cycle resolved sequence of diesel combustion with EGR

The natural luminosity from spray combustion in c.i. engines is constituted by two parts: chemiluminescence and soot incandescence. The first mainly features the UV-visible spectral range while soot radiative emission is typical of visible-IR range [20, 21, 22, 23].

In conventional combustion regime, soot emission is much stronger than chemiluminescent signal, thus it is reasonable to argue that the soot can be well represented by the broadband luminosity [24][25][26]. Even if CMOS cameras are suitable for collecting the soot emission, the first exothermic reactions occur in the UV range, for this reason UV-visible imaging was performed through the ICCD camera and two pass-band filters were applied to distinguish the OH (310 nm) and soot emission (690 nm). In fact, the first stage of combustion is crucial for determining the combustion mechanism and for a deep understanding of its effect on the exhaust emission.

Figures 8 and 9 show the evolution of natural emission and chemiluminescence signals for selected operative conditions from the start of luminous combustion. Specifically, the effect of fuel was shown at 21% oxygen for Diesel and BU40. Spray combustion images were reported in pseudo-colour with red and dark-blue representing the flame and background, respectively, according to the intensity scale on the right of each sequence. Comparing figures 6 and 8 the higher sensitivity of UV-visible imaging compared to the cycle resolved is evident, as demonstrated by the advanced detection of the autoignition signal. Looking at BU40 effect on the combustion mechanism, the ignition delay increase and the lower emission intensity of the butanol blends compared to diesel should be noted, while it is difficult to evaluate a difference in the spatial distribution of the luminosity. Moreover, BU40 provided lower flame luminosity and soot intensity compared to diesel fuel, confirming lower soot formation.

Figure 10 shows the lift-off lengths evaluated from OH and soot emissions for each fuel injection strategy. As expected the lift-off length increased by increasing the butanol concentration. For each fuel, the EGR further extended the lift-off lengths. As aforementioned, the first exothermal reactions occur in the UV range; as an effect, the OH lift-off length resulted lower than soot one, for all the investigated conditions.

The lift-off length was considered as an indicator of the percentage of stoichiometric air, entrained up to the lift-off length for the spray jet flame. Thus a longer lift-off length demonstrated more space for air entrainment and hence a reduced local equivalence ratio. The spatially integrated luminosity obtained from UV-visible flame emission and from OH and soot chemiluminescence was calculated by integrating the pixel values over the entire image. The broadband flame signal allowed to estimate the ignition delay for each injection condition with an accuracy of 132 μs.

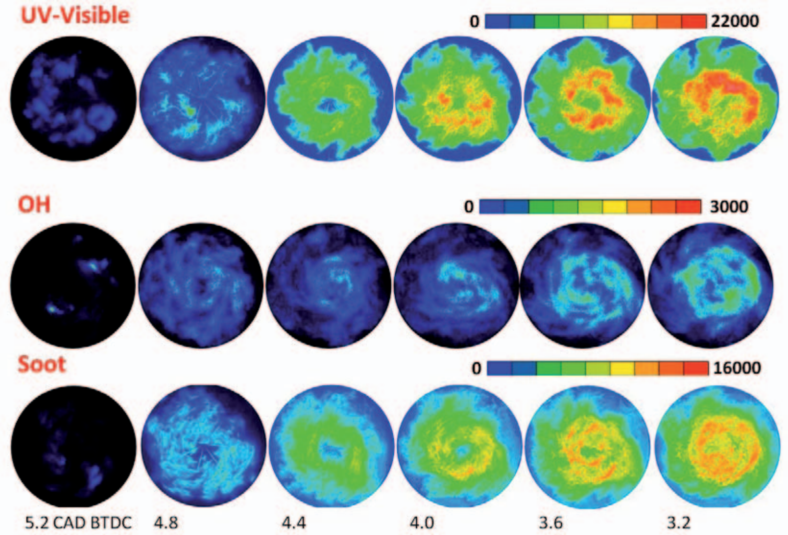

Figure 8. UV-visible flame, OH and soot emissions for Diesel combustion without EGR

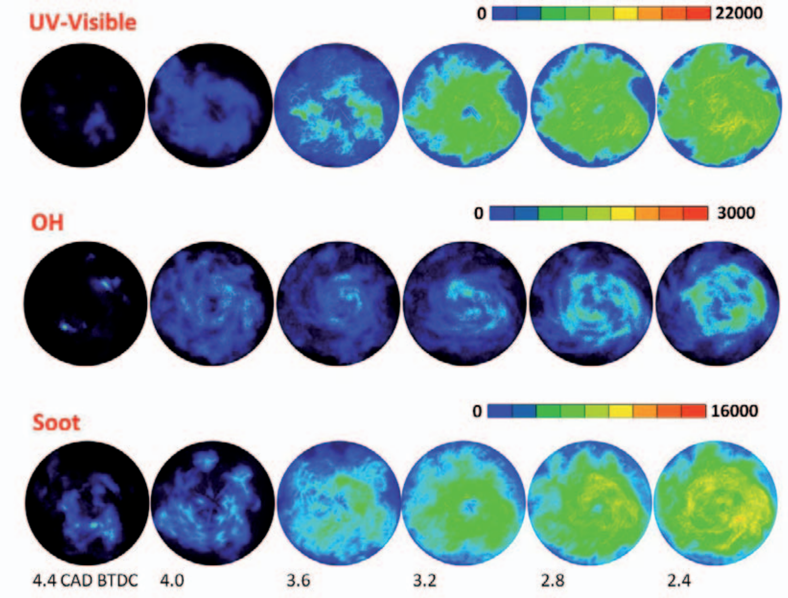

Figure 9. UV-visible flame, OH and soot emissions for BU40 combustion without EGR

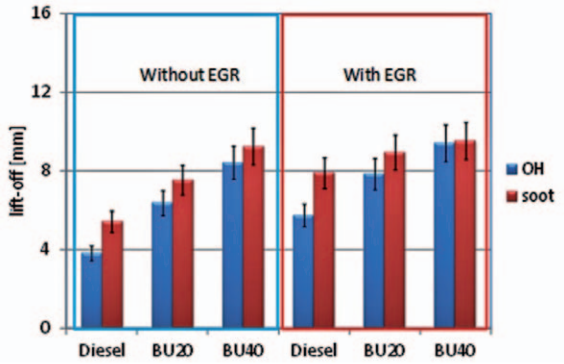

Figure 10. OH and soot lift-off length for all the tested fuels

Figure 11 shows the result of the optical measurements compared with thermodynamic data: as, expected, the ID estimated by optical values resulted lower than thermodynamic ones, due to the high sensitivity of the ICCD camera in the UV range where the first exothermal reactions occur. Figure 12 shows the temporal evolution of spatially integrated soot signals from the start of injection for all the test cases. Due to the delay in SOC induced by the n-butanol blends, the soot occurrence resulted delayed with the increase in butanol concentration. A decrease in the highest value of the soot luminosity was observed when the EGR was activated. This result was just apparently unexpected: in fact the lower oxygen content in the in-cylinder gas slows down the soot oxidation, as highlighted by the lower slope of soot signal during the decreasing stage.

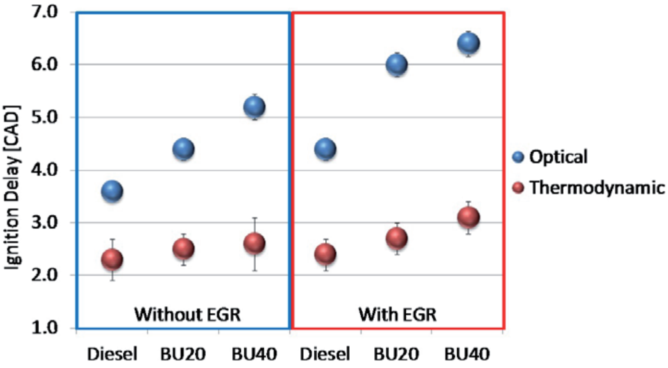

Figure 11. Comparison between ignition delay from thermodynamic data and UV-visible luminosity

As shown in Figure 13, higher OH radical concentration was detected for all the settings without EGR. This resulted in an enhanced oxidation phase and a faster soot reduction. Further, the soot oxidation phase was more significant for higher butanol volume fraction in the blends.

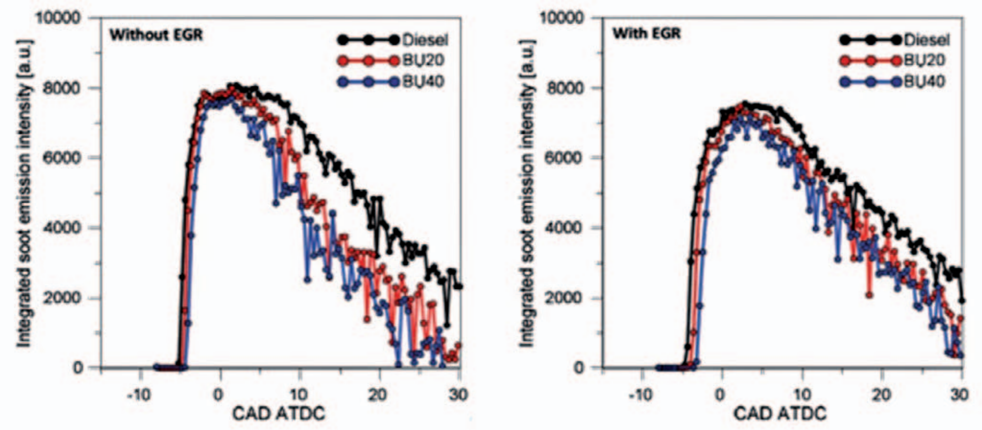

Figure 12. Soot integral emission intensity without (left) and with EGR (right) for all the tested fuels

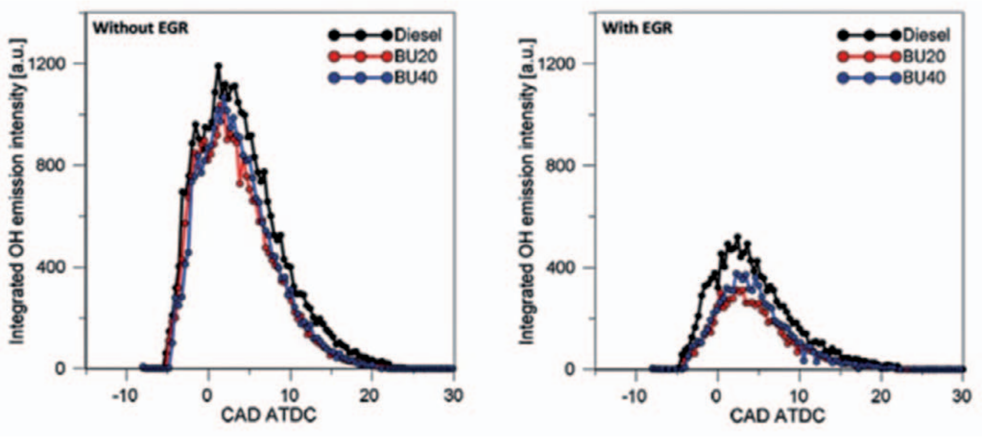

Figure 13. OH integral emission intensity without (left) and with EGR (right) for all the tested fuels

Conclusions

UV-visible digital imaging, cycle resolved visualization and 2D chemiluminescence were applied in a prototype optically accessible CI engine fuelled with blends of commercial diesel and n-butanol (20% and 40% volume fractions) to characterize the spray combustion process. The optical results were correlated to thermodynamic analysis and exhaust gas measurements. The effects of EGR on spray combustion process and emissions were investigated.

The combined effect of n-butanol and EGR delayed the autoignition, resulting in a reduction of local fuel-air equivalence ratio, combustion temperature and a decrease in NO_x emission. The oxygen content within the butanol molecule enhanced the soot oxidation and limited the smoke emission at the exhaust compared to the reference diesel. This result was also highlighted by the UV-visible flame emission with a lower emission intensity given by the butanol blends compared to diesel fuel.

The higher resistance to auto ignition of the butanol-diesel blends, accomplished a transition from the conventional to a partially premixed combustion for the butanol blend at higher volume fraction (BU40) and a reduction in the exhaust soot emission. This result was highlighted by the higher OH radicals detected by the flame emission measurements significant in an enhanced oxidation phase.

The lift-off length was evaluated: the values increased for higher n-butanol volume fraction and with the EGR activation.

References

[1] Yao, M., Zheng, Z., Liu, H.: *Progress and recent trends in homogeneous charge compression ignition (HCCI) engines*. Prog Energy Combust Sci, 35 (2009), pp. 398–437.

[2] Dec, J.E., Sjoberg, M.: *Isolating the effects of fuel chemistry on combustion phasing in an HCCI engine and the potential of fuel stratification for ignition control.* SAE 2004-01-0557; 2004.

[3] Bendu, H., Murugan, S.: *Homogeneous charge compression ignition (HCCI) combustion: Mixture preparation and control strategies in diesel engines*. Renewable and Sustainable Energy Reviews, 38 (2014), pp. 732-746.

[4] Kim, K., Wang, Z., Wang, B., Shuai, S., Yang, H., Bae, C.: *Load expansion of naphtha multiple premixed compression ignition (MPCI) and comparison with partially premixed compression ignition (PPCI) and conventional diesel combustion (CDC)*. Fuel, 136 (2014), pp. 1–9.

[5] Kiplimo, R., Tomita, E., Kawahara, N., Yokobe, S.: *Effects of spray impingement, injection parameters, and EGR on the combustion and emission characteristics of a PCCI diesel engine*. Applied Thermal Engineering 37 (2012), pp. 165–175.

[6] Chen, Z., Wu, Z.H., Liu, J.P., Lee, C.: *Combustion and emissions characteristics of high n-butanol/diesel ratio blend in a heavy-duty diesel engine and EGR impact*. Energy Convers Manag, 78 (2014), pp. 787–795.

[7] Siwale, L., Kristóf, L., Adam, T., Bereczky, A., Mbarawa, M., Penninger, A., *et al.*: *Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo--charged compression ignition engine*. Fuel, 107 (2013), pp. 409–418.

[8] Rakopoulos, D.C., Rakopoulos, C.D., Giakoumis, E.G., Dimaratos, A.M., Kyritsis, D.C.: *Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine*. Energy Conversion and Management, 51(10), 1989–1997, 2010.

[9] Zheng, Z.Q., Li, C.L., Liu, H.F., Zhang, Y., Zhong, X.F., Yao, M.F.: *Experimental study on diesel conventional and low temperature combustion by fueling four isomers of butanol*. Fuel, 141 (2014), pp. 109–119.

[10] Valentino, G., Corcione, F.E., Iannuzzi, S.E., Serra, S.: *Experimental study on performance and emissions of a high speed diesel engine fuelled with n-butanol diesel blends under premixed low temperature combustion*. Fuel, 92 (1) (2012), pp. 295–307.

[11] Liu, H.F., Wang, X., Zheng, Z.Q., Gu, J.B., Wang H., Yao, M.F.: *Experimental and simulation investigation of the combustion characteristics and emissions using n-butanol/biodiesel dual-fuel injection on a diesel engine*. Energy, 74 (2014), pp. 741–752.

[12] Lapuerta, M., Martos, F. J., & Cárdenas, M. D.: *Determination of light extinction efficiency of diesel soot from smoke opacity measurements*. Measurement Science and Technology, 16(10), 2048, 2005, doi:10.1088/0957-0233/16/10/021.

[13] Valentino, G., Merola, S., Marchitto, L., & Tornatore, C.: *Butanol-Diesel Blend Spray Combustion Investigation by UV-Visible Flame Emission in a Prototype Single Cylinder Compression Ignition Engine*. SAE International Journal of Engines 8.2015-24-2435 (2015).

[14] Gaydon, A.G.: *The Spectroscopy of Flames*. Chapman and Hall Ltd., London, 1974.

[15] Crosley D.R., Lengel R.K.: (1975). *Relative transition probabilities and the electronic transition moment in the A-X system of OH*. Journal of Quantitative Spectroscopy and Radiative Transfer 15(7–8), 579-591.

[16] Luque J. and Crosley D.R.: *LIFBASE: Database and spectral simulation (version 1.5)*. SRI International Report MP 99-009 (1999).

[17] Zhao, H., & Ladommatos, N.: *Optical diagnostics for soot and temperature measurement in diesel engines*. Progress in Energy and Combustion Science, 24(3), 221-255, 1998, doi:10.1016/S0360-1285(97)00033-6.

[18] Kosaka, H., Aizawa, T., & Kamimoto, T.: *Two-dimensional imaging of ignition and soot formation processes in a diesel flame*", International Journal of Engine Research, 6(1), 21-42, 2005, doi: 10.1243/146808705X7347.

[19] Otsu, Nobuyuki. "A threshold selection method from gray-level histograms." Automatica 11.285-296 (1975): 23-27.

[20] Dec, J. and Espey, C.: *Chemiluminescence Imaging of Autoignition in a DI Diesel Engine*. SAE Technical Paper 982685, 1998, doi:10.4271/982685.

[21] Fujimoto, H., Kurata, K., Asai, G., and Senda, J.: *OH Radical Generation and Soot Formation/Oxidation in DI Diesel Engine*. SAE Technical Paper 982630, doi:10.4271/982630.

[22] Merola, S.S., Vaglieco, B.M., Corcione, F.E., Formisano G.: *Spectral analysis of combustion process of common rail diesel engine*. SAE Paper 2002-01-1634; 2002.

[23] Dec, J. and Espey, C.: *Ignition and Early Soot Formation in a DI Diesel Engine Using Multiple 2-D Imaging Diagnostics*. SAE Technical Paper 950456, 1995, doi:10.4271/950456.

[24] Siebers, D., Higgins, B., and Pickett, L.: *Flame Lift-Off on Direct-Injection Diesel Fuel Jets: Oxygen Concentration Effects*. SAE Technical Paper 2002-01-0890, 2002, doi:10.4271/2002-01-0890.

[25] Pickett, L. M., & Siebers, D. L.: (2006). *Soot formation in diesel fuel jets near the lift-off length*. International Journal of Engine Research, 7(2), pp. 103–130.

[26] Donkerbroek, A. J., Boot, M. D., Luijten, C. C. M., Dam, N. J., & Ter Meulen, J. J.: (2011). *Flame lift-off length and soot production of oxygenated fuels in relation with ignition delay in a DI heavy-duty diesel engine*. Combustion and Flame, 158(3), pp. 525–538.

Utilization of Renewable Alcohol in an Internal Combustion Engine with Thermo-Chemical Recuperation of the Exhaust Gas Energy

Wykorzystanie odnawialnego alkoholu w silniku spalinowym z termochemiczną rekuperacją energii gazów spalinowych

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Abstract

Internal combustion engines (ICEs) are greatly responsible for fossil fuels consumption and environmental pollution. Development of more fuel-efficient ICEs together with alternative fuels is, therefore, of great importance. ICE's. overall efficiency can be improved by utilization of the thermal energy wasted with the exhaust gases. One method of exploiting this energy is by promoting endothermic fuel reforming reactions that increases the lower heating value (LHV) of the fuel introduced to the engine and allows combustion of a hydrogen-rich gaseous fuel. This method is commonly called thermo-chemical recuperation (TCR). Although TCR is feasible with conventional fuels, it is frequently realized with alcohol fuels that can be synthesized from methane or biomass, since their reforming temperature is lower. For this study, a gen-set gasoline-fed carburetor single-cylinder SI engine was modified to allow working with gasoline and methanol steam reforming (MSR) products. It was found that engine feeding by MSR products has a great potential for pollutant emissions mitigation as compared with gasoline. Harmful emissions of the pollutants CO, NO_x and the GHG gas CO_2 were reduced by 96%, 99% and 32% respectively. Particle number (PN) emissions were reduced by 99.7%. The achieved energy efficiency improvement of the engine fed by the methanol reformate was found to be from 20 up to 70% when compared with gasoline.

Keywords: Internal combustion engine, thermo-chemical recuperation, waste heat recovery, methanol, steam reforming, nanoparticles

1. Introduction

ICE's have been widely used as the main power plant in the transportation sector. Their operation is, thus, responsible for extensive usage of petroleum products worldwide. In the USA about 95% of the energy consumption in the transportation sector in the year of 2014 came from fossil fuels [1]. Moreover, they greatly contribute to climate change and environmental pollution due to their greenhouse gas and hazardous pollutant emissions. Therefore it's. of crucial importance to develop more efficient vehicles powered by low-carbon intensity fuels.

One way of increasing the powertrain overall efficiency is by recuperating the energy contained in the exhaust gases. It's. well documented that this energy corresponds to about 30% of the total energy delivered by the fuel [2] and it's. usually wasted. This process is called waste heat recovery and it can be performed in different ways, turbocharging being the most common [3]. Another way is by using the thermal energy of the exhaust gases to promote endothermic reactions of fuel reforming, which is often called thermo-chemical recuperation (TCR).

Energy transfer in TCR is not limited by isentropic expansion, as in turbocharging [4]. Moreover, the gaseous mixtures of the reforming products are often hydrogen-rich, which grants better combustion properties, such as a higher LHV, higher octane number, higher flame speed and wider flammability limits [5].

TCR can be performed with virtually any primary fuel, but alcohols are excellent candidates due to their relatively low reforming temperature (as compared to petroleum-based fuels) and high hydrogen content. This study focuses on methanol reforming, since it can be reformed at about 300°C and is a promising renewable fuel, since it can be derived from biomass.

Moreover, combustion of the hydrogen-rich alcohol reforming products greatly mitigates the formation of hazardous emissions. This can be explained by the fact that the main combustion product of hydrogen is water. The wide flammability limits of hydrogen allow lean engine combustion, which greatly decreases nitrogen oxides (NO_x) emissions. Furthermore, lean combustion of gaseous MSR products usually containing hydrogen, CO and CO_2 mitigates particle matter (PM) formation.

TCR does not stand as a new idea. In fact, there was very intense research on the topic in the late 70's. and 80's. Petterson et al. [6] summarized most of the research on the theme conducted up to the early 90's. Enhancement on engine efficiency has been widely reported. Takayuki et al. [7] and Finegold et al. [8] have even built vehicles with on-board methanol decomposition and reported up to 40% efficiency increase. Similar study was performed also by Brinkman and Stebar [9], where they pointed out that the main reason for efficiency improvement is the better combustion properties of decomposition products, namely higher flame speed, higher octane number and wider flammability limits.

Some major problems, however, have also been reported. The major obstacles that researchers dealt with were backfire, pre-ignition, reduced maximal power and difficulty at cold-start and transient operating modes [9]. Backfire and pre-ignition were caused by the highly flammable nature of hydrogen-rich gaseous fuel, while reduced maximal power was due to the lower volumetric efficiency, since the admission of the gaseous fuel into the engine intake manifold reduces the mass of fresh air that can be ingested. Cold-start and transient behavior problems derived from the absence of the available heat at engine's. starting and reactor dynamics limitations. These problems could not be overcome at that time and as a result most research activities on methanol TCR were stopped.

Nonetheless, by virtue of the technological development over the last decades, it's. now possible to overcome such problems. Wimmer et al. [10] showed that for a hydrogen-fueled engine direct injection (DI) into the cylinder can solve the problems of backfire and pre-ignition, since fuel does not get mixed with air nor gets in contact with potential hot spots through the intake manifold. Moreover, DI allows greater volumetric efficiency and maximum power comparable to gasoline engines. Poran and Tartakovsky suggested in [11] that high-pressure TCR may allow direct injection of the reforming products into the engine cylinder with the subsequent benefits. Furthermore, Tartakovsky et al. [12] suggested the usage of a hybrid propulsion system as a solution to the cold start and transient behavior problems, since the ICE could always be operated at optimal regime and the electric engine could be used to deal with the different regimes requirement. An additional energy source available in the hybrid propulsion system may allow its startup at cold starts.

The main goals of the present study were to adapt a conventional gasoline engine to operate with DI of methanol-reformate fuel and to assess changes in energy efficiency and pollutants emission.

2. Methodology

2.1 Experimental setup and measurement procedures

A gen-set gasoline-fed carburetor single-cylinder SI engine was modified to permit work with both liquid gasoline and gaseous methanol reforming products. For gasoline feeding, the original configuration was used. For reformate feeding, the gaseous mixture was directly-injected into the engine cylinder to prevent the pre-ignition and the backfire problems. For this purpose a dedicated gaseous fuel direct injector was developed. The experimental overall setup and the equipment used can be seen in Figure 1.

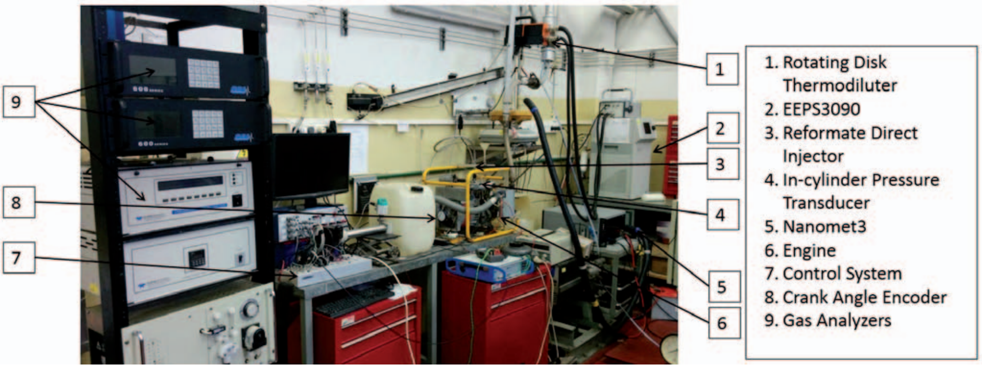

Figure 1. Experimental overall setup

The engine was tested with both gasoline (95 RON) and syngas imitating methanol reformate. The composition of the syngas is shown in Table 1 and it was found to be the most probable product of the reforming process in the case of molar steam-to-methanol ratio value of 1:1 [4].

Table 1. Syngas composition

H_2 molar/ mass fraction [%]	CO_2 molar/ mass fraction [%]	Air/Fuel stoichiometric ratio	LHV [MJ/kg]
75/12	25/88	4.13	14.61

Various ignition timings were tested, and the maximal engine efficiency (minimal specific fuel consumption) operating point was found. After that, the characteristic load curve at the rated engine speed and optimal ignition timing was measured. The following engine parameters were measured or calculated:

- Engine speed and power;
- In-cylinder maximal pressure and maximal pressure-rise rate (indicatory diagram);
- Exhaust gas temperature;
- Air flow-rate;
- Fuel consumption;
- Air excess factor (lambda);
- Concentrations of gaseous pollutants NO_x, CO, and the greenhouse gas CO_2 in the exhaust;
- PN emissions.

A rheostat was used to impose the gen-set loading. For this reason, the generator electric power was used as a basis for referring the entire engine performance parameters. The rated value of the generator was measured to be 1.6 kW at 3000 rpm, while the engine brake power was 2.2 kW. That value closely corresponds to the nominal efficiency of this generator, which is 73% [16]. Before taking measurements, a warm-up period was allowed. Reformate pressure at the injector inlet was set to the range of 30 – 50 bar. Lambda value was set to 1 at gasoline feeding and was changed from 1 to 1.5 (lean operation) at reformate feeding. The in-cylinder pressure transducer provided data on maximal pressure and the maximal pressure rise rate. Based on that, indicatory diagrams for each operating regime were built. Mean weighted values of 100 consecutive working cycles were used as the measurement results.

2.2 The engine

ROBIN EY20-3 air-cooled naturally aspirated, single-cylinder spark-ignition 4-stroke engine was selected for the laboratory experiments. It was coupled, as a gen-set, with the SINCRO GP100 2.2 kW AC 230V generator. The main motivation for selecting this engine was that it has side valves location that allows more space in the cylinder head for installing an in-cylinder pressure transducer and a direct fuel injector. The main parameters of the engine can be seen in Table 2.

Table 2. Specification of the ROBIN EY20-3 engine

Engine	Gen-set ROBIN EY20-3 / SINCRO GP100 2.2 kW AC 230V
Bore x Stroke, mm	67x52
Displacement, cm^3	183
Compression ratio	6.3
Power, kW @ speed, rpm	2.2 @ 3000
Lubrication	Splash type
Carburetor	Horizontal draft, Float type
Gasoline feed system	Gravity type
Ignition system	Flywheel magneto
Spark plug	NGK B6HS
Starting system	Recoil starter
Governor system	Centrifugal flyweight type

2.3 Fuel delivery

For gasoline feeding, the original fuel tank was used. Fuel was mixed with air and introduced into the intake manifold by means of the conventional carbureted fuel supply system of the engine.

For reformate feeding, the fuel was supplied from a high-pressure cylinder provided by a gas supplier company. The reformate was directly injected into the cylinder. In order to do so, a dedicated gaseous fuel injector had to be used. At the time of the present study, there were no market-available injectors suited for this task. Therefore, an injector originally designed for operating with liquid fuel was adapted. Similar efforts had been reported in the past [13, 14, 15].

Magneti-Marelli gasoline direct injector model IHP072 has been chosen as the basis for modification. The nozzle part that restricts the fuel flow was removed. Figure 2 shows the original injector, some of the work done and the final configuration of the gaseous direct injector.

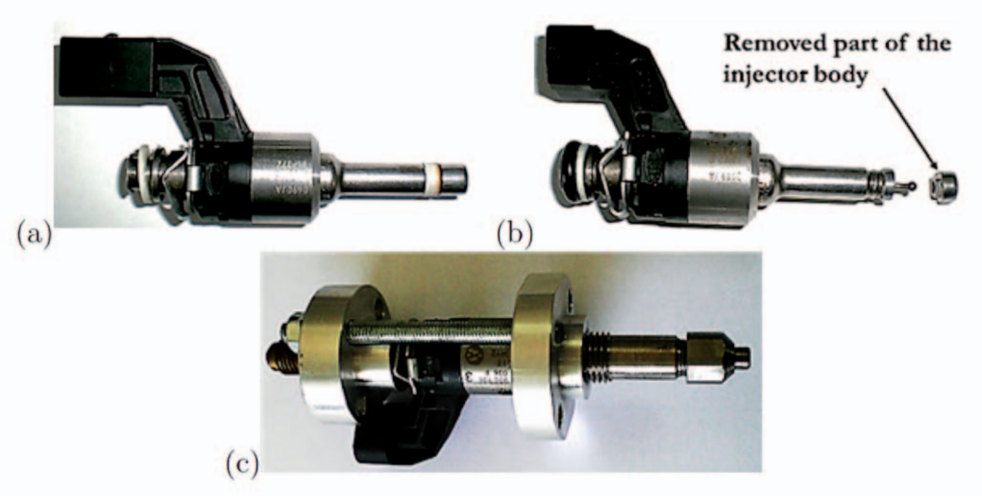

Figure 2. Gaseous reformate direct injector: (a) original IHP072 GDI injector; (b) injector preparation; (c) final reformate injector design

The engine was run at stoichiometric fuel-air ratio ($\lambda=1$) when powered with gasoline. With reformate feeding, however, engine operation with lean mixtures ($\lambda>1$) was also examined, since this is one of the advantages of the studied fuel. The leanest mixture used corresponds to λ=1.5.

2.4 Emissions measurement

The concentration of pollutants in the exhaust gases of the engine had been analyzed for operation with both gasoline and methanol reformate. For this purpose the following equipment was used:

- For Particles Size Distribution: **Engine Exhaust Particle Sizer (EEPS) Spectrometer 3090 – TSI**. Particles pass through an electrical diffusion charger where they get a predictable charge level based on their size. An electric field drags the particles in the sizing region where 22 sensing electrometers are installed. Particles, which land on the sensing electrodes, transfer their charge. The equipment measures particles from 5.6 to 560 nm with particle size resolution of 16 channels per decade (32 in total) and time resolution of 10 readings per second.
- For Total PN: **NanoMet3 – Matter Aerosol**. The sample is thermally conditioned to eliminate the volatile fraction. It is also based on electrical charging to count particles, but there is no size distribution assessment. The equipment measures particles from 10 to 700 nm. NanoMet3 was equipped with a sampling line at the temperature of 300°C. This heating prevents the condensation of volatiles in the raw aerosol. This procedure allows the measurement of solid particle number concentrations (SPNC), as described by the Particle Measurement Program (PMP) [17].
- For NO_x: **Nitrogen Oxides Analyzer 200EH – Teledyne**. The equipment uses the chemiluminescence measurement principle. The measured concentration ranges from 0-5 ppm to 5000 ppm with 0.5% of reading precision.
- For CO/CO_2: **NDIR/O2 Analyzer 600 – CAI**. The equipment is based on the infrared absorption characteristics of gases. A modulated single infrared light beam is used. The measured concentration ranges from 0-50 ppm to 100% with 1% of repeatability and linearity.
- For diluting the sample: **Rotating Disk Thermodiluter 379020A – TSI**. The equipment is suited for sampling, diluting, and conditioning exhaust particles prior to their measurement in dedicated equipment. A small quantity of the raw exhaust is captured by a cavity of the rotating disk and

transported to the measurement channel where it is mixed with HEPA-filtered, particle-free dilution air. Dilution ratio can be adjusted from 15:1 to 3000:1 and heated diluter temperatures can be set up to 150°C. The dilution accuracy is rated as 10%.

For the nanoparticle size distribution measurement, the engine was operated at 700W power and at 2800 rpm. Thermo-dilution was performed at 150°C, which corresponds to the maximum available temperature of the Rotating Disk Thermodiluter. A dilution factor of 105 was implemented.

2.5 In-cylinder pressure analysis

A pressure transducer installed inside the cylinder and an encoder provided data on pressure and crank angle position. 100 consecutive cycles were measured and their mean weighted values were obtained. Instantaneous cylinder volume was calculated according to the following equation:

$$V = V_c\left\{\left(1+\frac{1}{2}(r_c-1)\left[R+1-\cos\theta-(R^2-\sin^2\theta)^{1/2}\right]\right)\right\}$$

Where V_c is the clearance volume, r_c is the compression ratio, R is the ratio of the connecting rod length to the crank radius and θ is the crank angle.

3. Results

Different values of ignition timing were tested. Figure 3 shows that the maximal engine efficiency with gasoline was achieved at 32° before top dead center (BTDC). This is a typical value for gasoline-powered engines [18]. The same procedure was performed for methanol reformate feeding, and the obtained ignition timing for minimal Specific fuel consumption (SFC) was found to be around 14° BTDC. The retarded ignition timing for reformate feeding is a direct implication of the higher flame speed of the mixture, which allows quicker combustion.

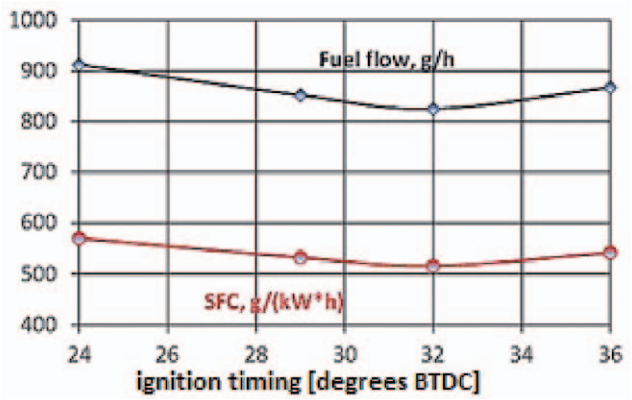

Figure 3. Engine SFC as a function of ignition timing for gasoline feeding

3.1 Engine efficiency

The generator efficiency of 73% was used to calculate the engine efficiency. The efficiency calculation was performed based on the primary liquid consumption (gasoline and methanol). The obtained values of the engine efficiency under operation with gasoline and methanol reformate are shown in Figure 4. Figure 5 presents the improvement in engine efficiency with methanol reformate as compared to gasoline.

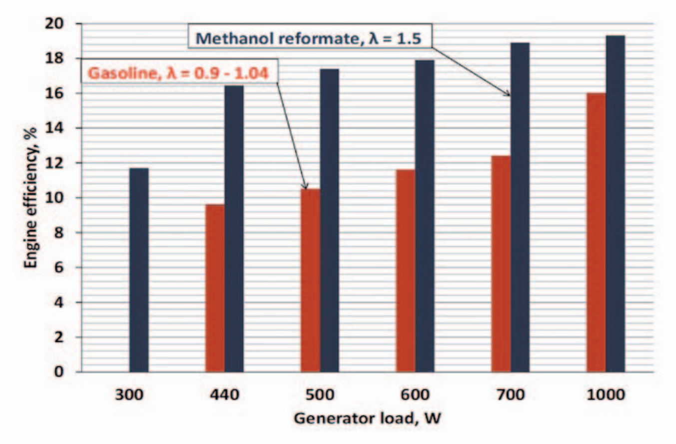

Figure 4. Engine efficiency with gasoline and methanol reformate

One of the first things that can be noticed is the relatively low values of the engine efficiency (less than 20% for every measured regime). This can be explained by the low-load regimes in which the experiment was performed and the low engine compression ratio (of only 6.3). However, it's. possible to notice a clear increase in efficiency when the engine is operated on methanol reformate. The increase is about 20% at 1000 W and up to 70% under low loads, which is due to the combined effects of two main factors: the lean-burn operating achieved with hydrogen-rich reformate fuel and the better technology of direct fuel injection. Tartakovsky et al. [19] studied the contribution of the lean-burn operation with reformate. According to the results of this study, there can be an improvement of up to 13% in engine efficiency due to lean burning of the methanol reformate fuel.

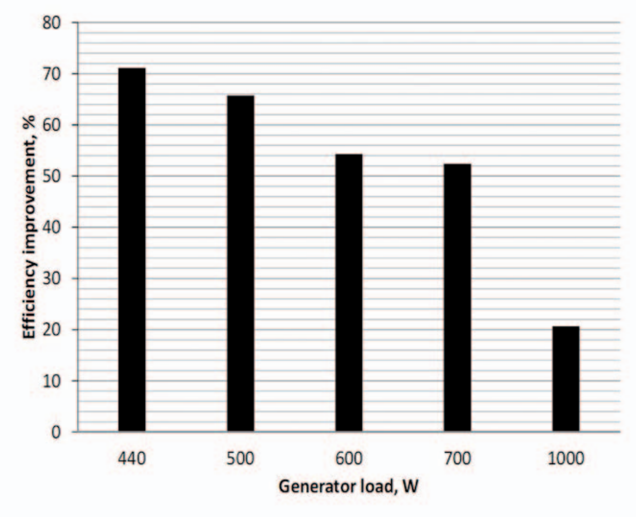

Figure 5. Engine efficiency improvement under methanol reformate feeding over gasoline feeding

3.2 Pollutants emissions

Figure 6 presents the results of emissions for the measured pollutants CO_2, CO and NO_x at engine operating with gasoline at stoichiometric mixture and also methanol reformate at lambda values of 1 and 1.5. Engine was operated at rated power of 1000W and 2800 rpm. For all the three measured pollutants, the same trend was observed. There was a decrease in the gaseous pollutant emissions when the engine was operated with reformate instead of gasoline, and an even greater decrease for lean operation. Table 3 shows the relative reduction of gaseous pollutants emissions when the engine was powered with methanol reformate at stoichiometric and lean operation. CO concentrations in the exhaust gas were reduced by about 75% for a stoichiometric air/fuel mixture and by 96% under lean operation. Reduction of 99% in the NO_x emissions can be explained by the relatively low temperatures obtained in the combustion of reformate.

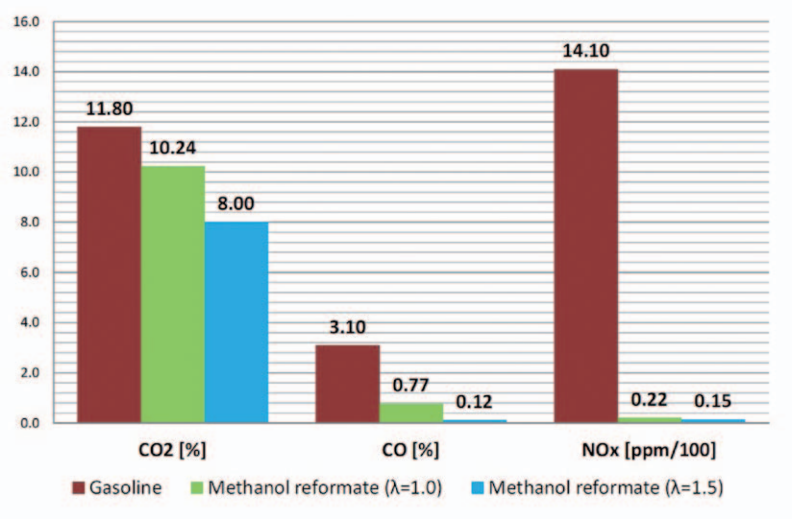

Figure 6. Gaseous emissions

Table 3. Relative reduction of gaseous emissions under reformate feeding

Relative improvement (from gasoline)	CO_2 [%]	CO [%]	NO_x [%]
Methanol reformate (λ = 1.0)	13.2	75.2	98.4
Methanol reformate (λ = 1.5)	32.2	96.1	99.0

Figure 7 presents the results of size distribution for gasoline and stoichiometric reformate mixture. It can be seen that in both situations the obtained profile is similar, with methanol reformate combustion nanoparticles being slightly smaller.

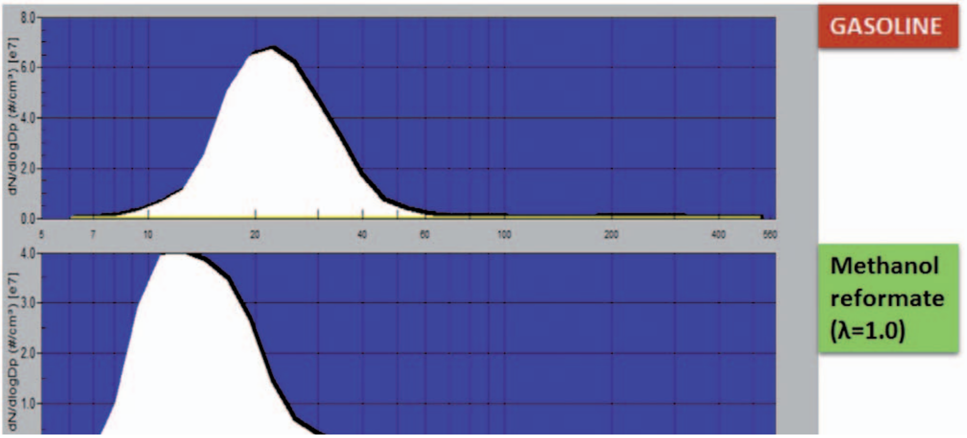

Figure 7. Nanoparticle size distribution

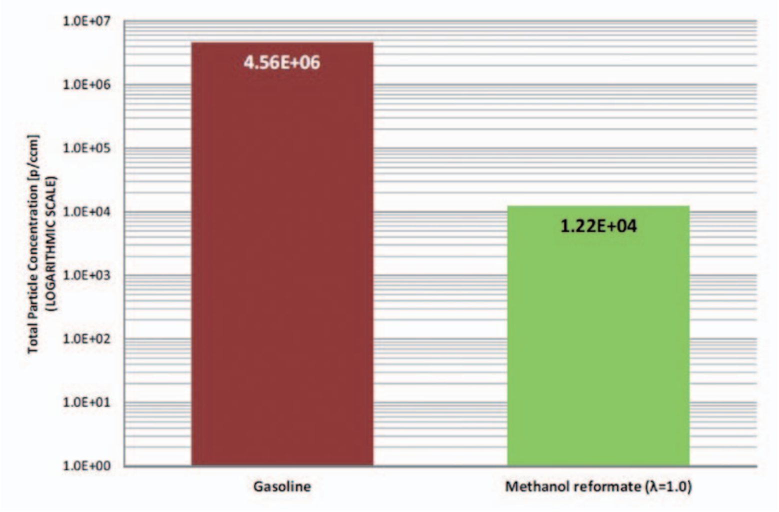

Figure 8. Total particle concentration

It's important to notice, however, that the relatively low dilution temperature of only 150°C leads to a significant amount of volatile nanoparticles. Therefore, another nanoparticle measuring equipment Nanomet-3 was used. This equipment can't measure nanoparticle size distribution, but can dilute the aerosol at the temperature of 300°C with a dilution factor of 100. By means of this, a larger portion of the volatiles were eliminated, and a more significant fraction of the solid particles were left. Particles within the size range from 10 to 700 nm were measured. Figure 8 presents the obtained concentrations for the total solid nanoparticles. As can be seen, operation with gasoline led to 4.56×10^6 particles per cubic centimeter, while stoichiometric operation of the engine with reformate led to only 1.22×10^4 particles per cubic centimeter. This represents a total PN reduction of 99.7%. We suppose that in the case of reformate combustion there may be significant contribution to nanoparticle formation due to the combustion of engine oil.

3.3 In-Cylinder Pressure Analysis

Results of the in-cylinder pressure analysis are presented in Figure 9. The pressure values of 100 consecutive cycles and their average (in red) are plotted against crank-angle for engine operating with gasoline at stoichiometric mixture and also methanol reformate at lambda values of 1 and 1.3. Average cycle pressure against cylinder volume diagrams are presented on the right. Table 4 presents results for maximum achieved pressure, spark ignition timing, maximum pressure timing and time lag between those two events for engine operating in the mentioned regimes.

Table 4. In-cylinder pressure analysis data

	α_{spark} [°]	α_{Pmax} [°]	$\Delta\alpha$ [°]	P_{max} [bar]
Gasoline	330.00	375.75	45.75	15.78
Methanol reformate ($\lambda = 1.0$)	346.00	376.25	30.25	14.33
Methanol reformate ($\lambda = 1.3$)	346.00	377.75	31.75	14.42

Due to the higher LHV of gasoline, engine operation with this fuel provided higher maximum pressure. It can also be observed that in the three engine operation modes, maximum pressure is achieved on about the same spot, 376°. However, combustion of reformate is faster compared with gasoline, due to its higher flame speed. Moreover, although engine's. efficiency is higher at lean operation, combustion is faster with a stoichiometric mixture. Efficiency improvement at lean operation is explained by lower heat transfer losses in the latter case.

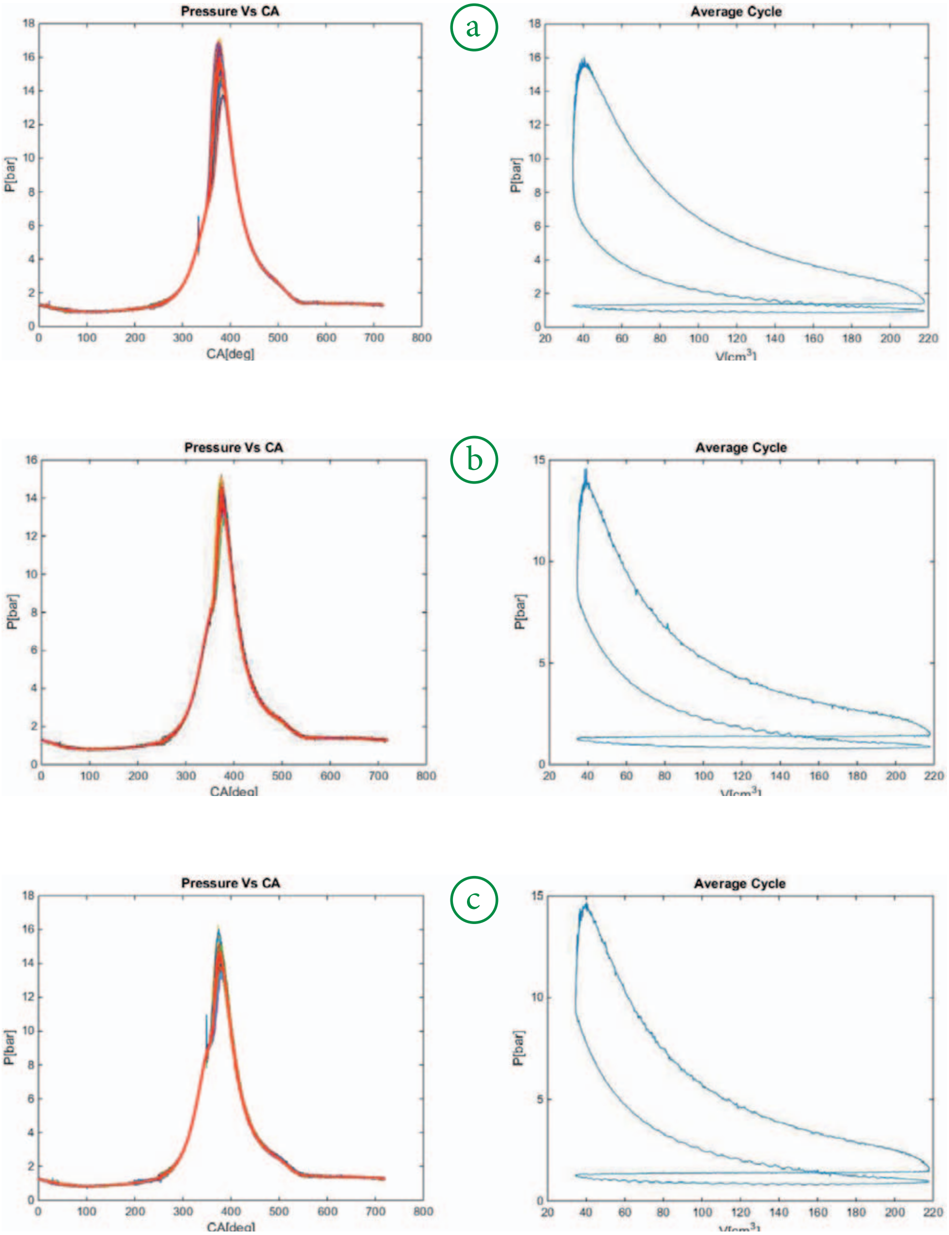

Figure 9. P-CA and P-V diagrams:
(a) Gasoline (λ = 1.0); (b) Reformate (λ = 1.0); (c) Reformate (λ = 1.3)

4. Conclusions

This work has analyzed the utilization of methanol in an ICE with TCR of the energy of the exhaust gases. It presents first results of the experimental study.

A gen-set carbureted engine was modified to operate both with gasoline and methanol reforming products. For this purpose a direct injector was developed for the operation with the gaseous fuel. An in-cylinder pressure sensor was used to provide combustion related data. It was found that engine efficiency can be increased up to 70% under low loads with methanol reformate, compared with gasoline. Engine exhaust analyzers were used to measure the concentration of the pollutants emissions. Toxic CO was reduced by about 75 and 96% under stoichiometric and lean operation, respectively. NO_x reduction was over 98%. Particle number concentrations were reduced by 99.7%.

Acknowledgements

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References

[1] US EIA. Monthly energy review, March 2015, 2015.

[2] He, M., Zhang, X., Zeng, K., Gao, K.: (2011). *A combined thermodynamic cycle used for waste heat recovery of internal combustion engine*. Energy, 36(12), pp. 6821–6829.

[3] Tartakovsky, L., Gutman M. and Mosyak A.: (2012). *Energy efficiency of road vehicles – trends and challenges. Chapter 3* in the Edited Collection “Energy Efficiency: Methods, Limitations and Challenges”, Emmanuel F. Santos Cavalcanti and Marcos Ribeiro Barbosa (editors). Nova Science Publishers, pp. 63–90.

[4] Poran, A., Artoul, M., Sheintuch, M., and Tartakovsky, L.: (2014). *Modeling Internal Combustion Engine with Thermo-Chemical Recuperation of the Waste Heat by Methanol Steam Reforming*. SAE Int. J. Engines 7(1):234–242.

[5] Rakopoulos, C. D., Scott, M. A., Kyritsis, D. C., Giakoumis, E. G.: (2008). *Availability analysis of hydrogen/natural gas blends combustion in internal combustion engines*. Energy, 33(2), pp. 248–255.

[6] Pettersson, L. and Sjöström, K.: (1991). *Decomposed Methanol as a Fuel – A review*. Combustion science and technology, 80(4–6), pp. 265–303.

[7] Sakai, T., Yamaguchi, I., Asano, M., Ayusawa, T., Kim, Y. K.: (1987). *Transient Performance Development on Dissociated Methanol Fueled Passenger Car*. SAE Technical Paper 871169.

[8] Finegold, J. G. (1984). Dissociated methanol vehicle test results (No. SERI/TP-234-2245; CONF-840543-2). Solar Energy Research Inst., Golden, CO (USA).

[9] Brinkman, N. D. and Stebar, R. F.: (1985). *A Comparison of Methanol and Dissociated Methanol Illustrating Effects of Fuel Properties on Engine Efficiency –Experiments and Thermodynamic Analyses*. SAE Technical Paper 850217.

[10] Wimmer, A., Wallner, T., Ringler, J., Gerbig, F.: (2005). *H2-direct injection–a highly promising combustion concept*. SAE Technical Paper 2005-01-0108.

[11] Poran, A. and Tartakovsky, L.: (2015). *Energy efficiency of a direct-injection internal combustion engine with high-pressure methanol steam reforming*. Energy 88:506–514.

[12] Tartakovsky, L., Mosyak, A., Zvirin, Y.: (2013). *Energy analysis of ethanol steam reforming for hybrid electric vehicle*. International Journal of Energy Research 37: 259-267.

[13] Mohamad, T. I.: (2010). *Compressed Natural Gas Direct Injection (Spark Plug Fuel Injector)*. INTECH Open Access Publisher.

[14] Varde, K. S. and Frame, G. A.: (1985). *Development of a high-pressure hydrogen injection for SI engine and results of engine behavior*. International Journal of Hydrogen Energy 10(11): 743–748.

[15] Hassan, M. H., Kalam, M. A., Mahlia, T. I., et al.: (2009). *Experimental test of a new compressed natural gas direct injection engine*. Energy & Fuels 23(10): 4981–4987.

[16] Linz Electric. Products overview, 04–14.

[17] Giechaskiel, B., Mamakos, A., Andersson, J., et al.: (2012). *Measurement of automotive nonvolatile particle number emissions within the European legislative framework: A review*. Aerosol Science and Technology 46(7): 719–749.

[18] Heywood, J. B.: (1988). *Internal combustion engine fundamentals* (Vol. 930). New York: Mcgraw-Hill.

[19] Tartakovsky, L., Baibikov, V., Veinblat, M.: (2013). *Comparative Performance Analysis of SI Engine Fed by Ethanol and Methanol Reforming Products*. SAE Technical Paper 2013-01-2617.

Paliwa etanolowe dla transportu – zagadnienia normalizacyjne

Ethanol fuels for the transport – standardization issues

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Abstract

The article discusses the formal aspects of the development standards. In particular discusses legal and standardization issues of standard PN-EN 15376:2014-11 – English version, Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań, introducing the EN 15376:2014 *Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods.* Given the information of the technical bodies dealing with ethanol fuels for the transport: in European Committee for Standardization CEN – Technical Committee CEN/TC 19 *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin,* in particular Work Group CEN/TC19/WG21 *Specification for unleaded petrol,* and in Polish Committee for Standardization PKN – Subcommittee PKN/KT222/PK1 *Liquid fuels* of PKN/KT222 *Petroleum and related products.* The article presents standardization documents – specifications feeding requirements for biofuels: E10 and E85+.

Keywords: ethanol fuels for the transport, standardization, CEN and PKN procedures.

Streszczenie

W artykule przedstawiono formalne aspekty opracowania norm. W szczególności omówiono prawne i normalizacyjne zagadnienia dotyczące normy PN-EN 15376:2014-11 – wersja angielska, *Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań*, wprowadzającej EN 15376:2014 *Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods.* Podano informacje o organach technicznych zajmujących się tematyką paliw etanolowych dla transportu, którymi są: w Europejskim Komitecie Normalizacyjnym CEN – Komitet Techniczny CEN/TC 19 „Paliwa ciekłe i gazowe, środki smarowe i produkty podobne pochodzenia naftowego, syntetycznego i biologicznego" (*Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*), w szczególności Grupa Robocza CEN/TC 19/WG 21 „Specyfikacja dla benzyny bezołowiowej", a w Polskim Komitecie Normalizacyjnym PKN – Podkomitet PKN/KT 222/PK 1 Paliw Płynnych Komitetu Technicznego PKN/KT 222 Przetworów Naftowych i Cieczy Eksploatacyjnych. Przedstawiono dokumenty normalizacyjne – specyfikacje podające wymagania dla biopaliw E10+ i E85.

Słowa kluczowe: paliwa etanolowe dla transportu, normalizacja, procedury CEN i PKN.

Dlaczego normalizacja?

Normy są dobrowolne, obowiązują nas rozporządzenia, ale samochody jeżdżą na paliwach, których właściwości określają normy.

Obowiązujące akty prawne dla bioetanolu – etanolu stosowanego jako komponent benzyny silnikowej

Obowiązującymi aktami prawnymi podającymi wymagania jakościowe i metody badań dla biokomponentów są:

- Rozporządzenie Ministra Gospodarki z dnia 14 maja 2015 r. zmieniające rozporządzenie w sprawie wymagań jakościowych dla biokomponentów, metod badań jakości biokomponentów oraz sposobu pobierania próbek biokomponentów [1];
- Rozporządzenie Ministra Gospodarki z dnia 17 grudnia 2010 r. w sprawie wymagań jakościowych dla biokomponentów, metod badań jakości biokomponentów oraz sposobu pobierania próbek biokomponentów [2].

Załącznik nr 1 rozporządzenia z 14 maja 2015 r. *Wymagania jakościowe dla bioetanolu* zawiera wszystkie aktualnie obowiązujące wymagania. Metody badań podaje załącznik nr 3 *Metody badań jakości biokomponentów* rozporządzenia z 17 grudnia 2010 r., w punkcie I. *Metody badań jakości bioetanolu, w zakresie poszczególnych parametrów tego biokomponentu* [2], oraz zmieniające go rozporządzenie z 14 maja 2015 r. § 1 pkt 4a [1].

Aktualna norma PN-EN 15376:2014-11 – wersja angielska

Aktualną – nie „obowiązującą" – Polską Normą na etanol jako komponent benzyny silnikowej jest norma PN-EN 15376:2014-11 – wersja angielska, *Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań*. Norma ta wprowadza europejską normę EN 15376:2014 *Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods* [3]. W tabeli 1 zestawiono dane zaczerpnięte z obu ww. rozporządzeń i z Polskiej Normy.

Tabela 1. Wymagania dla etanolu paliwowego w aktualnej normie i obowiązujących rozporządzeniach

Norma/rozporządzenia	PN-EN 15736	Rozporządzenia
Właściwości	Metoda badań	Metoda badań
Zawartość etanolu + wyższe nasycone alkohole	EN 15721	PN-EN 15721

Zawartość wyższych nasyconych (C3–C5) alkoholi jednowodorotlenowych	EN 15721	PN-EN 15721
Zawartość metanolu	EN 15721	PN-EN 15721
Zawartość wody	EN 15489 EN 15692	PN-EN 15489 PN-EN 15692
Całkowita kwasowość (wyrażona jako zawartość kwasu octowego)	EN 15491	PN-EN 15491
Przewodność elektryczna	EN 15938	PN-EN 15938
Wygląd	EN 15769	PN-EN 15769
Zawartość chlorków nieorganicznych	EN 15492	PN-EN 15492
Zawartość siarczanu	EN 15492	PN-EN 15492
Zawartość miedzi	EN 15488 EN 15837	PN-EN 15488 PN-EN 15837
Zawartość fosforu	EN 15487 EN 15837	PN-EN 15487 PN-EN 15837
Zawartość suchej pozostałości po odparowaniu	EN 15691	PN-EN 15691
Zawartość siarki	EN 15485 EN 15486 EN 15837	PN-EN 15485 PN-EN 15486 PN-EN 15837

Kolorem zielonym zaznaczono tekst występujący i w rozporządzeniu, i w normie (w normie – w j. angielskim; zamieszczony tekst zaczerpnięto z opracowywanego projektu wersji polskiej) [4]; na niebiesko – zaczerpnięty z normy; na czerwono – z ww. rozporządzeń.

Metody badań przywołane w Polskiej Normie to normy europejskie, które są dokumentami w języku angielskim. Polska Norma jest identycznym tłumaczeniem normy europejskiej; nie ma już od wielu lat w polskich normach produktowych załącznika krajowego informacyjnego, wskazującego, która Polska Norma jest odpowiednikiem powołanej normy europejskiej. Natomiast wszystkie normy europejskie wprowadzane są przez kraje członkowskie Europejskiego Komitetu Normalizacyjnego (CEN) w języku oryginału w ciągu pół roku od zatwierdzenia. Wynika to z faktu, że Polski Komitet Normalizacyjny jest członkiem CEN [5].

Metody badań przywołane w rozporządzeniach to Normy Polskie, które wprowadzają odpowiednie normy europejskie. Wprowadzona Norma Polska może być opublikowana w języku angielskim, ale zanim zostanie powołana w przepisach, musi być opublikowana w języku polskim, co wynika z ustawy o normalizacji.

Co wynika z ustawy o normalizacji?

Ustawa o normalizacji z dnia 12 września 2002 r. stanowi, że Polski Komitet Normalizacyjny (PKN) jest krajową jednostką normalizacyjną. Misją PKN jest sprawnie organizować działalność normalizacyjną zgodnie z rozwiązaniami europejskimi i międzynarodowymi. Ustawa o normalizacji w rozdziale 3 *Polskie Normy i inne dokumenty normalizacyjne* definiuje Polską Normę jako normę krajową, przyjętą w drodze konsensu i zatwierdzoną przez krajową jednostkę normalizacyjną, powszechnie dostępną, oznaczoną – na zasadzie wyłączności – symbolem PN. Polska Norma może być wprowadzeniem normy europejskiej lub międzynarodowej. Wprowadzenie to może nastąpić w języku oryginału [6]. Symbol PN-EN oznacza Polską Normę wprowadzająca normę europejską EN [4]. Stąd wynika sytuacja, że aktualna Polska Norma może być w języku angielskim; poza stroną tytułową i informacją o treści normy zamieszczoną na stronie PKN.

Ustawa w rozdziale 3 w punkcie 4 stanowi: „Polskie Normy mogą być powoływane w przepisach prawnych po ich opublikowaniu w języku polskim” [6]. W ramach systemu normalizacji dobrowolnej istotne znaczenie ma zasada, zgodnie z którą normy opracowują dla siebie sami zainteresowani ich stosowaniem. PKN, jako krajowa jednostka normalizacyjna, nie tworzy norm ani też nie ingeruje w merytoryczną treść norm na żadnym etapie ich opracowania. Organizuje natomiast działalność normalizacyjną, w tym m.in. na wniosek zainteresowanych przeprowadza odpłatnie procedurę zmierzającą do uzgodnienia i zatwierdzenia Polskiej Normy lub Polskiego Dokumentu Normalizacyjnego, na podstawie dostarczonego przez zamawiającego gotowego projektu [4]. Normy tworzą zainteresowani, na własne potrzeby i z własnych środków. Budżet PKN jest tworzony wyłącznie na organizowanie działalności normalizacyjnej [7].

Ustawa w rozdziale 3 stanowi: „Stosowanie Polskich Norm jest dobrowolne” [6]. W poprzednim systemie, do 31 grudnia 1993 r., było ono obowiązkowe – normy pełniły rolę przepisów. Od 1 stycznia 1994 r. stosowanie Polskich Norm jest dobrowolne, przy czym do 31 grudnia 2002 r. istniała możliwość, przez właściwych ministrów i w pewnych przypadkach, nakładania obowiązku ich stosowania. Od 1 stycznia 2003 r. stosowanie Polskich

Norm jest całkowicie dobrowolne. Często jeszcze spotykane niepoprawne sformułowanie „obowiązująca norma" dotyczy faktycznie aktualności normy.

Informacje o PN-EN 15376 dostępne na stronie PKN

Na stronie internetowej PKN, po wpisaniu numeru w wyszukiwarce na stronie głównej, uzyskuje się informację o wszystkich wydaniach normy (numer, tytuł i norma wprowadzana). W zakładce „Dowiedz się więcej" podany jest zakres normy PN-EN 15376:2014-11: „W niniejszej Normie Europejskiej określono wymagania i metody badań dotyczące etanolu będącego przedmiotem obrotu handlowego, stosowanego jako składnik paliwa do pojazdów samochodowych z silnikami benzynowymi, zgodnego z wymaganiami EN 228. Norma ta ma zastosowanie do etanolu dodawanego do paliwa do pojazdów samochodowych na każdym poziomie do 85% (*V/V*) włącznie" [4].

Przedstawiona jest również informacja o możliwościach nabycia normy. Zgodnie z ustawą o normalizacji „Polskie Normy korzystają z ochrony jak utwory literackie, a autorskie prawa majątkowe do nich przysługują krajowej jednostce normalizacyjnej" [2]. Dokumenty normalizacyjne można nabyć w PKN w wersji papierowej bądź elektronicznej. Cena zależy od formy udostępnienia: np. wersja elektroniczna – 32,80 PLN (z VAT: 40,34 PLN), wersja drukowana – 43,70 PLN [4].

Tabela 2. Informacje dodatkowe o normie PN-EN 15376:2014-11 – wersja angielska [4]

Numer normy	PN-EN 15376:2014-11 – wersja angielska
Tytuł	Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań
Data publikacji	27-11-2014
Liczba stron	10
Grupa cenowa	E
Sektor	SCH, Sektor Chemii
Organ Techniczny	KT 222/PK 1, Paliw Płynnych

Numer normy	PN-EN 15376:2014-11 – wersja angielska
Wprowadza	EN 15376:2014 [IDT]
Zastępuje	PN-EN 15376:2012 – wersja polska
ICS	75.160.20, 71.080.60

Organ Techniczny, w którego zakresie znajduje się norma, to Podkomitet ds. Paliw Płynnych Komitetu Technicznego 222 ds. Przetworów Naftowych i Cieczy Eksploatacyjnych KT 222/PK 1. Całość prac normalizacyjnych związanych z wprowadzeniem wersji angielskiej – uznaniowej norm EN, a następnie opracowaniem wersji polskiej tych norm (w przypadku zainteresowania środowiska takim działaniem) prowadzona jest za pośrednictwem właściwego Organu Technicznego PKN – w tym przypadku KT 222/PK 1.

[IDT] to symbol stopnia zgodności – oznacza normę PN identyczną z wprowadzoną normą.

Zamieszczone w ostatnim wierszu tabeli 2 kody liczbowe ISC (*International Classification for Standards*) to wyróżniki Międzynarodowej Klasyfikacji Norm, stanowiącej podstawę do szeregowania dziedzinowego norm w katalogach, oznaczające odpowiednio:

75.160.20	dziedzina	75	Technologia przetwórstwa ropy naftowej i technologie związane
	grupa	75.160	Paliwa
	podgrupa	75.160.20	Paliwa płynne, w tym benzyny, olej napędowy, nafta itp.
71.080.60	dziedzina	71	Przemysł chemiczny
	grupa	71.080	Związki chemiczne organiczne
	podgrupa	71.080.60	Alkohole. Etery [4]

Normy na etanol paliwowy

Kolejne wersje PN-EN 15376 wprowadzającej EN 15376

Pierwsza europejska norma na etanol jako komponent benzyny silnikowej ukazała się w 2007 r. i zgodnie z procedurami z CEN/PKN została w ciągu sześciu miesięcy wprowadzona do zbioru PN w języku oryginału jako PN-EN 15376:2008 (*oryg.*) [8]. Niestosowane już obecnie oznaczenie „(*oryg.*)" było informacją, że norma ma polski tytuł i treść w języku angielskim. Jeżeli odpowiedni Komitet Techniczny (KT) opracował polską wersję językową, będącą dokładnym tłumaczeniem EN, nowa norma wycofywała z zastąpieniem wersję wprowadzoną do zbioru PN metodą uznania [9]. Aktualna norma EN 15376:2014 jest czwartą edycją normy europejskiej na etanol paliwowy. Do chwili obecnej PKN opublikował pięć kolejnych wydań normy: cztery w wersji angielskiej i jedno w języku polskim.

Poniżej przedstawiono wykaz kolejnych wersji normy PN-EN 15376 wprowadzającej EN 15376.

Normy wycofane:

- PN-EN 15376:2008 – wersja angielska; wprowadza: EN 15376:2007
  wycofana i zastąpiona przez PN-EN 15376+A1:2009 – wersja angielska
- PN-EN 15376+A1:2009 – wersja angielska; wprowadza: EN 15376:2007+A1:2009
  wycofana i zastąpiona przez PN-EN 15376:2011 – wersja angielska
- PN-EN 15376:2011 – wersja angielska; wprowadza: EN 15376:2011
  wycofana i zastąpiona przez PN-EN 15376:2012 – wersja polska
- PN-EN 15376:2012 – wersja polska; wprowadza: EN 15376:2011
  wycofana i zastąpiona przez PN-EN 15376:2014-11 – wersja angielska

Norma aktualna:

- PN-EN 15376:2014-11 – wersja angielska, wprowadza: EN 15376:2014 [4]

Obecnie w Podkomitecie KT 222/PK 1 trwa procedura opracowania polskiej wersji normy PN-EN 15376:2014-11. Norma PN-EN 15376 w wersji polskiej ukaże się w połowie 2016 r. i będzie miała ten sam numer referencyjny co wersja angielska PN-EN 15376:2014-11. Norma ta nie zastąpi aktualnej normy w języku angielskim. Obie wersje będą miały ten sam numer referencyjny, mimo że nie ukazały się w tym samym czasie. Wynika to z przyjętych przez PKN zasad numeracji Polskich Norm. Numer Polskiej Normy jest stałym i niepowtarzalnym identyfikatorem tematu normalizacyjnego objętego normą i nie ulega zmianie w związku z nowelizacją normy: np. PN-EN 15376. Numer referencyjny Polskiej Normy jest identyfikatorem normy, związanym z datą jej publikacji: np. PN-EN 15376:2012. Od 2013 r. PKN wprowadził nowe zasady: numer referencyjny zawiera dodatkowo miesiąc publikacji normy, np. PN-EN 15376:2014-11 (listopad). Wszystkie wersje językowe PN mają ten sam numer referencyjny – niezależnie od różnych dat publikacji wersji językowych PN [9].

Normy ASTM i GB na etanol paliwowy

Aktualna norma ASTM na etanol paliwowy do benzyny zgodnej z ASTM D4814 *Standard Specification for Automotive Spark-Ignition Engine Fuel* dodawany w ilości 1–10% (*V*/*V*) to: ASTM D4806-15 *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel* [10]. Norma ASTM D4806-15 jest kolejną, dwudziestą szóstą wersją normy wydaną od 1999 r. W 2006 r. ukazały się cztery wydania tej normy [11].

Norma ASTM na biopaliwo *ethanol flex-fuel* o zawartości 51% do 83% (*V*/*V*) etanolu ASTM D-5798-14 *Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines* miała pierwsze wydanie w 1999 r., było ono walidowane w 2004 r. i zastąpione nową wersją w 2006 r. Aktualna norma z 2014 r. jest trzynastym wydaniem [11].

Normy GB (*Guobiao Standards*) to normy krajowej jednostki normalizacyjnej Chin – Standardization Administration of China (SAC). Chińska norma krajowa na etanol paliwowy GB 18350-2013 *Denatured fuel ethanol* miała poprzednie, pierwsze wydanie w 2001 r. Natomiast chińska norma krajowa na benzynę z dodatkiem etanolu GB 18351-2001 *Ethanol gasoline for motor vehicles* była w tym czasie nowelizowana pięciokrotnie. Zatwierdzona w maju 2015 r. norma na benzynę E10 to GB 18351-2015 *Vehicle ethanol gasoline (E10)*. Chińskie normy dostępne są w angielskiej wersji językowej; przykładowa cena aktualnej normy GB 18350-2013 *Denatured fuel ethanol* w zależności od wersji językowej to: chińska – 23 USD, angielska – 597 USD [12].

Paliwa etanolowe w CEN i PKN

Europejski Komitet Normalizacyjny (CEN) zrzesza 33 członków. Członkami CEN są krajowe jednostki normalizacyjne 28 państw Unii Europejskiej oraz Macedonii, Turcji, Islandii, Norwegii i Szwajcarii [13]. PKN jest członkiem CEN od 1 stycznia 2004 r. W wyniku tego wszystkie normy europejskie stają się zgodnie z procedurami CEN Normami Polskimi [5].

W CEN tematyka paliw płynnych, obejmująca również paliwa etanolowe, umiejscowiona jest w Komitecie Technicznym CEN/TC 19 *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, w szczególności w Grupie Roboczej (WG) CEN/TC 19/WG 21 *Specification for unleaded petrol* [13]. Polska jest reprezentowana w Grupie Roboczej (WG) CEN/TC 19/WG 21 przez dwóch ekspertów delegowanych, zgodnie z procedurami PKN, za pośrednictwem PKN/KT 222.

W PKN tematyka paliw płynnych umiejscowiona jest w Sektorze Chemii w KT 222/PK 1 ds. Paliw Płynnych. Sekretariaty Komitetu Technicznego PKN/KT 222 i Podkomitetu KT 222/PK 1 prowadzi Instytut Nafty i Gazu – Państwowy Instytut Badawczy.

Organ Techniczny PKN – KT 222/PK 1 jest wiodący w zakresie współpracy z odpowiednimi organami technicznymi CEN: Komitetem Technicznym CEN/TC 19 i Grupą Roboczą CEN/TC 19/WG 21. Przewodniczącym KT 222/PK 1 jest Martynika Pałuchowska, sekretarzem –Iwona Doening. Liczba członków Podkomitetu wynosi 18, a liczba delegowanych przez podmioty reprezentantów – 31. Każdy podmiot ma prawo delegować trzech reprezentantów, przy czym w zgłoszeniu określa, który z reprezentantów ma prawo głosu [4].

Tabela 3. Podmioty – członkowie KT 222/PK 1 ds. Paliw Płynnych [4]

BP EUROPA SE Spółka Europejska Oddział w Polsce	ONICO SA
Grupa LOTOS SA	Operator Logistyczny Paliw Płynnych Sp. z o.o.
Instytut Badań i Rozwoju Motoryzacji BOSMAL Sp. z o.o.	ORLEN GAZ Sp. z o.o.
Instytut Nafty i Gazu – Państwowy Instytut Badawczy	ORLEN Laboratorium Sp. z o.o.
Instytut Techniczny Wojsk Lotniczych	ORLEN Południe SA
Instytut Transportu Samochodowego	Polska Izba Paliw Płynnych
LOTOS Lab Sp. z o.o.	Polska Organizacja Przemysłu i Handlu Naftowego
LOTOS Paliwa Sp. z o.o.	Polski Koncern Naftowy ORLEN SA
OBR SA	Przemysłowy Instytut Motoryzacji
Uwaga: W pracach każdego Organu Technicznego uczestniczy z ramienia Polskiego Komitetu Normalizacyjnego Konsultant.	

Wszystkie metody badań etanolu powołane w rozporządzeniach zostały opracowane w wersji polskiej przez Podkomitet ds. Paliw Płynnych KT 222/PK 1.

Prace w CEN i w odpowiednich Organach Technicznych PKN obejmują również specyfikacje paliw o wyższej zawartości etanolu, takich jak E85 oraz paliwo E10+ (od 20% do 25% (*V*/*V*) etanolu).

Specyfikacja techniczna na paliwo etanolowe (E85) do pojazdów samochodowych CEN/TS 15293:2011

Aktualnym dokumentem CEN ujmującym wymagania na paliwo etanolowe (E85) jest specyfikacja techniczna CEN/TS 15293:2011 *Automotive fuels – Ethanol (E85) automotive* *fuel – Requirements and test methods*. Dokument ten zastępuje CEN/CWA 15293:2005 *Automotive fuels – Ethanol E85 – Requirements and test methods* [14]. Prace nad dokumentem CWA (*CEN Workshop Agreement*) rozpoczęto w CEN/TC 19 w 2003 r. w grupie warsztatowej (Workshop) powołanej specjalnie do spraw tego rodzaju paliwa silnikowego. Opracowany dokument CWA 15293 oparty został na normie amerykańskiej ASTM D5798-99 i szwedzkiej SPSE-424/2002-02-01 [15]. Dokument CWA ma inny status niż norma europejska – tak jak w przypadku specyfikacji technicznej CEN nie ma obowiązku wprowadzania go do zbioru norm państw członkowskich CEN. Tak jak specyfikacja techniczna nie może być sprzeczny z normą europejską.

Podkomitet ds. Paliw Płynnych KT 222/PK 1 opracował polską wersję specyfikacji technicznej CEN/TS 15293:2011 *Automotive fuels – Ethanol (E85) automotive fuel – Requirements and test methods* [16], którą jest PKN-CEN/TS 15293:2012 – wersja polska, *Paliwa do pojazdów samochodowych – Paliwo etanolowe (E85) do pojazdów samochodowych – Wymagania i metody badań* [17].

Zakres dokumentu: „W niniejszej Specyfikacji Technicznej określono wymagania i metody badań paliwa etanolowego (E85) do pojazdów samochodowych będącego przedmiotem obrotu. Niniejsza specyfikacja jest przeznaczona do paliwa etanolowego (E85) do pojazdów samochodowych stosowanego w silnikach samochodowych o zapłonie iskrowym zaprojektowanych do pracy na paliwie etanolowym (E85). Nominalnie paliwo etanolowe (E85) do pojazdów samochodowych jest mieszaniną 85% (*V/V*) etanolu spełniającego wymagania EN 15376 i benzyny silnikowej spełniającej wymagania EN 228, lecz zakłada się możliwość wytwarzania różnych »sezonowych rodzajów« paliwa etanolowego (E85) do pojazdów samochodowych zawierających więcej niż 50% (*V/V*) etanolu" [4]. Opracowany przez CEN raport techniczny CEN/TR 15993:2013 *Automotive fuels – Ethanol (E85) automotive fuel – Background to the parameters required and their respective limits and determination* dostarcza informacji o pracach związanych z powstaniem specyfikacji dla E85 [18].

Paliwo etanolowe E10+

Komitet Techniczny CEN/TC 19 w czerwcu 2013 r. przedstawił raport techniczny CEN/TR 16514:2013 *Automotive fuels – Unleaded petrol containing more than 3,7% (m/m) oxygen – Roadmap, test methods, and requirements for E10+ petrol* [19]. Dokument ten zawiera omówienie planowanych zadań w zakresie przygotowania wymagań i metod badań dla przyszłej benzyny o zawartości tlenu powyżej 3,7% (*m/m*), nazywanej benzyną E10+, przy czym będzie preferowana benzyna o zawartości od 20% do 25% (*V/V*) etanolu. Przewidywane właściwości benzyny E10+, takie jak większa zawartość tlenu i wyższe liczby oktanowe – w porównaniu do obecnych wymagań jakościowych dla benzyny o zawartości do 10% (*V/V*) etanolu – powinny zapewnić osiągnięcie dalszych ograniczeń emisji CO w przyszłych silnikach przeznaczonych do wykorzystania tego gatunku paliwa. Z powodu spodziewanych w przyszłości bardziej rygorystycznych wymagań dotyczących zanieczyszczeń emitowanych z silnika oraz w celu zapewnienia trwałości silnika i układu oczyszczania spalin – w przygotowywanej normie dla E10+ należy spodziewać się wprowadzenia nowych limitów w stosunku do chlorków nieorganicznych, fosforu, siarczanów i zawartości popiołu. Ponadto przed zdefiniowaniem ostatecznych wartości granicznych dla poszczególnych parametrów jakościowych benzyny E10+ należy zbadać wpływ zawartości tlenu powyżej 3,7% (*m/m*) na takie właściwości jak: liczby oktanowe, właściwości jezdne, ilość zanieczyszczeń i emisja CO_2. W raporcie technicznym CEN/TR 16514 zwrócono uwagę, że każdy limitowany parametr jakościowy benzyny E10+ wymaga zastosowania jednej lub więcej metod badawczych. Zakłada się, że obecnie wykorzystywane metody analityczne będą używane do badań jakości benzyny silnikowej lub wystąpi konieczność dostosowania ich do potrzeb benzyny E10+ [20].

Podsumowanie

Specyfikacje określające wymagania dla paliw i biokomponentów są istotnymi dokumentami dla całego środowiska związanego z produkcją i dystrybucją paliw, dla producentów silników, konsumentów, jak i dla zajmujących się paliwami od strony legislacyjnej. Normy, tak jak rozporządzenia, muszą uwzględniać wymagania zawarte w dyrektywach. Dostępne na rynku paliwo ma spełniać wymagania właściwych rozporządzeń i norm – ponieważ producenci silników samochodowych określają numerem normy rodzaj paliwa przeznaczonego do danego silnika. Norma ujmuje wszystkie wymagania, nie tylko te zawarte w dyrektywach wynikające z troski o środowisko, ale również te, które gwarantują prawidłową eksploatację silników, chroniąc interesy konsumenta – użytkownika samochodu.

Cel artykułu to przybliżenie tematyki prac normalizacyjnych w obszarze paliw etanolowych dla transportu. Działalność normalizacyjna związana z obszarem paliw płynnych, w tym paliw etanolowych dla transportu, prowadzona przez Podkomitet PKN/KT 222/PK 1 ds. Paliw Płynnych daje możliwość zainteresowanym podmiotom uczestniczenia w pracach normalizacyjnych już na najwcześniejszym etapie powstawania projektów norm w CEN, dostarcza informacji o planowanych zmianach dotyczących wymagań, jak i metod badań.

Zaangażowanie zainteresowanych środowisk – członków Podkomitetu pozwala na sprawną realizację zadań normalizacyjnych wynikających z członkostwa PKN w CEN.

Wykaz oznaczeń i akronimów występujących w tekście

ASTM	American Society for Testing and Materials (Amerykańskie Stowarzyszenie Badań i Materiałów)
CEN	Comité Européen de Normalisation (Europejski Komitet Normalizacyjny)
EN	symbol normy europejskiej
ICS	*International Classification for Standards* (Międzynarodowa Klasyfikacja Norm)
KT	Komitet Techniczny PKN
PK	Podkomitet Techniczny PKN
PKN	Polski Komitet Normalizacyjny
SAC	Standardization Administration of China (krajowa jednostka normalizacyjna Chin)
TC	*technical committee* (komitet techniczny CEN)
TS	*technical specification* (specyfikacja techniczna CEN)
WG	*work group* (grupa robocza w CEN)

Artykuł powstał na podstawie pracy INiG – PIB pt. Podstawy merytoryczne dostosowania norm polskich z zakresu ropy i gazu do wymagań UE – nr zlecenia: 82/TN/DN/11, nr archiwalny: DK-5100-55/14.

Literatura

[1] Rozporządzenie Ministra Gospodarki z dnia 14 maja 2015 r. zmieniające rozporządzenie w sprawie wymagań jakościowych dla biokomponentów, metod badań jakości biokomponentów oraz sposobu pobierania próbek biokomponentów.

[2] Rozporządzenie Ministra Gospodarki z dnia 17 grudnia 2010 r. w sprawie wymagań jakościowych dla biokomponentów, metod badań jakości biokomponentów oraz sposobu pobierania próbek biokomponentów.

[3] PN-EN 15376:2014-11 – wersja angielska, *Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań*.

[4] Polski Komitet Normalizacyjny, http://www.pkn.pl (dostęp: wrzesień 2015).

[5] CEN/CENELEC: *Przepisy wewnętrzne. Część 2: Wspólne reguły prac normalizacyjnych*. Styczeń 2012 r., PKN.

[6] Ustawa o normalizacji z dnia 12 września 2002 r.

[7] *Uwagi PKN do oświadczenia Pana Senatora Stanisława Gorczycy*. Pismo Prezesa PKN skierowane do Marszałka Senatu RP PR.080.50/2014, http://www.senat.gov.pl (dostęp: wrzesień 2015).

[8] PN-EN 15376:2008 *Paliwa do pojazdów samochodowych – Etanol jako komponent benzyny silnikowej – Wymagania i metody badań*.

[9] Błaszkiewicz Z.: *Zmiany w procedurach normalizacyjnych – numeracja Polskich Norm i czwarta wersja językowa Normy Europejskiej*. Nafta-Gaz 2014, nr 10, s. 728–733.

[10] ASTM D4814-14 *Standard Specification for Automotive Spark-Ignition Engine Fuel*.

[11] ASTM International, Amerykańskie Stowarzyszenie Badań i Materiałów, http://www.astm.org (dostęp: wrzesień 2015).

[12] *Chinese Standard (National Standard, Industry/Professional Standard)*, http://www.chinesestandard.net (dostęp: wrzesień 2015).

[13] CEN Europejski Komitet Normalizacyjny, http://www.cen.eu (dostęp: wrzesień 2015).

[14] CEN/CWA 15293:2005 *Automotive fuels – Ethanol E85 – Requirements and test methods*.

[15] Pałuchowska M., Danek B.: *Specyfikacje jakościowe bioetanolu i biopaliw do silników o zapłonie iskrowym*. Nafta-Gaz 2009, nr 2, s. 174–182.

[16] CEN/TS 15293:2011 *Automotive fuels – Ethanol (E85) automotive fuel – Requirements and test methods*.

[17] PKN-CEN/TS 15293:2012 – wersja polska, *Paliwa do pojazdów samochodowych – Paliwo etanolowe (E85) do pojazdów samochodowych – Wymagania i metody badań*.

[18] CEN/TR 15993:2013 *Automotive fuels – Ethanol (E85) automotive fuel – Background to the parameters required and their respective limits and determination.*
[19] CEN/TR 16514:2013 *Automotive fuels – Unleaded petrol containing more than 3,7% (m/m) oxygen – Roadmap, test methods, and requirements for E10+ petrol.*
[20] Danek B.: *Biopaliwo o zawartości 20÷25% (V/V) etanolu, wybrane właściwości fizykochemiczne*. Nafta-Gaz 2015, nr 4, s. 223–229.