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Abstract

In spite of its relevance, the prospective energetic valorization of crude glycerol (CG), a major by-product of biodiesel production, remains nowadays unfulfilled in the industry because of the significant challenges posed by its combustion properties. Besides some basic post-treatments such as desalting (to obtain desalinated crude glycerol, DG), its blending with other industrial by-products could improve crude glycerol properties, while maintaining the renewable nature of the fuel. A secondary product obtained from the FAGE process, consisting in a mixture of acetals named GF*, has been proposed in this work as a suitable fuel for this purpose. The combustion characteristics of these by-products have been tested along with different CG-GF* and DG-GF* blends by employing single droplet combustion experiments and semi-industrial furnace tests. Single droplet results point to widely different behaviors between GF* and the glycerols, the latter displaying much lower burning rates and violent microexplosions ascribed to salt content as well as to the broad differences in their constituent's boiling points. Relevant differences were noted between DG and CG modes of microexplosion, presumably due to the lower salt content of the former. Both CG-GF* and DG-GF* mixtures presented similar behaviors to CG, although with a noticeably faster conversion. The furnace tests revealed that GF* addition widened the range of stable conditions in the burner, significantly improving flame stability and reducing CO emissions. NOx emissions slightly increased, although they could be reduced through burner aerodynamics optimization, facilitated by the improvement in flame stability. The reported results support the potential use of GF* as auxiliary fuel for enhancing the combustion behaviors of crude glycerol.

Keywords	Crude Glycerol; Acetals; Semi-industrial Furnace; Droplet Combustion; Microexplosion.
Taxonomy	Combustion, Multiphase Flow, Fluid Mechanics
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62 **Abstract**
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65 major by-product of biodiesel production, remains nowadays unfulfilled in the industry
66 because of the significant challenges posed by its combustion properties. Besides some
67 basic post-treatments such as desalting (to obtain desalted crude glycerol, DG), its
68 blending with other industrial by-products could improve crude glycerol properties,
69 while maintaining the renewable nature of the fuel. A secondary product obtained from
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71 this work as a suitable fuel for this purpose. The combustion characteristics of these by-
72 products have been tested along with different CG-GF* and DG-GF* blends by
73 employing single droplet combustion experiments and semi-industrial furnace tests.
74 Single droplet results point to widely different behaviors between GF* and the
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76 ascribed to salt content as well as to the broad differences in their constituent's boiling
77 points. Relevant differences were noted between DG and CG modes of microexplosion,
78 presumably due to the lower salt content of the former. Both CG-GF* and DG-GF*
79 mixtures presented similar behaviors to CG, although with a noticeably faster
80 conversion. The furnace tests revealed that GF* addition widened the range of stable
81 conditions in the burner, significantly improving flame stability and reducing CO
82 emissions. NOx emissions slightly increased, although they could be reduced through
83 burner aerodynamics optimization, facilitated by the improvement in flame stability.
84 The reported results support the potential use of GF* as auxiliary fuel for enhancing the
85 combustion behaviors of crude glycerol.
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Keywords

Crude Glycerol, Acetals, Semi-industrial Furnace, Droplet Combustion, Microexplosion

Abbreviations

CG - Crude glycerol

DG - Desalted crude glycerol

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121 FAGE - Fatty acid glycerol formal esters
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123 FAME - Fatty acid methyl esters
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125 GF - Glycerol formal
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127 GF* - Mixture of acetals of industrial relevance
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129 NGOM - Non-glycerol organic matter
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131 PG - Pure glycerol
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133 **1. Introduction**

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135 The extensive manufacture of biodiesel during the last decades has indirectly increased
136 the production of glycerol, a by-product of the transesterification process, where
137 vegetable oils or animal fats react with short-chained alcohols. The obtained glycerol
138 stream, usually denominated crude glycerol, is far from being chemically pure, typically
139 consisting of a mixture of glycerol, water, alcohol, soap, FAMEs and alkaline catalyst
140 residues [1, 2]. These impurities severely hinder its use in high added value processes,
141 being crude glycerol (CG) of very little economic value nowadays [1, 2]. In view of the
142 large surplus of this by-product, and as viable high-end alternatives are very limited
143 with the current refining technologies and market position, its energetic valorization in
144 industrial boilers has been proposed as a feasible solution to the large amounts of CG
145 produced in biodiesel plants.

146
147 In principle, the characteristics of CG are compatible with its potential use as fuel in
148 industrial power plants, either completely replacing or co-fired with fossil fuels. Some
149 works in the literature reported favorable results in terms of the co-combustion of
150 glycerol with other fuels (e.g., biomass [1]). Most of those studies analyzed the effect of
151 using glycerol (or other bioliquids) as fuels in small-scale test facilities on the
152 combustion characteristics (specially emitted pollutants) with respect to those obtained
153 from burning traditional fuels (e.g., [3-8]). However, there are still relatively few studies
154 on the use of crude bioliquids in commercial heat/power generation plants [9] due to the
155 modifications required for existing systems [10]. In the case of CG, there are significant
156 differences between its physicochemical properties and those of conventional fossil
157 fuels, namely: low calorific value, high water content, high autoignition temperature,
158 production of toxic acrolein gases, high viscosity at room temperature and high mineral
159 content. These properties significantly hinder the use of CG in combustion-related

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180 applications [3, 4] or may involve significant modifications in existing burners [8, 11].
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182 In particular, the lower calorific value of CG (~16 MJ/kg) compared to that of fossil
183 fuels (e.g. 44 and 46 MJ/kg for diesel and propane, respectively), forces to consume a
184 significant amount of an auxiliary fuel, typically natural gas or propane, to ensure a
185 good quality combustion with stable flame.
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188 An alternative option to overcome the challenges posed by burning neat CG is to blend
189 it with other liquid by-products which can improve its combustion behavior. In doing
190 so, the obtained fuel would be entirely considered as waste-derived, as opposed to its
191 prospective blending with conventional petro-fuels such as diesel. A novel process,
192 described in [12, 13], has been developed to produce Fatty Acid Glycerol formal Esters
193 (FAGE), a fuel of similar characteristics to that of the widespread FAME. This process
194 is reported to yield a by-product consisting in a mixture of acetals, being glycerol
195 formal (GF) the predominant one. This by-product stream is reported to display much
196 more suitable physicochemical properties for its combustion when compared with CG
197 [13], and therefore their potential blending could significantly improve the prospects of
198 a successful valorization of the crude glycerol surplus, while also consuming the
199 aforementioned FAGE by-products. In addition, as detailed in [12, 13], the FAGE
200 manufacture process uses glycerol as feedstock, even further increasing therefore its
201 consumption.
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204 In this work, the combustion characteristics of crude glycerol (as received from a
205 biodiesel plant and also desalted), an acetal mixture (GF*) and their blends were
206 experimentally studied at two different scales. Their combustion properties were
207 obtained under well controlled conditions in single droplet experiments, whereas their
208 behaviors under realistic conditions were assessed from tests in a semi-industrial
209 furnace. The objective was to characterize the behavior of those fuels and to determine
210 the potential benefits of blending crude glycerol, which has been reported to display
211 significant difficulties for its appropriate stand-alone combustion, with GF*.
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243 2. Experimental method
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250 2.1 Fuels investigated
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254 A crude glycerol sample (CG) provided by Meruria Biofuels as a by-product of their
255 biodiesel manufacture was, after a proper homogenization and filtration process,
256 physicochemically characterized prior to its combustion tests. The main results of this
257 characterization are outlined in Table 1.
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260 Table 1. Main chemical components and properties of
261 the crude glycerol (CG) studied.
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264 Parameter	265 Value
266 Glycerol (% m/m)	267 81.4
268 Water (% m/m)	269 2.8
270 Methanol (% m/m)	271 0.1
272 NGOM ^a (% m/m)	273 7.5
274 Sulfur (% m/m)	275 1.1
276 HHV (MJ/kg)	277 12.7-15.8 ^b
278 Density, 30°C (kg/m ³)	279 1290
280 Viscosity, 80 °C (cP)	281 67

282 ^a Non-Glycerol Organic Matter
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285 ^b The Higher Heating Value was determined four times,
286 with a significant data dispersion (standard deviation of
287 1.63 MJ/kg). Thus, the upper and lower values, rather
288 than their average, are displayed.
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290 As introduced before, this work aims to explore the possibility of improving the CG
291 combustion characteristics by blending it with a FAGE by-product, consisting in a
292 series of acetal compounds denoted GF and GFOMOM. For the interested reader,
293 information regarding the FAGE, GF and GFOMOM production and characteristics can
294 be found in [12, 13]. A mixture of both by-products was supplied by Inkemia IUCT, in
295 a proportion of industrial relevance for the FAGE production process. This blend was
296 named GF*, and its behavior will be explored along with that of different CG-GF*
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298 mixtures, both in single droplet combustion tests and in the furnace. Three CG-GF*
299 blends were prepared for the droplet experiments, with 7, 15 and 30 vol. % of GF*. In
300 addition, neat glycerol (Panreac, 99.5 % purity) was also included in order to provide a
301 reference baseline.
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304 It is well known that the high mineral content of CG can seriously damage the
305 combustion facilities [5] and for that reason, the 'raw' crude glycerol was processed to
306 remove most of its salt content. Dissolved salts in the CG were removed by solvent
307 precipitation followed by filtration of the solid salts. The solvent was recovered by
308 distillation and reused. With this procedure, the salt content can be reduced up to 80%,
309 depending on the nature of the solvent. The advantage of salt precipitation with respect
310 to the alternative process of glycerin distillation is the lower capital cost of the process
311 equipment. Furthermore, the operating cost of solvent desalting is also lower than
312 glycerin distillation, even if its industrial implementation has several disadvantages (the
313 main one being the need to manipulate the solid salt in the presence of a volatile
314 solvent). Further process optimization is needed in order to successfully scale-up the
315 desalting technology. Even so, this process was applied to a batch of CG, obtaining a
316 representative sample of desalinated crude glycerol (DG), whose salt content analysis is
317 compared to that of the original CG in Table 2. Namely, an ICP-AES (Inductively
318 Coupled Plasma Atomic Emission Spectroscopy) analysis was performed at ICB-CSIC
319 in order to quantify the main cations present in both glycerols. This information was
320 complemented with that of the total ash content, measured by means of a burner and a
321 muffle-type furnace. Using this latter parameter as a global indicator of salt presence,
322 the desalination process achieved a reduction of 64.3 % of the total ash content initially
323 present in the CG sample. Once obtained and characterized, the combustion of DG, both
324 neat and blended with GF*, was also analyzed in the droplet facility and in the semi-
325 industrial furnace.
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357 Table 2. Salt content in the crude and desalinated glycerol samples.
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^a Detection Limit

2.2 Droplet combustion facility

The single-droplet evaporation and combustion characteristics of the examined fuels were obtained through the Droplet Combustion Facility (DCF) developed at LIFTEC. These experiments provide insight into the intrinsic behavior of each fuel when tested under fixed and well characterized conditions. As these conditions are exactly the same for each sample, the observed differences are completely attributable to the studied fuels, and relative behaviors among them can be extracted in a simplified configuration. A detailed description of the experimental rig used for this purpose can be found elsewhere [14, 15].

The isolated, freely-falling droplets were originated at a piezoelectric device with initial diameters of $151.1 \pm 1.9 \mu\text{m}$ and subsequently injected within a hot coflow, where their evaporation and burning processes were recorded by optical means. In order to decrease the viscosity of the glycerol samples, the droplet generator had to be heated to temperatures up to 100°C . An interdroplet separation larger than 100 droplet diameters effectively prevented any interaction between droplets [16, 17]. In order to obtain a gaseous ambience representative of those found in real flames, a hot coflow consisting in the combustion products flowing out of a flat-flame burner was used. By adjusting the burner's feed flow rates, the composition and temperature of its exhaust gases could be modified, providing therefore different atmospheres for studying the droplet combustion process. Three conditions were selected, with 0, 3 and 10% of oxygen

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416 molar fraction (dry basis) in the coflow. As in real flames the oxygen availability can
417 significantly vary within flame regions, the chosen conditions are thought to cover a
418 varied range of common ambiences observed by droplets within real spray flames.
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421 The single droplet evaporation and combustion characteristics were entirely gained by
422 means of optical methods. A CCD camera (QImaging Retiga SRV) fitted with a
423 telemicroscope and backlit through a LED stroboscope used the double exposure
424 technique in order to extract not only the droplets size but also its velocity. With a delay
425 of 500 μ s between the LED's shots, a given droplet could be recorded multiple times in
426 the same picture. This is used for measuring the droplet velocity, but also for
427 characterizing other features such as the occurrence of microexplosions. Additionally, a
428 color DSLR camera (Nikon D5000) recorded the visible flame streak formed by the
429 freely-falling droplets, which provided insight into some macroscopically observable
430 features.
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433 2.3 Semi-industrial furnace

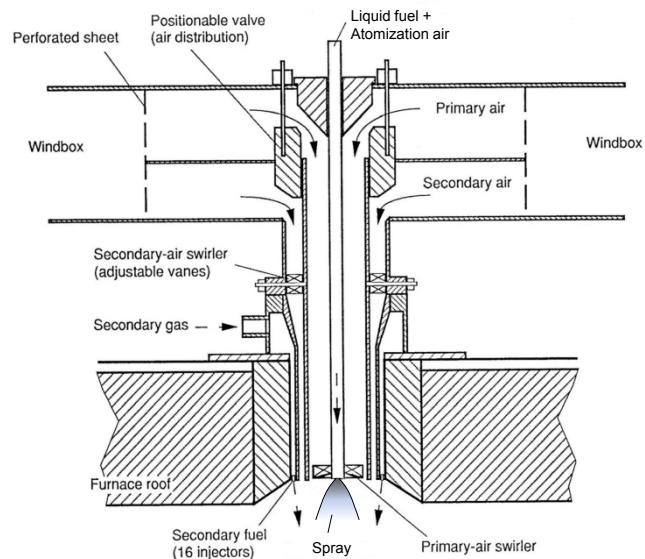
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435 The second stage of the combustion tests was conducted in a semi-industrial furnace,
436 under conditions representative of those found in real boilers. The experimental facility
437 has been described in detail in previous works [18, 19] and only their main
438 characteristics will be summarized here.
439

440 The combustion chamber is cylindrical and vertically oriented, with a total length of 3.5
441 m and a diameter of 0.83 m in the upper half, where the burner and the flame are
442 located. All furnace elements are cooled by individual water jackets and their inner
443 walls are refractory lined over the whole chamber length. Fig. 1 shows the geometry of
444 the burner installed in the furnace roof. It was designed to provide a broad flexibility, in
445 order to adapt to different fuels or to implement low-NOx measures (more details in
446 [19]). The combustion air is injected through two concentric ducts, in adjustable
447 proportions; the split was fixed at 68%/32% of primary/secondary air. The liquid fuels
448 were preheated to 80°C and injected by means of an air-assist atomizer. Due to the well-
449 known difficulties to achieve a stable flame with crude glycerol, the facility allowed for
450 the use of an auxiliary fuel (propane), which was injected through 16 injectors installed
451 in the periphery of the burner throat (see Fig. 1). Although the spray characteristics were
452 not determined, mean spray sizes are typically in the order of several tens of microns,
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475 with the distribution tail reaching the order of a hundred microns, as it can be confirmed
476 in [20-21], where the spray characteristics of a heavy oil tested at this same furnace
477 were analyzed. Thus, the droplet sizes used in the single droplets experiments (~150
478 μm) are expected to be close to the tail of the spray distribution obtained in the current
479 furnace tests.
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482 The main objective of these tests was to evaluate the stability and emissions achievable
483 with crude glycerol (both neat and desalinated) and its blends with GF*. Flue gas
484 composition was measured with individual on-line analyzers for O_2 , CO and NO_x
485 (repeatability < 1%, 0.5 % and 0.5 % of their respective full scale values). Given the
486 lack of generally-accepted methods to evaluate flame stability, some indices were
487 extracted from flame images and radiation. A video camera and a photomultiplier tube
488 fitted with a bandpass filter at $310 \pm 5 \text{ nm}$ (OH^* chemiluminescence band) were
489 installed at one of the side windows with that purpose.
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491



515 Fig. 1. Burner used for combustion tests in the semi-industrial furnace.
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519 3. Tests in droplet combustion facility 520

521 3.1 Base fuels 522

523 As introduced in Section 2.1, the droplet evaporation and combustion characteristics of
524 the industrial by-products CG, DG and GF* were extracted along with those of pure
525 glycerol (PG) by means of single droplet tests. These fuels are categorized as 'base
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fuels', to distinguish them from the CG-GF* and DG-GF* mixtures, which shall be presented in Section 3.2. Results are displayed in Fig. 2, with the droplet size evolution curves showed in the left column and the subsequently extracted burning rates ($K=-d(D^2)/dt$) provided in the right one. It should be noted that the droplet size curves are normalized by the initial droplet diameter (D_0), so that any small difference in D_0 among tests is automatically corrected. The $K-t/D_0^2$ curves are obtained as the time-derivatives of the size curves. For this purpose, the latter data was fitted to a 4th order polynomial, which was subsequently derived with respect to time. Regarding the uncertainty of the displayed curves, the error bars for a given droplet residence time have not been included because they are smaller than the symbols used in Fig. 2. Pure glycerol tests were repeated one month after their first run in order to check the procedure repeatability, providing a 6.80, 1.75 and 0.24% difference in time-averaged evaporation rate for the 0, 3 and 10% O₂ conditions, respectively. The first value is unusually high for these tests, which typically show a repeatability in the order of 1% for the time-averaged evaporation rate (e.g., 0.7% for a heating oil vaporization test in [15]). This lower repeatability is thought to respond to the significantly higher initial droplet velocities found for the PG repetition tests (especially for the 0% O₂ case), which would cause a quicker transit of the droplet along the gas coflow temperature profile. Any difference in the gas temperature around the droplet for a given residence time would have a bigger impact in the evaporation experiment, more sensitive towards this parameter because of the absence of a diffusion flame surrounding the droplet. In any case, all the experimental data presented in this work were obtained with initial droplet velocities much closer together than that of PG at the 0% O₂, and therefore their repeatability is expected to be considerably better.

Fig. 2 illustrates very similar evaporative behaviors between CG and PG during approximately the first half of the droplet lifespan for all the studied oxygen conditions. This is ascribed to the high content of glycerol in the studied CG (81.4%, according to Table 1). Both fuels display a prolonged initial heat-up transient with some thermal swelling (i.e., an increase of the droplet size due to its density decrease), primarily caused by their low tendency to evaporate at the droplet's injection temperatures. However, CG appears to show a more volatile behavior in that initial region, with slightly smaller normalized sizes and somewhat higher burning rates. The vaporization of the small fractions of NGOM and water present in the CG (Table 1) is thought to

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593 account for these differences. Over the course of this heat-up period, the PG droplets
594 gradually increase their burning rate until reaching a quasi-steady value which is kept
595 approximately constant until the droplet is completely vaporized, as stated by the well-
596 known d^2 -law. The CG curves, by contrast, are suddenly interrupted much before the
597 droplet burnout time due to the onset of violent microexplosions which shattered the
598 droplets. This kind of event was also observed in a previous work on crude glycerol
599 droplet combustion [14], and it is ascribed to the formation of internal vapor bubbles
600 which disrupt the liquid droplet upon their violent release. These disintegrations are
601 reported to be beneficial for the fuel conversion efficiency in real applications, as a
602 secondary atomization would not only significantly shorten the droplets' burnout time,
603 but also improve the fuel-gas mixing within the combustion chamber and reduce
604 pollutant emissions [14, 22]. Just before the microexplosion occurrence, the CG burning
605 rates appear to abruptly decay, departing from the PG behavior. This subtle feature was
606 also noticed in [23] for ethanol-TTIP mixtures, although relevant differences between
607 the microexplosion mechanisms might hamper comparison with the CG case (TTIP was
608 found to hydrolyze creating a solid shell at the surface). A hypothesis which might
609 explain this abrupt decay in K in the present work is based on the results presented by
610 Wang et al. for binary alkane mixtures [17], where it was found that the onset of the
611 first internal vapor bubble occurs much before this event can be inferred from
612 alterations in the droplet size, as the initial bubble size is too small to cause a significant
613 change in the droplet diameter. This initial bubble was reported to grow rather slowly
614 until reaching a turning point, where its size abruptly increased, causing the shattering
615 of the droplet. The progressive decay in the burning rate observed for CG in Fig. 2
616 could thus be ascribed to the formation of small bubbles inside the droplets just prior to
617 their fragmentation.

633
634 On the other hand, the desalinated crude glycerol displays a completely different behavior
635 when compared to both CG and PG. As illustrated in Fig. 2, DG droplets underwent an
636 abrupt swelling just after completing their initial heat-up transient. This swelling could
637 rapidly increase the droplet size by a factor of 2 prior to a puffing event or a weak
638 microexplosion. For most cases at the 0 and 3% O₂ conditions, these events achieved to
639 propel some small liquid fragments away from the parent droplet, significantly
640 decreasing its size. After this phenomenon, the DG droplets evaporated smoothly until
641 reaching a new microexplosion, this one analogous to that described for CG, which
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652 completely shattered the droplet. Because of the variable intensity of the weak
653 microexplosions, the DG droplet measurements displayed in Fig. 2 should only be
654 regarded as a sample of the range of sizes observed after this event. Depending on the
655 puffing intensity, the mass loss of the parent droplet varied, explaining therefore the
656 high dispersion found for this particular fuel. This high dispersion hindered the
657 extraction of evaporation and burning rates for DG in Fig. 2. For DG at the 10% O₂
658 condition, the puffing event was significantly more intense than those described for the
659 0 and 3% and, for most cases, achieved to shatter the parent droplet into several child
660 droplets of roughly the same size. This fact hampered droplet measurements after the
661 fragmentation point for DG at 10% O₂, as displayed in Fig. 2.
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663

664 Finally, the acetal mixture GF* presents a much shorter initial heating transient than the
665 glycerols, with substantially higher burning rates throughout the droplet lifespan.
666 Contrary to CG and DG, GF* droplets do not experience microexplosions, and their size
667 evolution curves proceed until the droplets are completely evaporated. In spite of their
668 considerably higher volatility, the total conversion of the GF* droplets is expected to
669 occur slightly after that of crude glycerol, as the shattering of the latter would drastically
670 reduce their consumption time afterwards (combustion time roughly scales with D^2 , as it
671 can be noticed in Fig. 2).
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674 When comparing among oxygen conditions for a given fuel, it is clearly ascertained
675 from Fig. 2 that higher oxygen availability accelerates the droplet conversion process,
676 enhancing burning rates and reducing droplet burnout times. This is due to the
677 formation of an envelope flame surrounding the droplet when oxygen is available. If the
678 oxygen fraction in the gaseous coflow is increased, the envelope flame displays a higher
679 temperature and is located closer to the droplet surface. Both effects significantly
680 enhance the heat transfer towards the liquid phase, accelerating therefore the droplet
681 evaporation process and the microexplosion occurrence.
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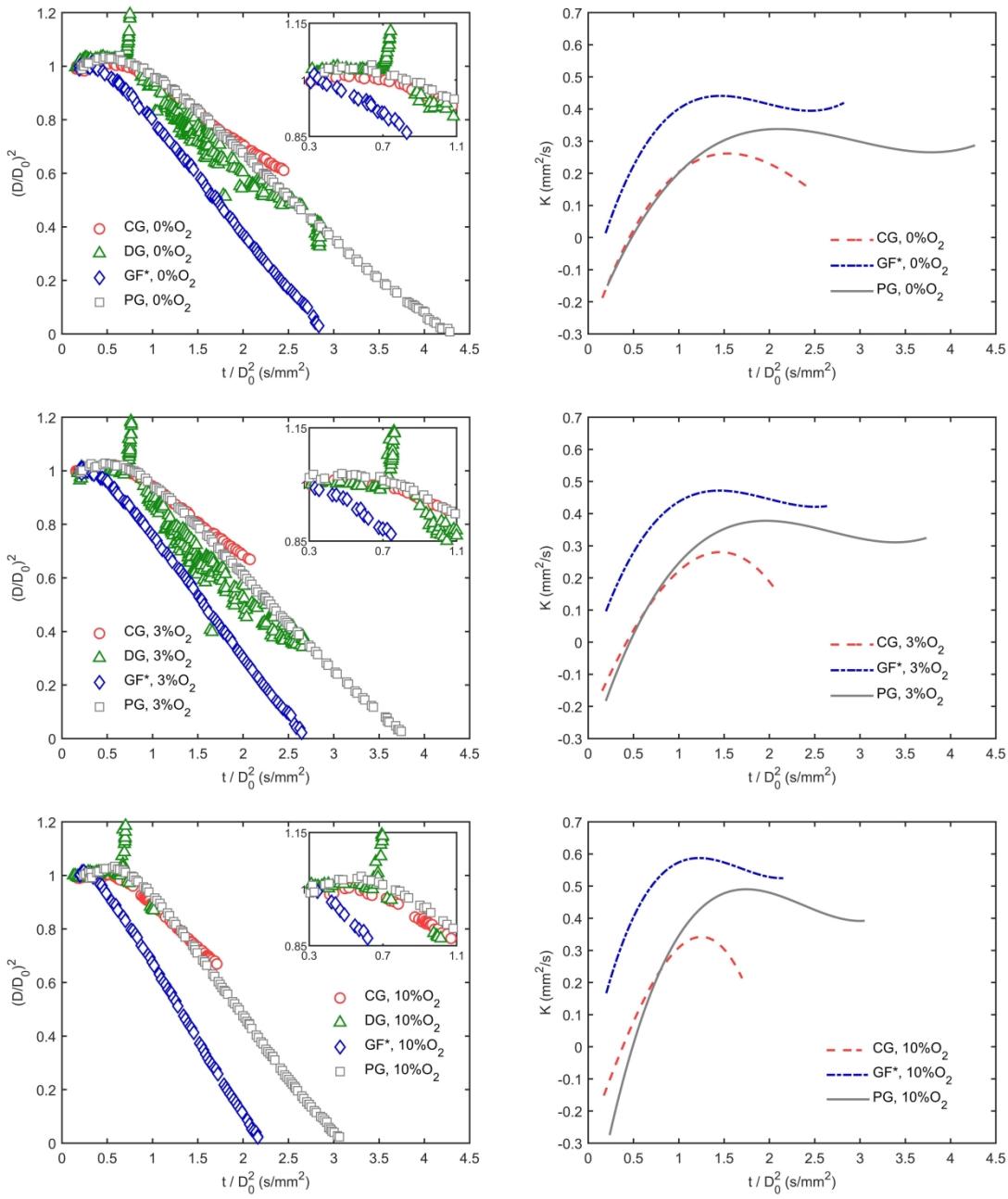


Fig. 2. Normalized droplet size and burning rate evolution for the three studied base fuels at different oxygen conditions (top: 0%, centre: 3%, bottom: 10%).

Fig. 3 illustrates an overview of some microexplosion sequences recorded for CG and DG at the evaporation condition (0% O₂ coflow). As detailed in Section 2.2, each picture displays multiple sequential shots of the same freely-falling droplet 0.5 ms apart. The upper row shows the already described DG swelling and puffing events, whereas the lower one illustrates the CG abrupt microexplosions. The first obvious difference between both is their occurrence point, considerably delayed for CG as it can be

confirmed in Fig. 3. The DG swelling starts just after its heat-up period, with droplet sizes in the order of D_0 (e.g., 153 μm for $t/D_0^2=0.708 \text{ s/mm}^2$ in Fig. 3) gradually increasing their diameter during the following few milliseconds ($\sim 2 - 4 \text{ ms}$) prior to their break-up and puffing, which can be observed in the triple-exposure pictures at $t/D_0^2=0.763$ and 0.902 s/mm^2 . On the other hand, microexplosions recorded for CG occur after a significant evaporation has already taken place (droplet sizes $\sim 120 \mu\text{m}$), with a much shorter characteristic time than the swelling and puffing events observed for DG. In the case of CG the upper droplets appear to be totally spherical, without any sign of microexplosion, whereas the lower ones are completely shattered by the bursting of the inner vapors. Therefore, the characteristic time for the recorded fragmentation events would be considerably lower than 0.5 ms for this fuel, even though the initial bubbles might have been building up during a longer time lapse (as observed for a different fuel in [17]). As already pointed out, an additional difference between the two kinds of microexplosions presented in Fig. 3 is the fact that CG microexplosions completely shattered the droplets, whereas the DG break-up phenomena was much weaker, with considerably larger child droplets which could even be tracked and measured downstream the bursting point for the 0 and 3% O_2 conditions (Fig. 2).

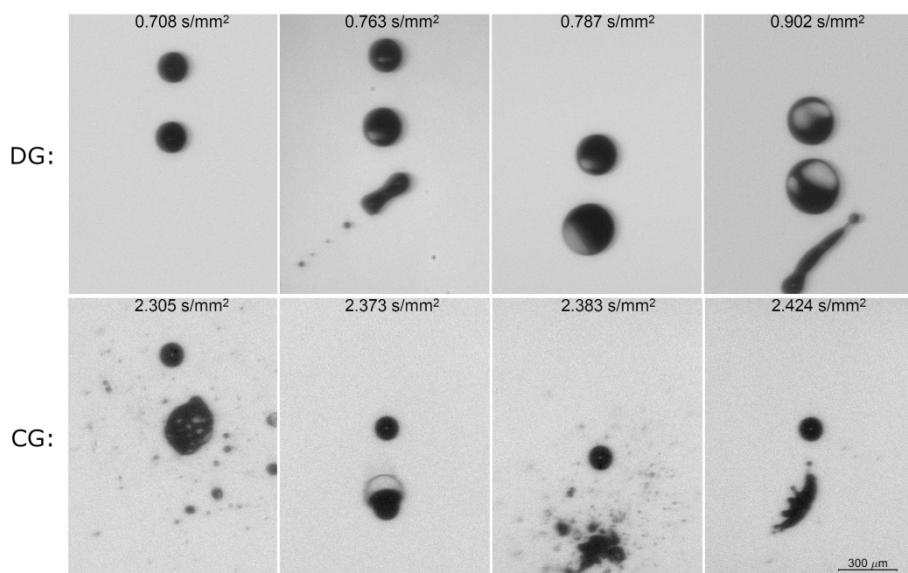


Fig. 3. Droplet swelling and microexplosion sequences for DG (upper row) and CG (lower row) at the 0% O_2 condition. For each sequence, the normalized time after injection (t/D_0^2) for the upper droplet is provided.

The CG microexplosions illustrated in the lower row of Fig. 3 display exactly the same features as those reported in [14] for a different crude glycerol sample, although also with significant differences when compared to [24], another of the few available works on CG droplet combustion. The broad differences between both experimental setups are thought to be responsible for the aforementioned discrepancies, as [24] employed a suspended droplet technique with bigger droplet sizes and lower ambience temperatures. The CG microexplosion typology reported here, with fast (< 0.5 ms) and violent droplet shattering, also differs from those described in several works on different mixtures and emulsions of alkanes, alcohols and water (e.g., [17, 25-27]). All the referred studies, performed by means of the freely-falling technique and avoiding therefore the potential influence of the solid filament, reported the occurrence of significant droplet swelling before its shattering. For instance, binary heptane-hexadecane droplets in [17] were found to increase their diameter by more than 60% prior to droplet burst, with a characteristic time in the order of a few milliseconds. Both microexplosion features appear to closely concur with the DG break-up phenomena illustrated in Fig. 3. Since the experimental configuration used in this work is analogous to that employed in [17, 25-27], the reported DG microexplosions are thought to respond to the same mechanisms proposed in those works, i.e., the homogeneous nucleation of the liquid mixture within the droplet. This local vaporization of the more volatile components (NGOM, water, methanol, even some non-recovered desalination solvent) would create a gas bubble within the liquid phase, whose growth explains the droplet swelling which precedes its break-up. As already discussed, a different case would be that of CG, whose fast and violent microexplosions concur with [14], where the droplet shattering was ascribed to the decomposition of alkali salts rather than to the evaporation of its lighter compounds, following therefore a different mechanism than those governing homogeneous nucleation between liquids. The fact that crude glycerol modifies its original abrupt microexplosions for the slower swelling-induced break-ups after the desalination process also suggests that salt content plays a relevant role in the droplet bursting mode. However, further investigation is clearly needed in order to better ascertain the differences between both microexplosion typologies.

The broad differences noted between the studied base fuels also lead to macroscopically observable distinct behaviors. This can be clearly ascertained from Fig. 4, where the flame traces formed by the combustion of the free-falling droplets are presented by

means of long-exposure photographs. All of them display a subtle blue streak stemming from the chemiluminescent emission of the droplets' envelope flames. However, whereas for pure glycerol and GF* this blue streak spans for the whole droplet burnout time, for CG and DG it is abruptly interrupted by a much more intense orangish emission. This luminosity was analyzed by a spectrometer (Ocean Optics HR2000), which found a marked peak at 589 nm, determining therefore that most of this radiation stems from the emission of excited sodium ions, released after the droplet shattering. This can be verified in Fig. 5, where the spectrum recorded for CG-GF*7 is presented. Thus, the onset of the orangish umbrella in Fig. 4 indicates the point of the first recorded microexplosion for the set of droplets captured in the long-exposure picture. In accordance with the curves presented in Fig. 2, DG droplets experience an earlier occurrence of microexplosions, although this difference is reduced compared to the 0% O₂ condition displayed in Fig. 3. The different modes of droplet shattering can also explain the noticeable differences found between both orangish umbrellas: whereas the CG sodium emission is more centered around a clearly more intense spot, the weaker microexplosions of DG provide a more distributed and asymmetrical sodium release along the child droplets trajectories.

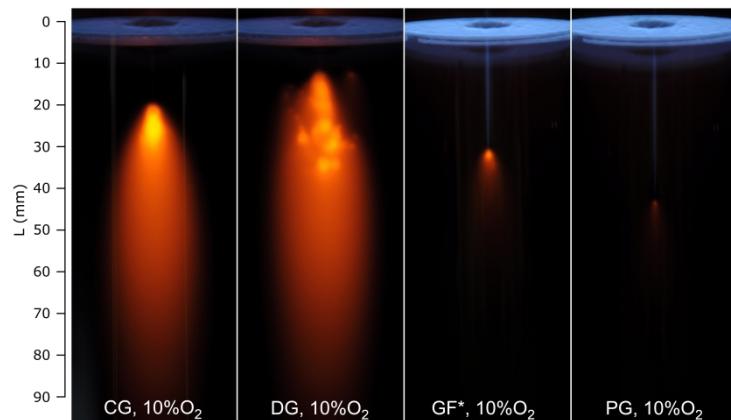
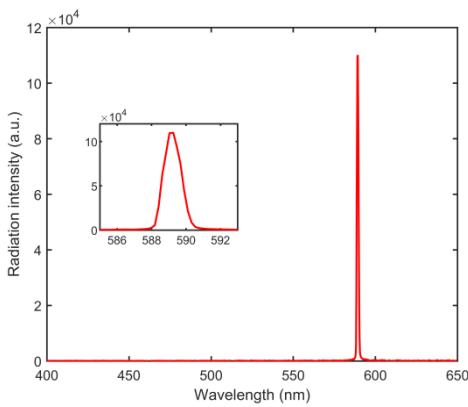


Fig. 4. Macroscopic flame traces created by the freely-falling droplets of the studied base fuels. An exposure time of 2 s was used for GF* and PG, whereas CG and DG pictures were captured with 1/3 s due to their higher luminosity.

The droplet burnout lengths for GF* and PG can also be clearly distinguished in Fig. 4, as they feature an orangish spark at the point of droplet depletion. The spectra recorded determined that these sparks were also caused by sodium emission, and therefore their occurrence is due to small contents of sodium in the GF* and PG, which are released

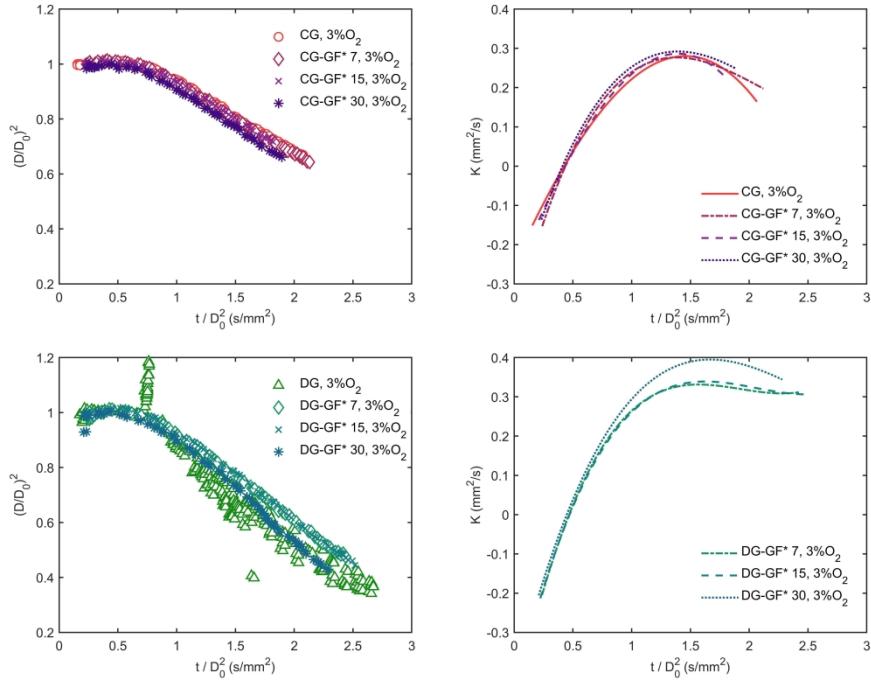
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947 into the hot ambience after the liquid has completely evaporated. This sodium can either
948 be contained within the original fuel samples or be a result of cross-contamination. In
949 any event, the amount of sodium present in GF* and PG is estimated to be negligible, as
950 the orangish luminosity does not arise until the very instant of droplet depletion. Both
951 the visible flame traces and the recorded spectra point to a negligible soot yield for all
952 the studied fuels, as the characteristic black-body continuum emission ascribed to soot
953 is absent (e.g., see the spectrum recorded for CG-GF*7 in Fig. 5).
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962 Fig. 5. Emission spectrum recorded in the combustion test of CG-GF*7 droplets (10%
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964 O_2 condition).
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972 3.2 Glycerol - acetal mixtures 973 974

975 As introduced before, one of the main objectives of this work is to evaluate the effects
976 of GF* addition on the evaporation and combustion characteristics of crude glycerol. To
977 this end, the tests described in the previous section were performed on different CG-
978 GF* and DG-GF* mixtures at the 3% O_2 coflow condition. The droplet size and burning
979 rate curves are displayed in Fig. 6 for both kinds of blends.
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Fig. 6. Normalized droplet size and burning rate evolution for CG-GF* and DG-GF* blends at the 3% O₂ condition.

It is noteworthy that CG and its mixtures with GF* show very similar behaviors throughout all the droplets combustion history. The three studied blends presented the same microexplosion typology than that described for CG in Fig. 3, and their macroscopically observable flame traces were also akin to those recorded for the neat crude glycerol (Fig. 4). Regarding the quantitative evaporation data, it can be inferred from Fig. 6 that GF* addition slightly accelerated the droplet evaporation process, although this effect is barely noticeable for the mixtures with lower GF* content, being clearer for the CG-GF*30 blend.

On the contrary, the addition of GF* drove relevant changes in the combustion features of DG, such as the suppression of the swelling and puffing stages. In [25-27] it was experimentally concluded that, for homogeneous nucleation to occur, the initial concentration of the most volatile constituents (e.g., water, NGOM, non-recovered desalination solvent or methanol in the case of DG) must be within a limited range defined by the relation of the homogeneous superheat limit of the mixture to the boiling point of these less volatile compounds. If, as it was proposed in Section 3.1, the swelling events displayed by DG are indeed caused by homogeneous nucleation within the droplet, the addition of a compound such as GF* could shift the mixture to a

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1065 concentration range out of the superheat limits, hindering therefore the initial swelling
1066 and puffing phenomena. As it can be noticed in Fig. 6, DG-GF* droplets vaporized
1067 smoothly until $(D/D_0)^2 \sim 0.45$, where an abrupt microexplosion led to a complete
1068 droplet breakup such as those observed for CG and its mixtures. These kind of
1069 microexplosions are ascribed to salt content, and therefore the lower salt concentration
1070 of DG is consistent with the delayed occurrence of the droplet shattering for DG-GF* in
1071 comparison with CG-GF*, which burst around $(D/D_0)^2 \sim 0.66$. As it was observed for
1072 CG mixtures, the burning rate enhancement with GF* blending is more pronounced for
1073 a 30% GF* addition, being the evaporation process of DG-GF*7 and DG-GF*15
1074 virtually the same. These results would be in accordance with the behaviors reported for
1075 the base fuels in Section 3.1, where the considerably higher volatility of GF*, both in
1076 terms of higher burning rates and shorter heat-up periods, was highlighted.
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1084 1085 4. Tests in semi-industrial furnace

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1087 The combustion characteristics of crude glycerol have been also investigated in a
1088 configuration representative of industrial facilities by means of tests performed with
1089 CG, DG and their blends with GF* in a semi-industrial furnace. The study has focused
1090 on analyzing the range of conditions allowing a stable combustor performance and the
1091 need of a support fuel to ensure flame stability. In the tests, the mass flow rate of
1092 glycerols, CG-GF* and DG-GF* mixtures was fixed at ~ 17 kg/h. Propane was used as
1093 auxiliary fuel, with flow rates in the range 0-3 Nm³/h.
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1096 A first, basic requirement concerns the stability of the flame, as in many cases glycerol
1097 burners need to be supplied with a secondary fuel in order to achieve a stable, attached
1098 flame [4, 5, 7]. Thanks to its broad flexibility, the burner used in this study (Fig. 1)
1099 could be adjusted to maintain a stable flame without any support fuel. Nevertheless, the
1100 operating range and the combustion quality (e.g. in terms of CO emissions) varied with
1101 the fuels fed to the burner. For example, in the case of unblended desalted glycerol, DG,
1102 a minimum of 5.8% excess oxygen (by vol., dry basis) was needed when no propane
1103 was used; this limit gradually decreased with the amount of propane fed through the
1104 secondary injectors (see Fig. 1), so that it was below 1.4% for 1 Nm³/h of propane. The
1105 addition of GF* also had a clearly beneficial effect in this respect: the minimum of
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1124 5.8% excess oxygen dropped to 2.4% and <3.3%¹ when the proportion of GF* in the
1125 liquid fuel was 15% and 30%, respectively. This is a first evidence of the positive effect
1126 of blending with GF*, as it could alleviate the need for premium fuels to stabilize the
1127 flame.
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1131 The CO and NOx emissions measured for the different tests with DG are represented in
1132 Fig. 7 and provide a clear picture on the effect of either propane or GF* addition. A
1133 limit of 100 ppm was arbitrarily selected as a threshold between ‘good’ and ‘bad’
1134 combustion qualities (the legal limit of 1000 ppm is too high for this purpose). Due to
1135 the wide range of CO emissions, a logarithmic scale has been used. It should be noted,
1136 however, that this magnifies the region of very low emissions (let’s say, <20 ppm),
1137 where the variations may be due to minor experimental uncertainties and, hence, not
1138 always are meaningful.
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1141 The use of 0.5 Nm³/h of propane (Fig. 7, left) leads in all cases to lower CO emissions
1142 than if DG or its blends are burned alone. Given the strong influence of excess oxygen
1143 on CO and the fact that its range not always overlapped for the different fuels, a direct
1144 method to compare the various situations is to determine the oxygen concentration
1145 required to keep CO emissions below the 100 ppm threshold. The addition of 0.5 Nm³/h
1146 of propane diminishes in all cases the excess air required to reach the CO limit, the
1147 reduction being more marked for DG (<7.3% to 4% O₂) than for DG+15%GF* (4.5% to
1148 3%) and DG+30%GF* (<3.3% to <2.9%). This gradation seems logical, as the margin
1149 for improvement is larger for unblended desalinated glycerol and gradually narrows as the
1150 amount of GF* increases. The positive effect of GF* on combustion quality can be
1151 clearly observed by comparing the different curves for fixed propane. The excess
1152 oxygen required to keep CO below 100 ppm is a useful index for this purpose: by
1153 adding 15% GF*, the oxygen concentration decreases from 4% to 3% for 0.5 Nm³/h of
1154 propane and from >7.3% to 4.5% when no support fuel is used. If the proportion of GF*
1155 is increased to 30%, an additional displacement of CO curves to lower excess oxygen is
1156 evident for both test series.
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1159 ¹ Actually, good flame stability was verified with 30% GF* down to 1.5% oxygen, but this was measured
1160 in a test with a higher fuel flow rate. Although this does not necessarily affect the result, it was preferred
1161 not to include this lower limit in Fig. 7.
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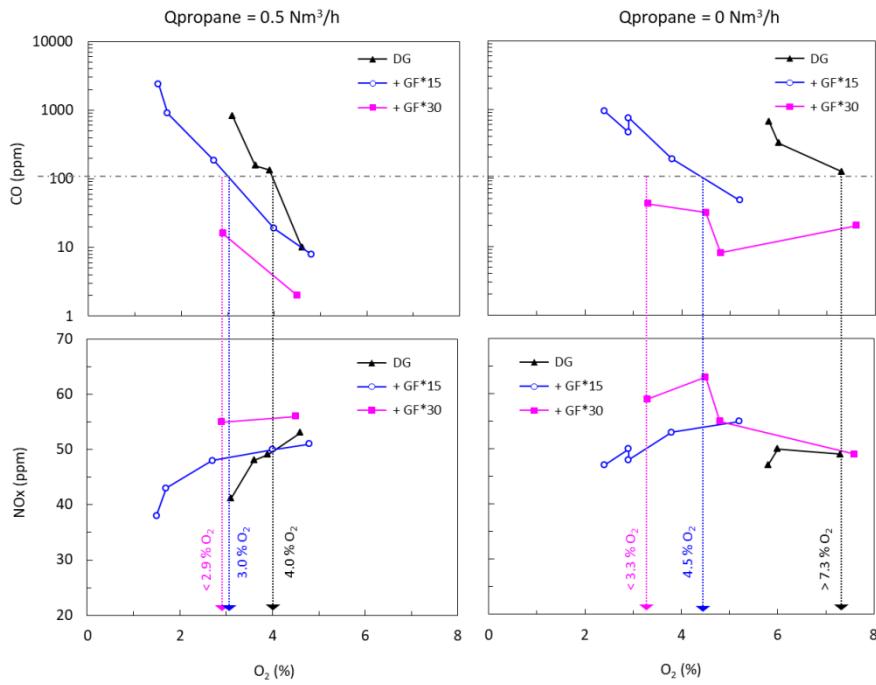


Fig. 7. Emissions of CO (top) and NOx (bottom) measured in the tests with DG and its blends with GF* when burning with 0.5 (left) and 0 Nm^3/h (right) of propane. The excess oxygen required in each case for quality combustion ($\text{CO} < 100 \text{ ppm}$) are also indicated.

NOx emissions tend to increase with the amount of GF*. This can perfectly be the consequence of a 'better' combustion (higher temperature, better dispersion of fuel vapor in the air flow). In principle, this could be compensated by modifying the burner aerodynamics (e.g., the split between primary and secondary air), especially when the fuel allows a relatively wide range of stable flame operating conditions, but this was not the objective of the study and no attempt in this regard was made.

As in the case of single droplets tests, the behavior of unblended crude (not desalinated) glycerol and the effect of acetals addition were also investigated in the semi-industrial furnace. The results obtained are displayed in Fig. 8 in terms of the CO and NOx emissions measured for the different test series performed with CG, DG and their corresponding blends with GF*30. The curves show that CG combustion is also improved by GF* addition but this effect is much less intense (for 0.5 Nm^3/h of propane, excess oxygen decreases only from <3.4% to 2.5%) than in the tests with DG where a reduction of several orders of magnitude in the CO levels is achieved (Fig. 7).

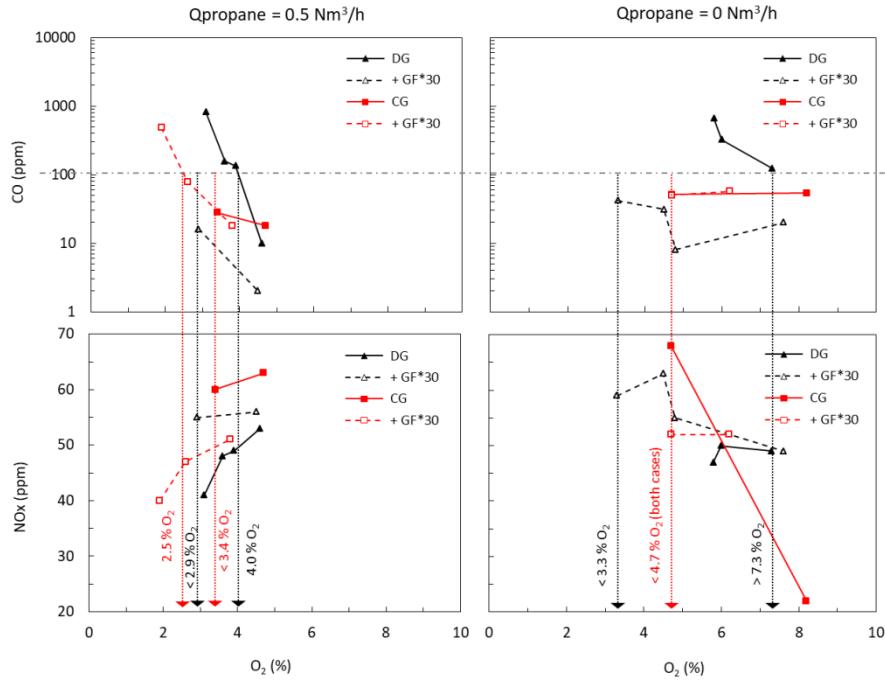
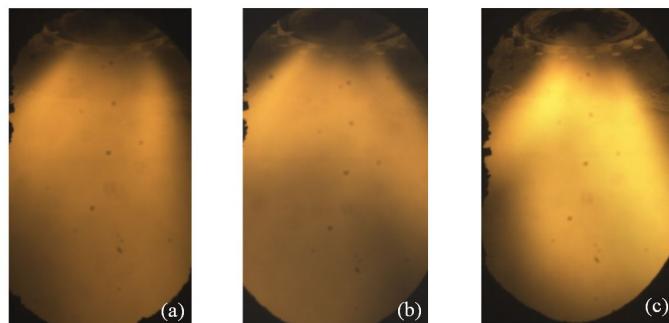


Fig. 8. Emissions of CO (top) and NOx (bottom) measured in the tests with crude and desalinated glycerol (CG and DG, respectively) and their blends with 30% GF* when burning with 0.5 (left) and 0 Nm³/h (right) of propane. The excess oxygen required in each case for quality combustion (CO<100 ppm) are also indicated.

Conversely, it is observed that the desalting process seems to have a negative effect on glycerol combustion as it rises significantly the CO levels, especially when no auxiliary fuel is used: whereas for CG less than 4.7% oxygen is enough to keep CO emissions below the 100 ppm threshold, it must be increased over 7.3% when burning DG. Although the great differences in scale of the facilities used in this work prevents a direct comparison of the results here discussed, this effect could be related to the distinct combustion behavior noticed in the DG droplet tests. As previously explained, DG droplets undergo an initial period characterized by both swelling and puffing events not observed with CG, but the final shattering due to microexplosions is delayed with respect to CG. This is expected to result in a slower and delayed production of fuel vapor in the DG flame, which may also negatively affect the fuel-air mixing and explain the higher excess oxygen required to achieve good flame stability and a nearly-complete conversion to CO₂. In any case, further research would be needed to ascertain these phenomena which are out of the scope of this work.

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1301 Information about the flame configuration and appearance was gained from color
1302 images recorded with a video camera. The acquisition rate was fixed at 117 fps,
1303 resulting in 351 snapshots for each condition, which were subsequently processed to
1304 derive a representative mean image. Fig. 9 is an example of the flame appearance for
1305 the three fuels tested. The images reflect the commented differences in the combustion
1306 behavior, showing brighter flames as the acetal percentage in the mixture is increased.
1307 As found for the droplet tests (Fig. 5), the spectrograph confirmed that the orangish
1308 color corresponds to the emission band of excited sodium.
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1324 Fig. 9. Flame images with DG (a) and its blends with 15% GF* (b) and 30% GF* (c).
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1326 0.5 Nm³/h of propane in all cases. Oxygen concentrations were 3.6, 4.0 and 2.9%,
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1328 respectively.
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1332 The intensity distribution of each flame image was analyzed and the corresponding axial
1333 position of the center of mass was calculated. This parameter, represented in Fig. 10, is
1334 indicative of the location of the region where glycerol is burned (since luminosity is
1335 dominated by the orange emission due to sodium). In general, the addition of GF* tends
1336 to shorten that distance, which seems consistent with an enhanced flame stability.
1337 However, it should be noted that when GF* increases from 15% to 30%, the opposite
1338 trend is observed; a similar change appears when propane is added. The longer average
1339 distance when propane or a high amount of GF* is used might reflect the preferential
1340 burning of those more reactive fuels, whereas glycerol combustion (the main origin of
1341 the luminosity) is delayed. Therefore, in this case, the location of the visible flame may
1342 not always be a reliable stability index. An additional analysis was performed in terms
1343 of the amplitude of the oscillations of radiation in the OH* band measured by a
1344 photomultiplier. Fig. 10 shows the rms of the photomultiplier signal, normalized by the
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mean value. In all cases, the amplitude of the oscillations consistently decreased when either propane or GF* was added, as further confirmation of the improved stability achieved when using a supporting secondary fuel or blending glycerol with acetals.

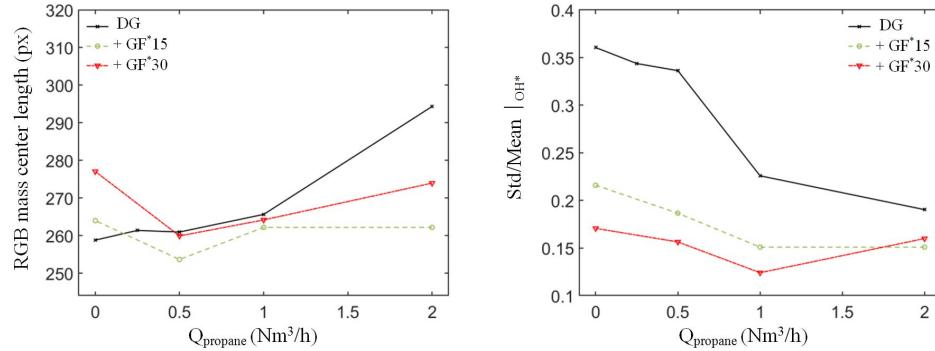


Fig. 10. Axial location of the centre of mass in flame images (left) and the fluctuations level (right) for the flames of DG and its blends with 15% GF* and 30% GF* for different mass flow rates of auxiliary gas (propane). Oxygen concentrations ranged from 2.9% to 6.0%.

5. Conclusions

The combustion characteristics of an industrial crude glycerol sample, both as received from a biodiesel plant (CG) and desalinated (DG), were studied along with those of a mixture of acetals named GF* and obtained as a by-product of FAGE production. The effect of GF* addition on the combustion of glycerol was studied at two different scales, namely through single-droplet combustion tests and by means of experiments in a semi-industrial furnace.

The single-droplet combustion tests showed that CG displayed very similar evaporation and burning rates to those of pure glycerol, although the consistent occurrence of microexplosions effectively reduced the CG droplet consumption times. The shattering events were reported to be considerably fast (< 0.5 ms) and violent, with the droplets being practically disintegrated afterwards. Desalinated crude glycerol on the other hand, exhibited a completely different behavior, with droplet swelling and puffing just after completing the initial heat-up period, and with a characteristic time in the order of a few milliseconds. These phenomena concur with other single droplet works on liquid mixtures and emulsions under similar experimental conditions, and is therefore ascribed

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1419 to the homogeneous nucleation of the most volatile compounds within DG. By contrast,
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1421 CG microexplosion typology is consistent with that of a previous work, where the salt
1422 content was found to be responsible for the shattering events. The acetal mixture GF*
1423 displayed a more conventional behavior, with markedly higher burning rates, shorter
1424 heat-up initial transients and a smooth and sustained evaporation which lasted until
1425 droplet burnout. The addition of GF* did not appear to drive drastic changes in the
1426 studied single droplet combustion behaviors for CG, although it suppressed the swelling
1427 and puffing stages for DG. In both cases, it progressively increased the burning rates
1428 and slightly accelerated the microexplosion onset favoring glycerol conversion.
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1434 The combustion behavior of the same fuels (CG, DG and mixtures with GF*) were also
1435 tested in a semi-industrial furnace. The results confirmed that the addition of GF*
1436 widened the range of stable combustion, significantly reduced CO emissions and
1437 notably improved flame stability (as determined from its flickering amplitude),
1438 especially in the case of DG. The blends showed a slight increase of NOx emissions,
1439 although this might be compensated by optimizing burner aerodynamics (facilitated by
1440 the enhanced flame stability). These benefits can also be interpreted from the
1441 perspective of a partial or total reduction in the use of premium fuels (natural gas,
1442 propane), as GF* can also act as a support fuel, with the advantage of being of
1443 renewable nature. In contrast, the results showed that glycerol desalting may result in
1444 some increase in the CO levels and, therefore, in the excess oxygen required to reach
1445 optimal flame stability and combustion efficiency.
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1463 his help in the experimental tasks.
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Declaration of interests

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The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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