

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

Michal Vojtisek-Lom and Vit Beranek
Czech Technical University

Jitka Stolcpartova
Institute of Experimental Medicine, AVCR

Martin Pechout
Technical University of Liberec

Vojtech Klir
Czech Technical University

ABSTRACT

N-butanol and isobutanol are alcohols that can be produced from biomass by fermentation and are possibly more compatible with existing engines than ethanol. This work reports on the effects of these two isomers on exhaust emissions of an unmodified direct injection spark ignition (DISI) engine. A Ford Focus car with a 1.0-liter Euro 6 Ecoboost DISI engine has been tested on a chassis dynamometer using WLTP and Artemis driving cycles, and on the road on a one-hour test loop containing urban, rural and motorway driving. Two isomers of butanol, 1-butanol and 2-methyl-propanol, were each blended with gasoline at 25% volume. Non-oxygenated gasoline and 15% ethanol in gasoline (E15) were used as reference fuels.

The vehicle performed well in terms of cold start, drivability, general performance, and off-cycle particle emissions, staying within several mg of particle mass and about 2×10^{12} particles (per PMP procedure) per km during laboratory tests. While E15 had little effect, both butanol blends have decreased PN emissions by about one half; effects on other pollutants were less consistent or not significant. Only roughly one half of particles was larger than 23 nm, and of these, only about half were non-volatile. Particle emissions during real driving were unevenly distributed, were not excessively different from the Artemis cycle, and were highest for gasoline, lower for E15, lower for 25% n-butanol, and lowest for 25% isobutanol, with most of the reductions taking place during high-power operation.

Overall, both n-butanol and isobutanol blends yielded a considerable reduction in particle number emissions relative to both gasoline and E15.

CITATION: 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.

INTRODUCTION

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. This paper reports on the effects of blends of n-butanol and isobutanol with gasoline on the emissions, primarily of particulate matter, from a production direct injection spark ignition (DISI) automobile engine.

Butanol, a four-carbon alcohol, is increasingly considered as an alternative, long-term fuel for spark ignition engines in addition to, or in lieu of, ethanol. Ethanol, produced from biomass, has been used both blended in low concentrations to gasoline for ordinary vehicles, and in high concentrations (E85) in flexible-fuel vehicles. Its drawbacks are miscibility with water and aggressivity towards materials.

There are four isomers of butanol: n-butanol (1-butanol); sec-butanol (2-butanol); isobutanol (2-methyl-1-propanol); and tertiary butanol (2-methyl-2-propanol). Of these, n-butanol and isobutanol can be produced from biomass [1, 2, 3, 4] and have been used in a few motor vehicle spark ignition engines [5, 6, 7, 8, 9, 10, 11, 12, 13]. Compared to

ethanol, both n-butanol and iso-butanol 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. Selected properties of gasoline, ethanol, n-butanol and isobutanol are listed in Table 1.

Operation of port fuel injection spark ignition engines on n-butanol has been reported to result in, relative to gasoline, worsened cold startability [14], worsened atomization of fuel [15-16], shorter duration of both early and main combustion stages [7, 8, 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 is no agreement among various studies as to the effects of nitrogen oxides (NO_x) emissions [9, 10, 11,13]. Isobutanol was reported to yield lower NO_x emissions than n-butanol [19]. Isobutanol exhibited 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 octane rating of the fuel [22].

In direct injection SI (DISI) engines, the usage of pure n-butanol was reported to be possibly problematic during engine cold start, because of worsened fuel atomization, impingement of the fuel on piston and cylinder liner and oil dilution [12]. At part load, both the combustion of n-butanol in a DISI engine and the resulting emissions were favorable, with an improvement of smoke opacity relative to gasoline [23,24]. The use of isobutanol-gasoline blends in different DISI engines has resulted in a reduction in emissions, notably decreased PM and particle number (PN) emissions for a spray-guided DISI engine [5,20].

Table 1. Selected properties of gasoline, ethanol, n-butanol and isobutanol (from [13], except for measured densities marked with (*)).

	Gasoline	N-butanol	Iso-butanol	Ethanol
Research octane number (RON)	95	94-96	113	110
Density [kg·m ⁻³] at 20 C (68 F)	~753*	~808*	~808*	790
Lower heating value [MJ·kg ⁻¹]	42.9	33.3	33.3	26.8
Volumetric lower heating value [MJ·dm ⁻³]	32.3	27.0	26.8	21.2
Latent heat of vaporization [kJ·kg ⁻¹]	380-500	716	579	904
Chemical formula	complex mixture	C ₄ H ₉ OH	C ₄ H ₉ OH	C ₂ H ₅ OH
Mass share of C [%]	86	65	65	52
Mass share of H [%]	14	13.5	13.5	13
Mass share of O [%]	0	21.5	21.5	35
Viscosity [mPa·s]	0.4-0.8	2.57	3.33	1.08
Boiling point [°C]	199 (FBP)	118	108	78
Stoichiometric air/fuel ratio [-]	14.7	11.2	11.2	9.0

It therefore appears that both n-butanol and isobutanol can be produced from biomass at a comparable cost [1] and both have a potential to reduce PM emissions, yet there are differences between these two isomers in terms of their production pathways, embedded fossil fuel energy which is lower for n-butanol [1], octane number which is higher for isobutanol [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] give reports on both isomers in port injection engines). There is generally less literature on the performance of butanol in DISI engines, and while n-butanol has been combusted in research DISI engines [23,24], most of the studies on production engines [5,11,20] are done with isobutanol and U.S. engines.

This study seeks to evaluate the effects of blends of both n-butanol and isobutanol with gasoline on exhaust emissions from a production DISI engine, so that both isomers can be compared between each other and with gasoline and ethanol-gasoline blend. E15 was chosen as it has been demonstrated as feasible at least for the U.S. market. Also, despite lower ethanol content in the gasoline throughout Europe, a wide variety of ethanol-gasoline blends prepared from a widely available commercial E85 and ordinary, low ethanol content gasoline are used in ordinary (non flexible fuel) automobiles throughout the Czech Republic [18,25,26]. For both isomers of butanol, a blend of 25% volume with gasoline was chosen as nominally matching the 5% by mass fuel oxygen content of E15.

As DISI engines exhibit, compared to port fuel injection spark ignition engines and diesel engines with a particle filter, relatively high emissions rates of particulate matter, and ultrafine particulate matter is probably the most detrimental pollutant emitted by internal combustion engines, particle emissions were the focus of this study. For this reason, multiple chassis dynamometer test cycles were chosen, along with a real driving emissions measurement.

EXPERIMENTAL

Vehicle and Fuels

A typical European small family car (C-segment production passenger car), 2013 Ford Focus station wagon, estate variant, with downsized three-cylinder 1.0 liter turbocharged gasoline direct injection EcoBoost engine (12-valve, 999 cm³ displacement, water cooled, air-to-air intercooler, bore × stroke 71,9 × 82 mm, compression ratio 10,0:1, rated power 92 kW @ 6000 rpm, rated torque 170 Nm @ 1400 - 4500 rpm 30s overboost @ 200Nm 1400-4500 rpm), 6-speed manual transmission, tire size 205/55 R16, 1242 kg curb weight, has been rented from a car rental agency and brought to a chassis dynamometer testing facility at the authors' laboratory. The vehicle was certified to Euro 6 standards, with rated fuel consumption of 5,8/4,2/4,8 l/100 km, rated CO₂ emissions 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.

Non-oxygenated gasoline with a nominal research octane number of 95, meeting ČSN EN228 specifications, has been obtained from a fueling station (EuroOil, Buštěhrad, Jirskéřská 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.

Laboratory Tests

The Worldwide harmonized Light vehicles Test Procedures (WLTP) Class 3 driving cycle, as defined by the United Nations Economic Commission for Europe (UNECE) Working Group 29 [27] and the Commom Artemis Driving Cycle, created to represent automobile driving patterns in Europe [28], were used as the base cycles. Speed points for these cycles were obtained from DieselNet [29].

The Artemis driving cycle comprises of the urban, rural and motorway section. Several versions of the motorway section, differing in maximum speed, are defined; unless otherwise noted, the version with a maximum speed of 130 km/h (81 mph) was run here.

The car has been subjected to several WLTP cycles on the fuel present from the tank to assess the overall emissions levels and to set up instrumentation and sampling system parameters. The fuel was then changed using the following procedure: The fuel was siphoned from the fuel tank to the maximum extent possible, the engine was operated until it has run out of fuel, and the tank was filled with test fuel. The car was then driven at various speeds and loads to allow for the Engine Control Unit (ECU) to adapt to the new fuel, after which a WLTP was run, and the car left overnight to equilibrate.

On each of the four fuels, the car has been subjected to the following test matrix:

- Cold WLTP
- Hot WLTP
- Four runs of Artemis urban, rural and motorway parts
- Two to three runs along the local test route

Additional cycles, including NEDC, USO6, and US EPA Highway Fuel Efficiency Test, have been run on either gasoline or E15 to further assess the effect of driving cycle on emissions.

For laboratory tests, the exhaust has been routed into a full-flow dilution tunnel with a constant volume sampler (CVS) operating at 10.8 m³/min.

The diluted exhaust was sampled with the following instrumentation for online measurements:

- a traditional suite of instruments (HC - heated flame ionization detector, CO and CO₂ - 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 cut-off point of 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 QM-A); 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 m³/h (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.

The results of the FTIR measurements, chemical analyses and toxicological assays, due to their complexity, will be reported at a later time.

On-Road Tests

Additionally, a 55-km local test route, including urban, suburban and motorway driving, was chosen for on-road testing. 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 speed in urban part is limited to 50 km/h, suburban to 90 km/h, motorway to 130 km/h. All runs were driven with the same driver in an attempt to compensate influence of different driving styles of different drivers.

Given the preliminary experience with the dynamometer performance of the vehicle, the regulated emissions (HC, CO, NO_x) as well as NO₂ were expected to be low. Therefore, a measurement of unregulated gaseous compounds by an FTIR spectrometer, and measurement of particulate matter were considered. For PM measurement, on-board EEPS was chosen as the most suitable instrument as the vehicle could not have been modified or disassembled in any way, the

installation of a heated sample line would have been difficult. Also, due to the space and equipment and battery mass constraints, simultaneous operation of FTIR and EEPS would have been difficult. Given the low levels of regulated gaseous pollutants observed during the dynamometer testing and the general concern about PM emissions from DISI engines, a decision was made to perform EEPS measurements only.

$$M [\text{ng}] = 7 \cdot 10^{-12} \cdot \text{particle diameter} [\text{nm}]^{2.37}$$

The concentrations were multiplied by the intake air flow reported by the EOBD to obtain emissions rates per second.

The PEMS data were used primarily to aid mass exhaust flow computations and synchronization of the data, as a cross-check for EOBD reported intake air flow, and, given the EEPS sensitivity to vibrations, to serve as a cross-check for quality control of the EEPS measurements.

RESULTS

Cycle Effects (Gasoline)

The assessment of the effect of the test cycle on emissions was carried on in full length on gasoline only, with the purpose to verify that the cycles selected are reasonably useful for comparison of different fuels.

The summary results for gaseous pollutants are shown in Fig. 2, and for particulate matter in Fig. 3. Four metrics are given for the PM emissions: particle mass emissions in mg/km as measured by gravimetric method, and three metrics of particle number (PN) emissions in trillions (10^{12}) of particles per km: PN measured according to PMP (Particle Measurement Program, non-volatile particles above 23 nm), PN from EEPS size distributions considering only channels 24 nm and higher, and PN from the entire EEPS size distribution.

It is apparent from the data that at least in terms of particulate matter, the vehicle was relatively very well behaved, with very little “off-cycle” emissions, which were essentially limited to several-fold increased NO_x in urban part of the Artemis cycle and in US06 cycle, an increase in CO during the US06 cycle, and a moderate PM mass increase during the US06 cycle. The increase of CO during US06 to 1.5 g/km is relatively harmless, as CO ceased to be an air pollution problem, and small non-road engines typically have an order of magnitude higher CO emissions (hundreds of grams per kg of fuel). The higher CO and higher PM mass, but much smaller increase in PN emissions, could be possibly caused by a slight overfueling, with volatile smaller particles and HC efficiently treated by the three-way catalyst.

The Examination of the second-by-second data (not shown in the paper) shows that short spikes associated with transients account for most of NO_x .

The PN emissions > 23 nm obtained from the EEPS size distribution were approximately double compared to the PMP-compliant measurement. Particles larger than 23 nm accounted for roughly half, and sometimes even less, of the total particles detected by the EEPS.

When comparing PMP to EEPS results, rather than assuming that all particles larger than 23 nm - and no particles smaller than 23 nm - are counted, realistic counting efficiencies of the PMP-compliant counter should be considered. The PMP used in this study used a TSI 3070 particle counter. For this purpose, the counting efficiencies were estimated in Table 2, based on published data [10,11] for diesel engines.

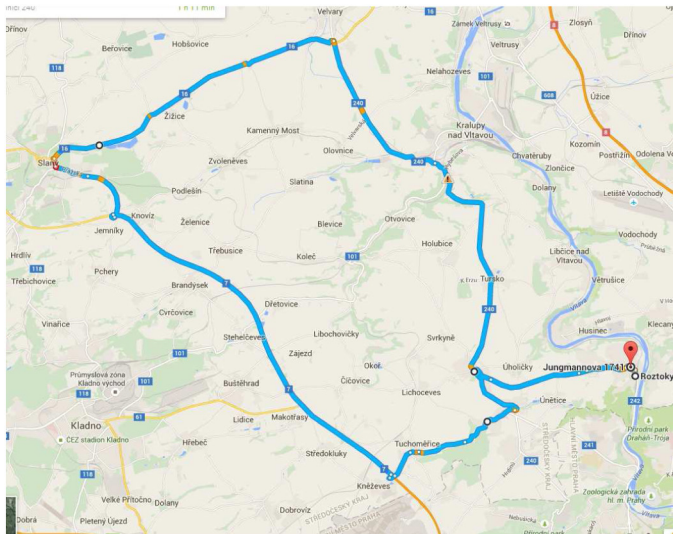


Figure 1. Map of test route.

A rotating disc microdiluter (MD-19, Matter Engineering) was located in the spare tire compartment, drawing exhaust from the tailpipe via a short (approx. 25 cm) insulated metal tubing into a dilution head heated to 150 C, providing a nominal dilution ratio of 90:1. Approximately 4.5 lpm of the diluted exhaust, along with approximately 4.5 lpm of HEPA-filtered ambient air, was then drawn, at a 180:1 total dilution ratio, by the EEPS located on the back seat.

Undiluted exhaust was also sampled by a miniature portable on-board monitoring system (PEMS) described earlier in [18,30] measuring HC, CO and CO_2 with NDIR analyzer, NO , NO_2 and O_2 with electrochemical cells, PM mass with a laser scattering device, and total PM length with a heated measuring ionization chamber. The PEMS also included a 5 Hz GPS for recording the actual position, altitude, and road speed. Engine operating data including road speed, engine rpm and intake air flow were recorded through the EOBD interface. Engine starts and free accelerations and abrupt accelerations and decelerations of the vehicle performed outside of the test route were used to synchronize the data from all instruments.

The EEPS was used as the authoritative source of PM emissions data. From the measured size distributions, total particle number concentration (5-560 nm), total number concentrations of particles greater than 23 nm (24-560 nm), and particle mass concentration were calculated. Two approaches were used for determining the particle mass concentrations: In one, a particle effective density of 0.8 g/cm³, a value based on review of published mass-mobility relationships [31,32,33,34], was chosen. In the second approach, the particle mass M as a function of its diameter was estimated using the following formula, chosen as the best fit based on [31-32]: