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Proceedings of the Combustion Institute

EVIER Proceedings of the Combustion Institute xxx (2010) xxx-xxx

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Glycerol combustion and emissions

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10 Abstract

11 With the growing capacity in biodiesel production and the resulting glut of the glycerol by-product, 12 there is increasing interest in finding alternative uses for crude glycerol. One option may be to burn it 13 locally for combined process heat and power, replacing fossil fuels and improving the economics of biodie-14 sel production. However, due to its low energy density, high viscosity, and high auto-ignition temperature, 15 glycerol is difficult to burn. Additionally, the composition of the glycerol by-product can change dramat-16 ically depending upon the biodiesel feedstock (e.g., vegetable oils or rendered animal fats), the catalyst 17 used, and the degree of post-reaction cleanup (\overline{q} .g., acidulation and demethylization). This paper reports 18 the results of experiments to (1) develop a prototype high-swirl refractory burner designed for retrofit 19 applications in commercial-scale fire-tube package boilers, and (2) provide an initial characterization of 20 emissions generated during combustion of crude glycerol in a laboratory-scale moderate-swirl refrac-21 tory-lined furnace. We report a range of emissions measurements, including nitrogen oxides, total hydro-22 carbons, and particle mass for two grades of crude glycerol (methylated and demethylated) and compare 23 these to No. 2 fuel oil and propane. We also present preliminary data on the emissions of select carbonyls 24 (by cartridge DNPH). Results indicate that a properly designed refractory burner can provide the thermal 25 environment to effectively combust glycerol, but that high particulate emissions due to residual catalysts 26 are likely to be an issue for crude glycerol combustion.

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28 Keywords: Glycerol combustion; Emission characterization; Bio-fuels; Burner development; Waste fuels 29

30 1. Introduction

Biodiesel fuels are produced through the
transesterification of triglycerides (fats, oils, or lip ids) into fatty acid methyl esters (FAME). During
this process, the triglyceride raw material reacts

with an alcohol (almost always methanol) and a 35 base catalyst (typically sodium or potassium 36 hydroxide) to produce FAME (biodiesel) and 37 glycerol (propane-1,2,3-triol) by-product. On a 38 39 molar basis, one mole of glycerol is produced for every three moles of FAME, and volumetri-40 cally, approximately 10% of the initial reactants 41 42 are converted to glycerol. Depending upon the feedstock and the process specifics, the glycerol 43 44 waste may also contain significant and variable

1540-7489/\$ - see front matter \odot 2010 Published by Elsevier Inc. on behalf of The Combustion Institute. doi:10.1016/j.proci.2010.06.154

Please cite this article in press as: M.D. Bohon et al., Proc. Combust. Inst. (2010), doi:10.1016/j.proci.2010.06.154

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M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx

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amounts of excess alcohol, water, catalyst, and a mixture of other organic material (soaps and unreacted fats and oils) collectively characterized as MONG (matiere organique non-glycerol). In 2009, the US biodiesel production capacity exceeded 10.2×109 L (2.7×10^9 gal) and is expected to increase another 1.63×10^9 L (4.3×10^8 gal) by 2011 [1]. Recent decreases in the price of crude oil and the slim margins associated with biodiesel production have negatively affected the industry such that it is estimated to be currently operating at less than 25% of this capacity. However, even at this reduced utilization, the market for the resulting glycerol (primarily cosmetics and food and beverage industries) is nearly saturated [2]. The current price of crude glycerol is so low (\$0.04-0.11/kg, \$0.02–0.05/lb) that many biodiesel producers are stockpiling it while they wait for better markets to materialize [3].

63 64 As biodiesel production evolves from a cottage 65 industry to become a viable alternative transpor-66 tation fuel, there will be a growing need to find 67 new value-added uses for the glycerol waste. This 68 presents opportunities for the industry to optimize 69 or transform the process to increase efficiencies, 70 and reduce or reuse wastes. Numerous alternative 71 uses of glycerol are currently being investigated. 72 These include conversion to commodity chemicals 73 (such as propylene glycol, propionic acid, and iso-74 propanol) with higher market values, use as fertil-75 izers, and as extenders in animal feeds [4]. 76 Another possible use is as a boiler fuel to produce 77 process steam and co-generate electricity. If com-78 bined with biodiesel production, this has the 79 added advantages of optimizing energy integra-80 tion, eliminating transportation costs, and displacing the need for fossil fuels. Utilizing 81 glycerol as a fuel has the potential of replacing 3.8×10^8 L/year (1.0×10^8 gal/year) of fuel oil, equivalent to 1.8×10^9 kg/year (1.3×10^6 tons/ 82 83 84 85 year) of carbon dioxide. Even though glycerol is 86 known to have a moderate heating value 87 $(\sim 16 \text{ MJ/kg})$, it has not previously been used as 88 a fuel. Glycerol has a very high activation energy 89 resulting in an auto-ignition temperature of 90 370 °C as compared to 210 and 280 °C for kero-91 sene and gasoline, respectively [5]. Pure glycerol 92 is also highly viscous (1030 cP at 22 °C), making 93 it difficult to pump and atomize. Finally, its chem-94 ical similarity to acrolein (propenal) causes con-95 cern if this toxic but normally unstable carbonyl 96 compound is formed as a product of combustion. 97 Patzer et al. [6] investigated glycerol combustion 98 in an unmodified package boiler, but were unable 99 to achieve stable glycerol flames until they co-fired 100 smaller amounts of glycerol with yellow grease. 101 This is consistent with the apparent issues of glyc-102 erol ignition and flame stability in package boilers 103 designed for high rates of heat transfer, cold walls, 104 short residence times (~ 2 s), and high gas-quench-105 ing rates (\sim 500 K/s)^{†7}]. In contrast, the research

106 presented here describes efforts to (1) develop a prototype high-swirl refractory burner designed 107 for retrofit applications in commercial-scale fire-108 tube package boilers and capable of stable opera-109 tion with 100% glycerol fuels, and (2) provide an 110 initial characterization of emissions generated 111 during combustion of crude glycerol fuels in a 112 similar laboratory-scale moderate-swirl refrac-113 tory-lined furnace. While data collected at the 114 US EPA/NRMRL from the refractory-lined fur-115 nace was performed under an approved quality 116 assurance project plan, the data pertaining to 117 the prototype burner were not subjected to the 118 119 Agency's required peer and policy reviews.

2. Materials and methods

2.1. Prototype 7 kW refractory burner 121

This study examined glycerol combustion in 122 123 two experimental systems. The first is a prototype 7 kW refractory burner based on a design 124 described by Chen et al. [8]. This burner, shown 125 in Fig. 1a, consists of an air swirl chamber, a ven-126 turi restriction, and a refractory-lined combustion 127 chamber. An air-assisted glycerol atomizing noz-128 zle (Delavan model 30609-3) is located along the 129 130 centerline of the swirl chamber and venturi resulting in an annular space for the swirling air. The 131 14.2 L combustion chamber is lined with cast 132 refractory 1.9 cm thick. In its current configura-133 tion, the prototype burner is equipped with a steel 134 restrictor at the exit of the combustion chamber to 135 promote internal recirculation. The assembly is 136 designed to be inserted into the first pass of a com-137 mercial fire-tube boiler, and provide an insulated 138 environment to promote ignition and flame stabil-139 ity. Axial and tangential air flowing through the 140venturi at the inlet of the combustion chamber 141 produces a swirling pressure gradient, creating 142 143 an intense recirculation zone into which the glycerol is sprayed. While a large range of swirl is 144 possible, swirl numbers between 2 and 10 were 145 examined and adjusted by varying the axial and 146 tangential air flow rates. The burner refractory is 147 first preheated with a traditional fuel, in this case 148 149 propane, and then transitioned to glycerol. Figure 1b illustrates the burner operating on 150 100% glycerol. Stable flames are possible through 151 a combination of the hot refractory walls and 152 153 intense gas recirculation. The prototype burner was mounted on a test stand under a large fume 154 155 hood. US Pharmacopeia (USP) grade glycerol was pumped (~ 28 g/min and 276 kPa) to the 156 spray nozzle and atomized with air (\sim 32 SLPM 157 and 172 kPa). Gas samples were collected through 158 an uncooled quartz probe at the throat of the 159 exhaust cap, cooled through an ice bath to remove 160 condensing water, and directed to a California 161 162 Instruments (model 400 HCLD, Orange, CA)

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M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx



Fig. 1. Experimental facilities used for glycerol combustion: (a) cross-sectional view of 7 kW prototype burner; (b) prototype burner operating on 100% USP grade glycerol; and (c) 82 kW refractory-lined furnace with sampling locations noted.

163 NO_x analyzer and an Infrared Industries (model 164 FGA-4000 XDS, Hayward, CA) exhaust gas ana-165 lyzer (O₂, CO, and CO₂). Exhaust temperatures 166 were measured using a bare type B thermocouple. 167 The prototype burner experiments included preli-168 minary measurements of selected volatile carbon-169 yls. A known volume (1.1 L) of burner exhaust 170 gas was drawn through a cartridge containing 171 2,4-dinitrophenylhydrazine (DNPH) impregnated 172 material purchased (Waters Corp., model 37500, 173 Milford, MA) for the purpose. DNPH reacts with 174 the carbonyls to create DNPH-carbonyl deriva-175 tives that were later dissolved in acetonitrile and 176 analyzed by high performance liquid chromatog-177 raphy. DNPH is also selective for NO_x species 178 and care must be taken so as not to saturate the 179 DNPH. DNPH saturation, however, is evident 180 during chromatography. In addition to USP 181 grade glycerol and an air blank, methane, pro-182 pane, and kerosene fuels were also characterized 183 for carbonyl emissions.

184 2.2. 82 kW refractory-lined furnace

The second experimental system, illustrated in Fig. 1c, is a laboratory-scale refractory-lined furnace. This system was equipped with an 82 kW rated International Flame Research Foundation (IFRF) movable-block, variable-air swirl burner which incorporated an air assisted atomizing nozzle positioned along its center axis. Swirl numbers up to 1.8 are possible. Additional details regard-192 ing this experimental system are presented else-193 where [9,10]. Based on its similar design to the 194 prototype burner (refractory-lined, adjustable 195 swirl, and air atomization), this system was also 196 used to examine operational issues (fuel delivery, 197 atomization, flame ignition and stability) as well 198 199 as provide a preliminary assessment of several emissions. Like the prototype burner, the labora-200 tory furnace was preheated (using natural gas) 201 202 and then transitioned to glycerol fuel. However, unlike the prototype burner, the laboratory fur-203 nace burned two formulations of crude glycerol 204 205 received from Foothills Bio-Energies Inc. (Lenoir, NC). These glycerol fuels were fed from drums 206 207 using an in-barrel heating system, insulated fuel 208 lines, and continuous circulation within a fuel loop with a portion directed to a Spraying Sys-209 tems Co. (model Air Atom 1/4-JSS) air-atomizing 210211 nozzle. Fuel temperature, air pressure, air flow, and air temperature were maintained at 93 °C, 212 213 204 kPa, 30 SLPM, and 150 °C, respectively. Preheating the crude glycerol in this manner reduced 214 its viscosity significantly (20 cP for pure glycerol 215 at 100 °C) allowing it to be handled similarly to 216 other fuel oils. Gas samples were extracted from 217 an exhaust location (see Fig. 1c) and directed to 218 a set of continuous emission monitors (CEMs). 219 220 These samples were conditioned and analyzed 221 for CO₂ (Beckman Corp., model 755, La Habra, 222 CA), O₂ (Beckman Corp., model 755, La Habra,

Please cite this article in press as: M.D. Bohon et al., Proc. Combust. Inst. (2010), doi:10.1016/j.proci.2010.06.154

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10 September 2010

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M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx

223 CA), CO (Thermo Electron Corp., model 48, 224 Franklin, MA), NO and NO2 (Teledyne Technol-225 ogy Co., model 200A4, San Diego, CA), and total 226 hydrocarbons (THC, Thermo Electron Corp., 227 model 43c, Franklin, MA), in accordance with Methods 3A, 7E, 10, and 25A [11]. Once steady-228 229 state operation with glycerol fuels was achieved, 230 particulate matter (PM) samples were collected 231 (in triplicate) on filters (Method 5) for mass deter-232 mination and limited chemistry [11]. PM samples 233 were also directed to a scanning mobility particle 234 sizer (SMPS, TSI Inc., model 3080/3022a, Shoreview, MN) and an aerodynamic particle sizer 235 236 (APS, TSI Inc., model 3321, Shoreview, MN) to 237 determine particle size distributions. Filter sam-238 ples were later examined for elemental carbon 239 and organic carbon (EC/OC) using a thermal/ 240 optical carbon analyzer (Sunset Laboratory Inc., 241 model 107, Tigard, OR) and inorganic elements 242 by wavelength dispersive X-ray fluorescence spec-243 troscopy (WD-XRF, Philips, model 2404 Panalyt-244 ical, Natick, MA). WD-XRF data were collected by Panalytical's SuperQ software and analyzed 245 246 using UniQuant 5 (Omega Data Systems, Veldho-247 ven, The Netherlands).

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248 2.3. Crude glycerol fuels

249 There is a great deal of variability in the feed 250 stocks and processes used to make and purify 251 the FAME product, recover useful reactants for 252 recycle, and process the glycerol by-product [12]. 253 Important glycerol post-processes include acidula-254 tion/neutralization to adjust the pH, and evapora-255 tion/distillation to separate the water and excess 256 methanol for reuse. Biodiesel manufacturers typically make efforts to reclaim the excess unreacted 257 258 methanol. However, based on the relative costs of 259 methanol recovery and purchasing new methanol, 260 this is not always the case. Further, as it may be 261 advantageous to utilize the methanol as a fuel 262 component, we decided to examine both methyl-263 ated and demethylated crude glycerol fuels. Meth-264 ylated crude glycerol typically contains (by 265 weight) 50-70% glycerol, 10-20% methanol, 5-266 10% salts, <3-10% water, <1-5% free fatty acids, 267 and <1-5% MONG. Demethylated crude glycerol 268 typically contains (by weight) 70-88% glycerol, <1% methanol, 5–15% salts, <5–15% water, <1– 269 270 5% free fatty acids, and <1-5% MONG [13]. 271 Table 1 presents an analysis of both crude glycerol 272 fuels as received from Foothills Bio-Energies pro-273 duced from the transesterification of low free fatty 274 acid chicken grease. Values for USP grade glyc-275 erol are included for comparison. All three fuels 276 (USP, methylated, and demethylated) contain sig-277 nificant amounts of oxygen (52, 43, and 17 wt%, 278 respectively). However, the low value measured 279 for the demethylated glycerol may indicate a fairly 280 low glycerol concentration and larger quantities 281 of MONG. Also notable are the low nitrogen

Fable 1					
Analysis	of th	nree	glycerol	fuels.	

	USP glycerol	Methylated	Demethylated
C (%)	39.1	42.05	67.27
H (%)	8.7	10.14	11.43
N (%)	0	<0.05	<0.05
O (%)	52.2	43.32	17.06
S (%)	0	0.078	<0.05
H ₂ O (%)	0	1.03	1.47
Ash (%)	0	3.06	2.23
Ca (ppm)		<23	119
Na (ppm)		11,600	17,500
K (ppm)		628	541
Cl (ppm)		124	154
Mg (ppm)		<8	29
P (ppm)		2220	1750
HHV (MJ/kg)	16.0	21.8	20.6

(<0.05 wt%) and sulfur (<0.05–0.08 wt%) contents 282 and high ash (2-3 wt%) contents of the two crude 283 glycerol fuels. This ash corresponds to very high 2.84sodium levels (1.2-1.8 wt%) consistent with the 285 use of NaOH catalyst. Other ash elements in nota-286 287 ble concentrations include phosphorus and potas-288 sium. The heating values determined for the methylated and demethylated fuels (21.8 and 289 20.6 MJ/kg, respectively) are also notably higher 290 than that for pure glycerol (16.0 MJ/kg). 291

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3.1. Prototype 7 kW refractory burner

USP grade glycerol combustion was examined 294 in the prototype refractory burner over a range of 295 swirl numbers and equivalence ratios and com-296 297 pared to operation with propane and No. 2 fuel 298 oil. All three fuels generated no or negligible 299 ash, as we wanted to avoid ash formation and deposition in these tests and concentrate on flame 300 ignition and stability issues. Propane was chosen 301 as it represents a similar (but non-oxygenated) 302 three-carbon alkane, similar to glycerol. No. 2 fuel 303 oil was chosen to examine and compare atomiza-304 305 tion using a common liquid fossil fuel. Both propane and No. 2 fuel oil have heating values 306 (46.2 and 42.5 MJ/kg, respectively) significantly 307 greater than glycerol. We decided to match the 308 burner load for all three fuels (7 kW). This corre-309 310 sponds to fuel feed rates of 28.0, 9.6, and 10.3 g/ min for USP glycerol, propane, and No. 2 fuel 311 oil, respectively. Glycerol combustion was exam-312 ined over a wide range of air flows and swirl. 313 Equivalence ratios were evaluated by using a pre-314 determined glycerol flow rate based on desired 315 power output and then airflow was adjusted (both 316 317 total and swirl) to achieve a stable flame, whereby the flame was entirely contained within the cham-318 ber through the full range of swirl. The highest air 319

10 September 2010

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320 flow was chosen where the glycerol could burn 321 through the full range of swirl without blowout. 322 Equivalence ratios were determined based on 323 measured air and fuel flows and confirmed from 324 measurements of exhaust O₂. Stable and optimum 325 operation was achieved over a range of three air 326 flow rates (210, 227, and 243 SLPM) for swirl 327 numbers from 2 to 10. Interestingly, accounting 328 for fuel oxygen, these conditions correspond to 329 low global equivalence ratios ($\Phi = 0.37 - 0.44$). 330 Corresponding air flows and swirl using both pro-331 pane and No. 2 fuel oil were not possible as the 332 flames tended to blowout. This was due to the 333 flow rate of air through the atomizing nozzle 334 required to atomize the highly viscous glycerol. 335 When the fuel was switched to a less viscous fuel, 336 the high air flow rate through the small orifice cre-337 ated too great a velocity which blew out the pro-338 pane and diesel flames. Stable operations were achieved at air flow rates of 180 and 202 SLPM 339 for propane and 172 and 195 SLPM for No. 2 fuel 340 341 oil for all swirl numbers (2-10) examined. These 342 conditions correspond to global equivalence ratios 343 between 0.48 and 0.65. Lower air flow rates for 344 the glycerol case did produce stable flames for 345 some swirl conditions, but not for the full range, 346 and thus it was difficult to resolve the disparity 347 in the equivalence ratios. The recirculation zone 348 strength will scale with the swirl number. For all 349 swirl numbers investigated here, the flame was sta-350 ble. The mean exhaust gas temperature decreased 351 with decreasing swirl number, and was fairly 352 insensitive to swirl number at high swirl.

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Table 2 summarizes emission measurements made at the burner exit. Emissions from USP glycerol combustion compare favorably with those from the other two traditional fuels. Emissions of CO were undetectable, and O₂ and CO₂ were consistent with corresponding stoichiometries and mass balances for complete combustion.



Fig. 2. NOx emissions corrected to 0% O₂ vs. swirl number for the 7 kW prototype burner.

Interestingly, NO_x emissions for the glycerol flames were exceedingly low $(7-10 \text{ ppm}, 0\% \text{ O}_2)$ compared to those for the two fossil fuels (110-140 ppm, 0% O₂). This was true even though O₂ levels during glycerol combustion were very high. Except for NO_x , these emissions did not have a notable dependence on the swirl number over that range examined. Figure 2 shows a slight influence of increasing swirl number on NO_x formation. Temperatures measured at the burner exit were fairly comparable, with those for glycerol perhaps somewhat lower than propane and No. 2 fuel oil. All three flames are predominately diffusion controlled, where peak flame temperatures occur at near stoichiometric equivalence ratios. Calculated stoichiometric adiabatic flame temperatures for glycerol, propane, and No. 2 fuel oil are 2201, 2394, and 2413 K, respectively. The adiabatic flame temperature for glycerol is slightly lower, which may contribute to the reduced NO_x formation. However, these differences in temperature

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Emissions measured fro	om 7 kW prototype	burner and 82 kW	refractory-lined furnace.
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	7 kW prototype burner					82 kW furnace			
	USP gl	ycerol		Propar	ie	No. 2 f	fuel oil	Methylated	Demethylated
Load (kW)	7.3	7.3	7.3	7.4	7.4	7.3	7.3	80.5	53.9
$arPhi^{\mathrm{a}}$	0.444	0.392	0.370	0.562	0.488	0.645	0.488	0.63	0.77
SR ^a	2.25	2.55	2.70	1.78	2.05	1.55	2.05	1.58	1.30
NO_x (ppm)	3.0	3.5	3.6	60.2	62.8	74.7	62.5	146.5	118.3
NO_x at 0% O_2 (ppm)	6.9	9.1	9.6	110.5	135.4	117.8	128.6	235.2	155.5
O ₂ (%)	11.8	12.9	13.3	9.6	11.3	7.7	10.8	7.9	5.1
CO ₂ (%)	7.3	6.7	6.3	6.8	5.9	7.0	6.2	12.5	15.4
CO (%)	0.0	0.01	0.0	0.01	0.00	0.0	0.0	_	_
THC (ppm)	-	_	_	_	_	_	_	4.7	7.1
Exit temp. $(^{\circ}C)^{b}$	958	901	877	1001	974	986	946	1041	1075
Flame temp. (°C) ^c	1201	1103	1060	1359	1213	1628	1343	1782	1716

^a Equivalence and stoichiometric ratios determined by excess O₂ in the exhaust.

 $^{\rm b}$ Temperature measured at the throat of the exhaust for the 7 kW prototype burner and at the exit of the 82 kW refractory-lined furnace.

^c Adiabatic flame temperature calculated at stoichiometric ratios listed above.

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M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx

381 are not large enough to account for all the dispar-382 ity. This may indicate that the thermal NO_x mech-383 anism is not the dominate mechanism, but NO_x 384 formation is rather a combination of thermal 385 and prompt mechanisms, both of which may be suppressed in the glycerol case. It is unlikely that 386 387 there is any significant contribution of fuel NO_x 388 formation due to very low levels of nitrogen in 389 all three fuels. One possibility is that there is 390 greater partial premixing in the glycerol case 391 which may contribute to reduced thermal NO_x 392 formation. Appleton and Heywood [14] show that with better atomization, NO_x formation is 393 394 reduced as global equivalence ratios decrease. 395 However, the glycerol case should exhibit lower 396 partial-premixing due to its higher boiling point 397 compared with No. 2 fuel oil. Additionally, pro-398 pane should exhibit the most premixing due to 399 being a gaseous fuel. Therefore, it seems unlikely 400 that glycerol has greater partial premixing. If large 401 differences in peak flame temperature and partial 402 premixing cannot explain the dramatically differ-403 ent NO_x levels, one possible explanation is the 404 very large fuel-bound oxygen content of the glyc-405 erol (\sim 52% by mass). Unfortunately, there is no 406 work in the literature with fuels with such high 407 fuel-bound oxygen contents and what effect this 408 may have on NO_x formation is not well under-409 stood. However, the presence of so much oxygen 410 within the fuel may contribute to a broadening 411 of the flame front, thereby reducing peak temper-412 atures. The presence of so much fuel-bound oxy-413 gen may also inhibit the prompt NO_x mechanism. The NO_x formation is not inhibited 414 415 by the presence of fuel-bound oxygen in the pro-416 pane and diesel flames and may proceed through 417 a combination of both prompt [15] and thermal 418 mechanisms, while both mechanisms could be 419 inhibited in the glycerol flame. It was attempted 420 to examine this effect by mixing glycerol with 421 other non-oxygenated fuels. However this effort 422 failed due to the high polarity of glycerol and its 423 immiscibility with most fuels. Further work needs 424 to be done to understand the effect of high fuel 425 oxygen content on NO_x emissions.

426 Table 3 presents preliminary emission mea-427 surements of formaldehyde, acetaldehyde, and 428 acetone from the prototype burner operating with 429 USP glycerol. As can be seen, aldehyde concentra-430 tions in the glycerol emissions were approximately

Table 3 Preliminary measurements of several carbonyls (ppm).

•		•	(II)
	Formaldehyde	Acetaldehyde	Acetone
Air	1.0	0.25	0.45
Methane	1.5	0.50	1.70
Propane	6.0	1.50	0.75
Glycerol	15.0	2.25	1.25
Kerosene	10.0	0.625	1.00

431 10 times those measured in the ambient air blank, slightly higher than those measured from methane 432 433 and propane, and comparable to those from kerosene. In no test was acrolein detected above 434 17.5 ppb. These preliminary data indicate that pri-435 mary carbonyl emissions from glycerol combus-436 tion may be comparable to those from other 437 conventional fossil fuels. 438

3.2. 82 kW refractory-lined furnace

Both methylated and demethylated crude glyc-440 erol fuels burned reasonably well in the refrac-441 tory-lined furnace without fossil fuel co-firing. In 442 fact, the warmed demethylated glycerol fed more 443 consistently through the air atomizer than the 444 445 methylated fuel which, due to its lower viscosity, required larger amounts of fuel and atomizing 446 air to produce a stable spray. This difference in 447 viscosity accounts for the higher load and excess 448 air reported in Table 2 for this fuel. The required 449 high fuel feed rates (due to low heating values) 450 produced long flames which were shortened by 451 maximizing the IFRF burner swirl (1.8). Interest-452 ingly, the refractory-lined furnace uses a UV-453 based flame safety system, and although both 454 fuels produced stable flames (base on visual obser-455 vations) the UV detector had difficulties establish-456 457 ing a stable signal. Eventually, a flame rod was substituted and stable flame signals were estab-458 lished. The equivalence ratios were determined 459 460 based on exhaust O_2 .

Table 2 presents the results of the gas-phase 461 emission measurements averaged over the course 462 of three replicate experiments. These results indi-463 cate that glycerol combustion in a refractory-lined 464 furnace produced gas-phase emissions compara-465 ble to previous experiences with fossil fuels (natu-466 ral gas and No. 2 fuel oil). Unfortunately, 467 accurate CO emissions could not be determined 468 due to instrument malfunction. However, both 469 470 total hydrocarbon concentrations as well as total carbon (TC) concentrations in the fly ash (see 471 Table 4) were consistently low and typical of emis-472 sions indicating reasonably complete combustion. 473 Oxygen levels were slightly elevated, but this was a 474 consequence of maintaining proper fuel atomiza-475 476 tion and the high inherent oxygen contents of 477 the glycerol fuels. Concentrations of NO_x $(\sim 150-240 \text{ ppm}, 0\% \text{ O}_2)$ were typical of the rela-478 tively high combustion temperatures and low fuel 479 480 nitrogen contents. The data suggest that the demethylated glycerol produced slightly less NO_x than 481 482 the methylated fuel. It is notable that the proto-483 type burner produces NO_x emissions significantly lower (~ 6 ppm, 0% O₂) than those measured in 484 the refractory-lined furnace. This difference in 485 NO_x emissions may be related to the variation 486 in swirl (1.8 compared to 2–10), but is most likely 487 related to the longer residence times in the refrac-488 489 tory-lined furnace. The prototype burner was able

M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx

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Table 4

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Fly ash elemental	analyzes (wt%).	
	Methylated	Demethylated
С	4.88	2.74
OC	1.31	0.53
EC	3.56	2.21
0	23.1	27.3
Na	41.8	45.8
Mg	0.033	0.067
P	4.56	5.98
S	0.99	1.48
Cl	0.96	1.45
Κ	1.45	1.53
Ca	0.338	0.46
Fe	0.114	0.143
Cu	0.013	0.009
Zn	0.781	0.688
Trace	1.850	1.940
Undetermined	19.2	10.4

490 to maintain stable glycerol flames at global equiv-491 alence ratios beyond the operating range for the 492 other fuels examined (propane and diesel). It 493 should be noted, however, that the crude glycerol 494 fuels examined in the refractory-lined furnace 495 were not the same as the USP glycerol examined 496 in the prototype burner. The presence of MONG 497 and other process by-products in the crude glyc-498 erol fuels reduces the fuel oxygen and may well 499 affect NO_x formation. Because of the large differ-500 ences in fluid dynamics, swirls, and residence 501 times between the two experimental systems, it is 502 difficult to compare NO_x emissions. However, 503 comparisons within their individual systems is 504 valid and of interest.

505 Mass concentrations of fly ash determined gravimetrically indicate average emissions of 506 3380 and 2200 mg/m³ for the demethylated and 507 508 methylated glycerol fuels, respectively. These are 509 very high values and are consistent with the high 510 ash concentrations of these fuels. These values 511 can be compared to concentrations of $\sim 90 \text{ mg/}$ 512 m³ measured in the same combustor burning a 513 No.6 fuel oil with an ash content of 0.1% [7]. In 514 fact, concentrations of 3000 mg/m^3 approach 515 those for coal combustion before particulate control. Particle size distributions measured from 516 517 emissions of the two fuels indicated a large dis-518 tinct accumulation mode ($\sim 100-110$ nm) suggest-519 ing vaporization, nucleation, and coagulation of a 520 significant amount of ash. These results are con-521 sistent with the very high alkali metal content of 522 the fuels. These data also indicate the presence 523 of a substantial coarse mode ($>5 \mu m$), especially 524 for the demethylated fuel.

Table 4 presents a summary of the elemental analyzes performed on the filter samples. For these measurements, it was assumed that total carbon (TC) is the sum of organic carbon (OC) and elemental carbon (EC). Other elements with

atomic numbers >9 (fluorine) were determined by WD-XRF. Carbon analyzes indicate that approximately 1% of the PM is organic carbon, and another 2-3% is elemental carbon. These values are comparable to those measured from traditional fossil fuels and are consistent with the low levels of hydrocarbons measured. Elements determined by XRF (and presented as stable oxides) accounted for approximately 80% and 89% of the particulate mass for the demethylated and methylated fuels, respectively. Major elements include Na, P, Cl, and K. Sodium specifically accounts for over 40% of the fly ash and its presence is the results of the NaOH catalyst used during the transesterification process. The other major elements (P, Cl, and K) are typical of biofuels. Between the unburned carbon and the inorganic elements measured, the majority of the particulate mass composition is identified.

4. Conclusions

Waste glycerol is produced in significant quantities during the transesterification of triglycerides to produce biodiesel fuels, and new value-added uses for this waste are needed to optimize process efficiencies and reduce the impacts of disposal. Although not an ideal fuel, waste glycerol might be used in boilers to produce process steam and co-generate electricity with the added advantages of optimizing energy integration, eliminating transportation costs, and displacing the need for fossil fuels. This work examined efforts to develop a prototype high-swirl refractory burner designed for retrofit applications in package boilers and provide an initial characterization of emissions generated during combustion of crude glycerol fuels. These results represent important first steps toward characterizing the use of waste glycerol as a boiler fuel. Study conclusions can be summarized as follows:

- (1) Stable 100% glycerol combustion was achieved for both a 7 kW prototype high swirl burner (using USP grade glycerol) and an 82 kW (rated) refractory-lined furnace (using crude methylated and demethylated glycerol wastes).
- (2) For the prototype burner, optimum glycerol combustion corresponded to operation at very high swirls (2–10) and excess air $(\Phi = 0.37-0.44)$. In contrast to glycerol, propane and No.2 fuel oil combustion became unstable at high excess air $(\Phi < 0.45)$.
- (3) With the exception of NO_x , both combustors produced gas-phase emissions similar to natural gas and distillate fuel oils indicating low total hydrocarbon emissions and efficient combustion.

glycerol

responsible.

of this work.

(4) Interestingly, NO_x emissions from the pro-

totype burner (7–10 ppm, 0% O₂) were 20

times lower than those from the refrac-

tory-lined furnace (160–240 ppm, 0% O₂).

Differences in burner swirl and excess air,

as well as differences in compositions

between pure glycerol and actual crude

emissions (by DNPH cartridges) indicate

formaldehyde and acetaldehyde emissions

only 10 times larger than an air blank,

and comparable to several common fossil

fuels. Acrolein was measured at less than

17.5 ppb. Continued measurements of car-

bonyls are one priority for a second phase

thylated glycerol wastes produces fly ash

concentrations (2200–3400 mg/m³) much

larger than residual fuel oils and compara-

ble to coal combustion before particulate

control. Particulate size distributions indi-

cate a large accumulation mode suggesting

(7) WD-XRF analysis indicates that 40-50% of

significant Na vaporization.

(6) Combustion of crude methylated and deme-

(5) Preliminary measurements of carbonyl

wastes are believed to be

M.D. Bohon et al. | Proceedings of the Combustion Institute xxx (2010) xxx-xxx

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- the fly ash (determined as stable oxides) is composed of Na with smaller amounts of
 - phosphorus (4-6%), potassium (1-2%), chlorine (1-2%), and sulfur (1%). This is consistent with unrecovered NaOH used as a process catalyst. Approximately 3-4% of the fly ash is unburned carbon. The large
 - concentrations of fly ash formed during glycerol combustion combined with the high alkali metal content of this ash presents a significant issue that needs to be addressed before crude glycerol fuels can

be utilized in boilers.

629 Acknowledgements

630 Portion of this work were sponsored under 631 Contract EP-C-09-027 with Arcadis G&M Inc., 632 the NCSU/EPA Cooperative Training Program 633 in Environmental Sciences Research, Training 634 Agreement CT8333235-01-0 with North Carolina 635 State University, and funds from the Diversified 636 Energy Corporation. The authors would like to 637 thank Seung-Hyun Cho and Daniel Janek for their 638 contributions. The US Environmental Protection Agency through its Office of Research and Devel-639 640 opment partially funded and collaborated in the

641 research described here. The views expressed by the individual authors, however, are their own 642 and do not necessarily reflect those of the US Envi-643 ronmental Protection Agency. 644

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