

Experimental Characterization of Diesel Combustion Using Glycerol Derived Ethers Mixtures

Gabriele Di Blasio
Istituto Motori CNR

Giuseppe Bonura and Francesco Frusteri
ITAE-CNR

Carlo Beatrice
Istituto Motori-CNR

Catia Cannilla
ITAE-CNR

Mauro Viscardi
Istituto Motori-CNR

ABSTRACT

In this paper the characteristics of a mixture of glycerol-based ethers usable in a compression ignition engine are investigated, in terms of efficiency and emissions. Alternative pathways for the energetic exploitation of biodiesel derived glycerol became of increasing interest as the biodiesel production was increased worldwide. Because of its detrimental physical and chemical properties, raw glycerol is hardly usable in conventional internal combustion engines (ICE). However, etherification of glycerol with *tert*-butyl alcohol and isobutylene allows obtaining a mixture mainly composed of higher glycerol ethers (GEM) suitable for compression ignition engines. Thus, the aim of this research study was to test a mixture of mono-, di- and tri-*tert*-butyl ethers of glycerol in blend with a commercial diesel fuel in a compression ignition engine, evaluating the fuel efficiency and the impact on the pollutant emissions.

The tests were performed on a single cylinder research engine derived from a Euro5 compliant four cylinder engine. The test methodology considers the comparison among three fuel blends: 1) a mixture consisting of 90% v/v diesel and 10% v/v of GEM; 2) a blend consisting of 80% v/v diesel and 20% v/v of GEM; 3) a reference diesel. The tests were carried out in five characteristic key points of the NEDC emission homologation cycle (New European Driving Cycle). These points allow estimation of the blends impact on the performance of a real four-cylinder engine (one cylinder of which is represented by the research engine) over the NEDC.

The results have shown the possibility to burn the diesel/GEM blends without significant impact on combustion characteristics and efficiencies while, due to the oxygen content of the GEM, important benefits are obtained in terms of NO_x-PM trade-offs and emission particles at the exhaust. At medium-high load conditions there is a maximum decrease of about 70% in terms of PM emissions compared to a slight increase of NO_x. At low load conditions, a maximum increase of HC and CO of about 50% has been detected.

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INTRODUCTION

In recent years, the interest in new sustainable energy resources is increasing worldwide, especially in the transportation sector where the market is mainly governed by petroleum derivative fuels. The interest originates from the future emission regulations, which will significantly limit the emissions of internal combustion engines, along with the global warming issues related to the greenhouse gases (GHG) and the need to reduce the dependency of the fossil fuels since the fuel demand has significantly increased worldwide. For these reasons, the European Union (EU) has imposed directives and legislations aiming at replacing 10% of transport fossil fuels with biofuels by 2020 [1] looking forward to large-scale production of second generation biofuels [2].

Biofuels can play an important role in addressing both the GHG emissions of transport and the dependency on mineral oil, although most of the reductions in emissions will be delivered by improved efficiency and electrification. Different global energy scenario studies indicate that in this century biomass may contribute much more: up to 40-60% of total energy demand by 2050 of which transportations represent about the 30% [3][4].

For this reason, the research for new biofuels has been becoming one of the major topics investigated by the scientific community.

The production of biodiesel is mainly supported in the EU [5] while in the US similar targets are in place [4]. Biodiesel is produced from triglycerides derived mainly from vegetable oils or animal fats. Recently, new biofuel production methods have been investigated such as oil produced from algae and oleaginous yeasts indicating new sources which, contrary to energy crops, do not conflict with the cultivation of land for food [5].

As a result of the increasing biofuel production, also the production of glycerol, which is the main by-product of the transesterification process, will grow proportionally.

So, the question arises from a cost-effective and efficient use of such a glycerol surplus. The combustion of glycerol "as it is" would represent a desirable solution. Unfortunately, because of its detrimental physical and chemical properties (e.g., high viscosity, low LHV, low autoignition quality) raw glycerol is hardly usable in conventional energy production plants, such as fuel burners or ICEs [6][7]. However, a proper design of the burner and refractory combustion chamber could allow to effectively burn crude glycerol, although a high particulate matter concentration is detected at the exhaust [8].

Alternative routes for glycerol recovery are represented by its energetic upgrading into high value products, such as synthesis of gases [9] and oxygenate additives for gasoline, biodiesel and diesel fuels [10].

In this respect, the present research aimed at defining and validating an etherification process of raw glycerol for the production of an oxy-fuel that can be blended with diesel and

biodiesel. An industrially relevant route for the conversion of glycerol into oxygenated chemicals involves the etherification with isobutylene (IB) or tert-butyl alcohol (TBA) to tert-butyl ethers [11,12,13,14,[15]. These oxygenated compounds, when blended with diesel or biodiesel fuels, improve engine performance leading to a reduction in particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes emission [15]. Specifically, higher ethers of glycerol possess suitable combustion properties, which improve the low temperature properties of diesel fuel (pour point and cold filter plugging point) and reduce the viscosity of biodiesel fuel. However, since mono-tert-butyl ethers of glycerol (1-MBG; 2-MBG) have a low solubility in diesel fuel, the etherification of glycerol, taking place with a consecutive reaction path, should be mainly addressed towards the formation of a mixture of di-tert-butyl ethers (1,3-DBG; 1,2-DBG) and/or tri-tert-butyl ether (TBG) (see Figure 1) [11,12,13,14,[15].

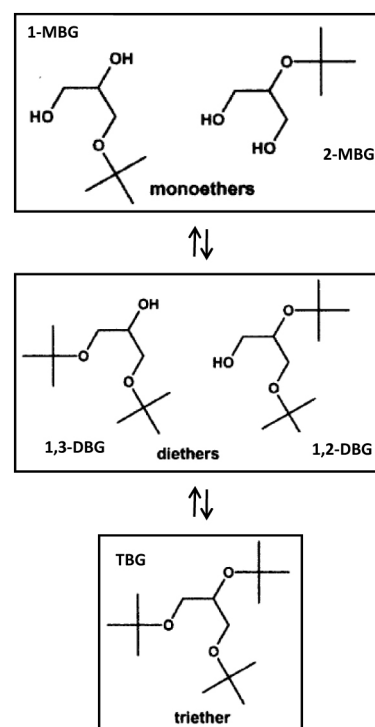


Figure 1. Molecular structure of glycerol tert-butyl ethers.

The project aims at a complete evaluation of the production process (in laboratory scale), as well as the validation of the GEM as fuel in experimental engine tests, with two main advantages: (i) the increase of the energy and CO₂ Well-To-Wheel (WTW) factor of the biodiesel supply chain; (ii) the addition of a high-quality oxy-fuel in the mineral fuels which contributes to the reduction of pollutant emissions from diesel engines.

Two mixtures of diesel-GEM at different volume ratio were tested, in order to assess their applicability within the CI

ICE. This research study aims to give a complete overview of the fuel-engine interaction.

Actually, this study involves many aspects such as effects on lubricity, corrosivity, elastomer deterioration, stability in the whole fuel line, impact on the injector nozzle etc. Of course, the characterization of all of these is a long-term work and requires proper fuel availability. In this framework, since GEM was produced in a lab-scale plant, its availability was very limited. Therefore, the study of fuel-engine interaction was limited to a detailed characterization of the impact of the alternative fuel on the combustion process as well as on the engine efficiency and pollutant emissions. When more fuel will be available, further investigations will involve also the above mentioned aspects.

EXPERIMENTAL SET UP AND METHODS

Catalytic System and GEM Production Process

Catalytic Systems for the Conversion of Glycerol into Diesel Fuel Components

A Hyflon®-SiO₂ catalyst (20 wt.%) was prepared by conventional incipient wetness method using an alcoholic solution of Hyflon® Ion S4X perfluorosulphonic ionomer (Solvay Solexis) as acid precursor. As carrier, a spherical silica (PQ Corporation), characterized by surface area of 300, was used. After impregnation, the catalyst was dried in air at 393 K for 12 h. The catalyst was characterized by different techniques in order to determine textural and morphological properties, thermal stability, loading of active phase and acid capacity, as elsewhere reported [15].

Plant and Catalytic Process

The etherification reaction was carried out at 343 K and autogenous pressure in liquid phase in a lab-scale stainless steel “jacketed-batch” reactor of 300 cm³, under a stirring frequency of 1200 min⁻¹ in order to limit the influence of external mass transfer phenomena.

Experiments were performed by operating at different *tert*-butyl alcohol/glycerol (R_{TBA/Gly}) or isobutylene/glycerol (R_{IB/GLY}) molar ratio (2.5-5.0) and by employing a catalyst amount of 0.3-7.5 wt.% referred to the glycerol weight (R_{cat/GLY}) at variable reaction time (6-17 h).

A well-defined amount of glycerol and dry catalyst were loaded into the reactor and, before the addition of TBA or IB, the reaction environment was flushed with nitrogen to remove air. A known amount of *tert*-butyl alcohol or liquid isobutylene, previously fed into a graduated tank, was injected into the reactor under 5 bar of nitrogen pressure. At the end of the run, the reactor was cooled down by an ice-bath, thus allowing all the gas phase compounds to be condensed.

Engine

The experimental activities were carried out on a prototype single cylinder (SC) research diesel engine which has a modern combustion system design derived from a Euro5 compliant four cylinders engine, which represents the state of the art of the automotive technology. The cylinder head is derived from production series, but it has been modified to work in single-cylinder mode. Differently from a real engine, the auxiliary systems (for boost, cooling, lubrication, etc.) are not directly coupled to the engine in order to allow for a maximum flexibility of their parameters without influencing the load conditions. A fully programmable ECU allows the operator to modify the fueling strategy, swirl ratio, EGR level, boost and backpressure values. This approach offers flexibility pertaining to operating conditions, without forfeiting state-of-the-art technology.

The fuel consumption is measured by mass flow meters AVL 733. The engine layout is laid out in [Figure 2](#), while in [Table 1](#) the engine properties are described.

Table 1. Engine characteristics

Displaced volume	475 cc
Stroke	90 mm
Bore	82 mm
Compression ratio	16.5:1
Number of Valves	4
Diesel Injection System	Common rail

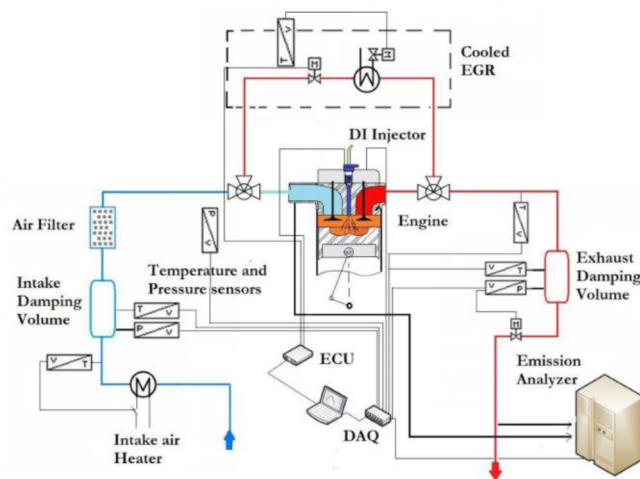


Figure 2. Research engine experimental layout

The pressure traces were recorded by a Kistler piezo quartz transducer fitted inside the combustion chamber. The net heat release rate (HRR) was calculated in real-time by the AVL IndiMicro indicating system. The filter smoke number (FSN) was measured by an AVL 415S smoke-meter and cross checked with the AVL Microsoot Sensor, when the values of smoke were at the limit of the sensitivity of the smoke meter. The gaseous emissions were recorded with an

ABB, Rosemount, Ecophysics and Hartmann&Braun device for UHC, CO, NO_x and CO₂-O₂ respectively.

Testing Methodology and Fuel Characteristics

The test procedure was chosen in order to provide additional experimental information when using GEM in blend with commercial diesel evaluating its impact/potential as fuel component. Differently from the preliminary engine tests made by the authors in previous experimental campaigns [6][7], the objective of this study is to make the results more valuable for practical application in the field of LD engines.

The operating points chosen for this research study are listed in Table 2. They were performed, using the Euro5 engine parameter calibration (injection, boost, swirl, EGR, etc.) derived from the real four-cylinder engine of equal unit displacement, at different engine speed and loads.

Table 2. Test points

Test point	RPM	IMEP [bar]	BMEP* [bar]	EGR [%]
1500x2	1500	3.3	2	40.5
2000x2	2000	4	2	39
2000x5	2000	7	5	33
2000x10	2000	12	10	21
2500x8	2500	10.4	8	25

BMEP of the real four-cylinder engine of equal unit displacement*

The points at 2 bar of Brake Mean Effective Pressure (BMEP) are representative of the low load operating conditions; the load point at 5 bar of BMEP, is identified as a critical operating point for soot and NO_x emission control; at medium load (8 and 10 bar of BMEP), the performance differences in terms of thermal efficiency, noise and impact on engine functionality are more noticeable.

The performed test points are widely used to evaluate the engine performance during the NEDC, even if they work in stationary operating condition. In confirmation of that, Figure 3 shows the position of the selected points in the speed-load plot of a vehicle with 1400 kg of inertial mass, equipped with the corresponding four-cylinder engine over the UDC+EUDC (Urban Driving Cycle + Extra Urban Driving Cycle), namely NEDC cycle.

Since previous studies [6][7] were concentrated predominantly at evaluating the fuel impact on the combustion behavior (single injection strategy, etc.), this research activity was aimed at investigating the engine-fuel interaction in conventional engine operating conditions, by using conventional engine calibration parameter settings (e.g. pilot plus main injection, etc.).

In the same test points, an additional analysis was executed adopting the same engine calibration but without using EGR. This has permitted evaluation of the GEM impact on the combustion characteristics (e.g. autoignition quality) more simply. Testing with and without EGR allow for a less convoluted interpretation of the results.

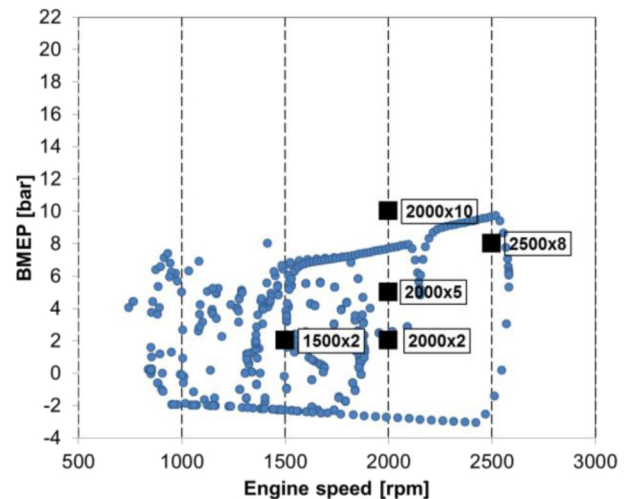


Figure 3. Position of the performed stationary operating points in the speed-load plot of a vehicle with 1400 kg of inertial mass, equipped with the multi-cylinder engine over the UDC+EUDC (NEDC) cycle

Moreover, during the tests, practical constraints such as maximum pressure rise rate (PRR) and IMEP coefficient of variation (COV-IMEP) were considered. The value for pressure rise was limited at about 7 bar/deg (80 bar/ms), according to the current comfort standards. The maximum admissible COV was limited to 3%. Before every measurement, about 2-3 minutes was necessary to stabilize the engine. The tests were repeated three times in each operating point in order to decouple the test-to-test measurement deviations from the fuel effects.

The GEM impact on engine combustion characteristics was evaluated by testing the following fuels:

- reference EN590 European commercial diesel;
- blend of 10% v/v of GEM in diesel (GEM10);
- blend of 20% v/v of GEM in diesel (GEM20).

The main physical and chemical characteristics of the pure GEM and the blends are listed in Table 3.

The choice of the GEM10 was driven by avoiding significant alterations of the fuel blend characteristics during the experiments ensuring engine reliability. Moreover, since biodiesel-derived raw glycerol is about 10 wt.% of the primary oil, GEM10 could represent a possible blending target, in the hypothesis that all the raw glycerol is converted into GEM.

The GEM20 was prepared with the objective to evaluate the impact on the engine combustion characteristics of blends with higher GEM ratios. This is useful to carry out trends on combustion and emission characteristics as a function of the GEM fraction in the blend.