Applied Energy 132 (2014) 236–247

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Mixture of glycerol ethers as diesel bio-derivable oxy-fuel: Impact on combustion and emissions of an automotive engine combustion system

Carlo Beatrice [a,*], Gabriele Di Blasio [a], Chiara Guido [a], Catia Cannilla [b], Giuseppe Bonura [b], Francesco Frusteri [b]

[a] CNR-IM, Istituto Motori, Via G. Marconi 4, 80125 Napoli, Italy
[b] CNR-ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126 Messina, Italy

HIGHLIGHTS

- Biofuels production from catalytic conversion of biodiesel derived glycerol.
- Impact of glycerol-derived ethers on regulated and unregulated pollutant emissions from automotive diesel engines.
- Effects of glycerol-derived ethers on size and number of the emitted particles from a diesel engine.
- Effect of glycerol-derived ethers on diesel combustion process and engine efficiency.

ARTICLE INFO

Article history:
Received 26 March 2014
Received in revised form 3 June 2014
Accepted 4 July 2014

Keywords:
Glycerol derived biofuel
Diesel engines
Diesel emissions
Particle size distribution
Aldehydes emissions
Fuel catalyst

ABSTRACT

The effects on combustion and emissions of a bio-derivable glycerol-based ethers mixture (GEM) usable in a compression ignition engine have been investigated. The tests were performed on a single cylinder research engine derived from a Euro5 compliant four cylinder engine for passenger car application. The experimental methodology has considered the comparison among three fuels: (1) a reference diesel; (2) a mixture consisting of 90 vol.% diesel and 10 vol.% of GEM; (3) a blend consisting of 80 vol.% diesel and 20 vol.% of GEM. The tests were carried out in some characteristic key points of the New European Driving Cycle (NEDC) emission homologation cycle. These points allowed an estimation of the blend impact on the performance of a real four-cylinder engine (one cylinder of which is represented by the research engine) over the NEDC. Both regulated and unregulated pollutant emissions have been measured during the test campaign. In particular, apart from the regulated emissions, the concentration of aldehydes and carbonaceous particles at the engine exhaust has been determined in some test points. The results have shown the possibility to burn the diesel/GEM blends without any significant impact on combustion characteristics and efficiencies, while, due to the oxygen content of the GEM, important benefits were obtained in terms of NOx-PM trade-off and emissions of particles at the exhaust. At medium–high load conditions, there was a maximum decrease of about 70% in terms of PM emissions compared to a slight increase of NOx. At low load conditions, a maximum increase of HC and CO of about 50% has been detected. Regarding the emissions of aldehydes, the results showed that the GEM addition favoured the increasing of carbonyl compounds at low engine loads, while at higher loads no significant variation has been detected by burning GEM.

1. Introduction

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 greenhouse gases (GHG) and the need to reduce the dependency on fossil fuels since the fuel demand has significantly increased worldwide [1].

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

* Corresponding author. Tel.: +39 081 7177 186.
E-mail address: c.beatrice@im.cnr.it (C. Beatrice).

http://dx.doi.org/10.1016/j.apenergy.2014.07.006
0306-2619/

Abbreviations

ATDC	After top dead center
B40	40 vol.% Biodiesel in blend with diesel
BMEP	Brake mean effective pressure
BTDC	Before top dead center
CAD	Crank angle degree
CN	Cetane number
CO	Carbon monoxide
CO_2	Carbon dioxide
COV-IMEP	Coefficient of variation for the IMEP
ECU	Engine control unit
EGR	Exhaust gas recirculation
GEM	Glycerol-derived ethers mixture
GHG	Greenhouse gases
HCs	Hydrocarbon emissions
HR	Heat release
HRR	Heat release rate
ICE	Internal combustion engine
IMEP	Indicated mean effective pressure
ISFC	Indicated specific fuel consumption
LHV	Lower heating value
MBF10,50	Mass burned fraction 10%, 50%
NEDC	New european driving cycle
NOx	Nitric oxides emissions
PM	Particulate matter
PRR	Pressure rise rate
PSDF	Particle size distribution function
SC	Single cylinder
SOI	Start of the main injection

contribute much more: up to 40–60% of total energy demand by 2050 of which transportations represent about the 30% [2].

In this framework, biodiesel represents one of the main products of the biofuel chain. It is mainly supported in the European Union (EU), while in the US similar targets are in place [3]. Recently, new biodiesel feedstocks have been considered, such as algae and oleaginous yeasts, indicating new sources which, contrary to energy crops, do not conflict with the cultivation of land for food [3,4]. As a result of increasing biodiesel production, also the production of glycerol, as main by-product of the transesterification process, will grow proportionally. Indeed, about 10 wt.% of the original oil is transformed into raw glycerol during the transesterification process.

So, the question arises from a cost-effective and efficient use of such a glycerol surplus, also considering the amount recycled in pharmaceutical industry. 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, poor lower heating value, low autoignition quality), raw glycerol is hardly usable in conventional energy production plants, such as fuel burners or internal combustion engines (ICEs) [5].

Especially for ICEs applications, alternative routes for glycerol recovery are represented by its energetic upgrading into high value products, such as syngas or oxygenated additives for gasoline and (bio-)diesel fuels. In the last years, such glycerol recovery routes have found more and more interest in fuel and engine research [6–8], especially for two main reasons: (i) the increase of the energy and CO_2 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.

In particular, the catalytic etherification of glycerol appears as an attractive solution to produce high-quality additives for diesel fuels [6–14]. However, only few studies dealing with the impact of glycerol ethers on engine performance are available in literature [6,7,15,16]. Yet, a comprehensive analysis of the impact of such oxy-fuels on engine performance, also including regulated and unregulated emissions, is not present in the scientific literature.

In this respect, the present research was aimed at the engine validation in terms of combustion characteristics and exhaust pollutant emissions of a blend fuel containing glycerol ethers. The attention was paid not only to the evaluation of the engine raw regulated emissions when glycerol-derived additives are employed, but also to the evaluation of the carbonyl compound concentration at the engine exhaust, along with the effects on the sizing and number of the carbonaceous particles.

Starting from the previous works dealing with the development of a production process of a glycerol ethers mixture (GEM) and a very preliminary characterization of its impact on engine performance as well [6,7], the present study extends the experimental analysis in terms of engine operating conditions and charcterization of pollutant emissions. In particular, several engine test points, representative of the engine operating conditions in the "New European Driving Cycle" (NEDC), were considered for the experiments and the impact of GEM on some unregulated emissions, like the concentration of aldehydes or the number of carbonaceous particles at the engine exhaust, was also investigated.

Actually, the research involves many aspects dealing with the effects of the fuel on lubricity, corrosivity, elastomer deterioration and stability in the whole fuel line, as well as the impact on the injector nozzle. Of course, such determinations require enough fuel availability. In this framework, being GEM produced in a lab-scale plant, the study of the fuel-engine "interaction" was primarily addressed to the impact of the diesel-GEM blends on combustion and emissions.

Therefore, after a brief description of the methodology used for the GEM production (see also [10]), the paper analyzes in detail the effects of the GEM addition to a commercial premium diesel fuel (in compliance with the EN590 regulation) on combustion and emissions of a single cylinder diesel engine in several test points. Two diesel-GEM blends at different volume ratio were tested. The results indicate no significant penalties on exhaust gaseous emissions, with remarkable effect on the reduction of both the particulate matter and particles number..

2. Materials and methods

Higher ethers of glycerol possess suitable combustion properties, which improve the low temperature properties of diesel fuel (pour point and cold filter plugging point), also reducing the viscosity of biodiesel fuel. Then, 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, must be mainly addressed towards the formation of a mixture of di-*tert*-butyl ethers (1,3-DBG; 1,2-DBG) and tri-*tert*-butyl ether (TBG) (see Fig. 1) [10,14].

2.1. Catalytic system and GEM production process

2.1.1. Solid acid catalyst for the conversion of glycerol into bio-additives for diesel fuel

A Hyflon®-SiO_2 catalyst (20 wt.%) was prepared by conventional incipient wetness method using an alcoholic solution of Hyflon®