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Executive Summary

The primary objectives of this work can be summed into two major categories. Firstly, the fundamentals of the combustion of glycerol (in both a refined and unrefined form) were to be investigated, with emphasis of the development of a system capable of reliably and repeatedly combusting glycerol as well as an analysis of the emissions produced during glycerol combustion. Focus was placed on quantifying common emissions in comparison to more traditional fuels and this work showed that the burner developed was able to completely combust glycerol within a relatively wide range of operating conditions. Additionally, focus was placed on examining specific emissions in more detail, namely interesting NOx emissions observed in initial trials, acrolein and other volatile organic emissions, and particulate and ash emissions. This work showed that the combustion of crude glycerol could result in significantly reduced NOx emissions as a function of the high fuel bound oxygen content within the glycerol fuel. It also showed that when burned properly, the combustion of crude glycerol did not result in excessive emissions of acrolein or any other VOC compared to the combustion from more traditional fuels. Lastly however, this work has shown that in any practical application in which glycerol is being burned, it will be necessary to explore ash mitigation techniques due to the very high particulate matter concentrations produced during glycerol combustion. These emissions are comparable to unfiltered coal combustion and are directly tied to the biodiesel production method.

The second focus of this work was directed to developing a commercialization strategy for the use of glycerol as a fuel replacement. This strategy has identified a 30 month plan for the scaling up of the laboratory scale burner into a pre-pilot scale system. Additionally, financing options were explored and an assessment was made of the economics of replacing a traditional fuel (namely natural gas) with crude glycerol from biodiesel production. This analysis showed that the cost of replacing natural gas with crude glycerol requires a strong function of the market price per unit of energy for the traditional fuel. However, the economics can be improved through the inclusion of a federal tax credit for the use of a renewable fuel. The conclusion of this analysis also shows that the ideal customer for energy replacement via crude glycerol is biodiesel producers who are located in remote regions, where the cost of energy is higher and the cost of crude glycerol is lowest. Lastly, the commercialization strategy analyzed competing technologies, namely traditional natural gas and electric heaters, as well as competing glycerol burners, and concludes with a discussion of the requirements for a pilot demonstration.

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Disclaimer:

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Introduction

As worldwide production capacity of biodiesel fuel increases, there will be ever greater opportunities to utilize glycerol, a byproduct of the biodiesel process, in transformative ways to increase the industrial energy efficiency and economic viability of both the biodiesel production process as well as other energy-intensive industries like aluminum. In the transesterification of fats, oils, or lipids into fatty acid methyl esters (FAME), glycerol is a necessary byproduct, accounting for approximately 10% of the initial feedstock mass. Depending upon the feedstock, the glycerol may contain alcohol, water, catalyst, and a whole host of other organic material collectively called MONG (mater organic non-glycerol). In 2009, the US biodiesel production capacity exceeded 2.24 billion gallons per annum and was expected to add another 1.2 BGY over the next 18 months, according to the US Biodiesel Board. Due to the poor economics however, the US is currently utilizing less than 25% of this capacity. The market for the resulting glycerol is already saturated, and when the actual production approaches the stated capacity, the degree of saturation will only increase. For example, crude glycerol is currently trading at \$0.02 – 0.05/lb, rendering it so low in value that many biodiesel producers are stockpiling it while they wait for a better use for it to materialize (hence the impetus for this proposal). Although pharmaceutical grade glycerol is selling for \$0.20/lb, the cost of purifying crude glycerol to this level of purity is not cost effective. Another option is to reform the glycerol by polymerization and this research is ongoing with some academic, but not necessarily practical, success. Yet another option is the gasification of glycerol into syngas – a high capital cost option. Perhaps the most economically viable solution for glycerol is the direct conversion of it into heat and work, using boilers or diesel engines. If this glycerol were burned in place of fossil fuels, it is estimated that the user could reduce their annual CO_2 emissions by 1.3×10^6 tons/yr.

In the search to find a value-added alternative that can be implemented locally at the biodiesel production facility to increase both energy efficiency and economics or sold to nearby energy-intensive industries, combustion may be one of the simplest and most feasible solutions. Both electrical and thermal inputs are required in almost all production processes, and these are costs, which the producer must cover, making already marginally competitive processes even more difficult. Additionally, these electrical and thermal inputs are typically supplied via fossil fuels. By locally burning the waste glycerol, the carbon footprint is reduced and the economics of the production process, biodiesel or other, are enhanced. Emphasis is placed on local consumption because the economics dictate that it is not cost effective to transport this low-value glycerol very far. In this phase of the project a team from NC State University, Alcoa Corporation, and Applied Combustion Technologies seek to further the development of clean glycerol burning technology and demonstrate the economic feasibility of converting waste glycerol into heat and/or power locally.

Due to physical properties such as a high viscosity (about 1.5 Pa-s at room temperature), low energy density (17 MJ/kg), high auto-ignition temperature (about 390°C) and low volatility (290°C boiling point), glycerol is more difficult to atomize, mix with air, and combust compared with other biofuels. A second difficulty with glycerol is that acrolein (the three carbon aldehyde), which is a toxic substance at the ppm level, is formed when glycerol thermally decomposes at temperatures above 350°C. A third difficulty is that the crude glycerol generated during biodiesel production contains catalyst salts, water, perhaps alcohol, and other impurities, depending upon the feedstock. The last difficulty is that there are many available feedstocks for biodiesel production and different feedstocks result in significant differences in the crude glycerol quality.

Before any of these processes utilizing glycerol may be realized, these difficulties must be addressed, which was the objective of the current work. Additionally, it was important to develop a commercialization plan in order to identify target crude glycerol end-users and develop a deeper understanding of the economics of glycerol combustion as a fossil fuel replacement for onsite heat and power generation.

Background

Glycerol has not previously been used as a low-cost, low-BTU fuel, and as such the combustion characteristics are not well understood. Therefore the primary objectives of this proposal are to develop a system capable of addressing the hurdles associated with effectively burning glycerol and then to characterize the emissions generated during combustion. As a subset of the first primary objective, several of the unique properties of glycerol must be accounted for.

The physical properties of glycerol make it a difficult fuel with which to work. The viscosity of glycerol is very high, approximately 1.5 Pa-s at room temperature. This high viscosity makes it difficult to properly atomize the fuel, thereby reducing the mixing of the fuel with air and resulting in larger droplets. This issue is compounded by the high auto-ignition temperature and low volatility (as defined by the boiling point) of glycerol (390°C and 290°C respectively). Lastly, glycerol has a relatively low energy density, resulting in a smaller release of energy per mass of fuel than other more traditional fuels. As a result glycerol is more difficult to create and sustain a proper flame. This issue is compounded by the similarity between the glycerol molecule and an acrolein molecule. Acrolein is the three-carbon aldehyde and is toxic at relatively low concentrations. Acrolein can form when glycerol is thermally decomposed at temperatures above 350°C, signifying that if glycerol is not properly and completely combusted, larger concentrations of acrolein can be produced.

The composition of crude glycerol is an additional issue. Crude glycerol is actually a catch all term for the non-biodiesel waste stream after the FAME has been removed. As such, crude glycerol often contains high concentrations of alcohol (most frequently methanol), metals and their salts (most frequently sodium from the sodium hydroxide catalyst as well as other metals), unreacted free-fatty acids and unreclaimed biodiesel, and some water. Additionally, this composition can vary widely based on many factors, ranging from the quality of the feedstock and the manufacturer's production and separation techniques. This requires that a system designed for glycerol combustion be very robust and compatible with a wide range of qualities of fuels.

In order to achieve the primary objectives listed above, the following steps comprise the technical approach for studying crude glycerol as a biofuel:

1. Characterize the quality and composition of the crude glycerol waste stream as a function of feedstock and production process.
2. Examine the spray characteristics of the varying glycerol compositions. It is vital is gain an understanding of the spray as a function of the properties of the fuel in order to ensure efficient atomization.
3. Measure combustion generated emissions from glycerol fueled flames utilizing an optimized atmospheric pressure swirl stabilized flame.

4. Measure the spray characteristics and emissions from combustion of crude glycerol in an industrial boiler to demonstrate the ability to scale-up the combustion technology.
5. Refine capital, operations, and maintenance projections of a commercial burner.
6. Assess the feasibility of integrating the glycerol burner technology into Alcoa's various processes.

Preliminary research had been done addressing some of these issues. Through internal funding from North Carolina State University, an initial design for a modified swirl burner capable of burning glycerol was investigated. This design incorporates a glycerol atomization system designed to address the difficulties associated with glycerol combustion described above. This system utilizes an air atomizing nozzle to reduce droplet size, thereby increasing the rate of evaporation of the droplet. This burner also utilizes an insulated combustion section to augment thermal feedback from the energy released in combustion back into the evaporating fuel. This system operates by first preheating with a traditional hydrocarbon fuel and then switching over to glycerol once the combustion chamber is hot.

Basic emissions measurements have been made using this modified swirl burner. These measurements include CO, NO_x, and unburned hydrocarbons. Initial results showed low levels of these emissions, however, future tests are needed to provide quantified results. Additionally, exhaust gas samples were collected and reacted with a DNPH-cartridge in order to measure aldehydes, such as acrolein. These tests showed aldehyde formation to be comparable to traditional hydrocarbon fuels. However, aldehydes are very difficult to measure and sample retention in the DNPH-cartridge is poor. Therefore, these tests also need to be repeated with a more accurate and sophisticated sampling technique intended for such complicated organic chemistry.

Burner Construction and Experimental Apparatus

The first step in the completion of the above objectives was to develop a more sophisticated burner set up to facilitate a greater suite of testing capabilities while maintaining the original geometries of the modified swirl burner which are designed for use in a practical boiler system. Figure 1 shows a series of photographs comparing the original modified swirl burner with the newly developed apparatus.

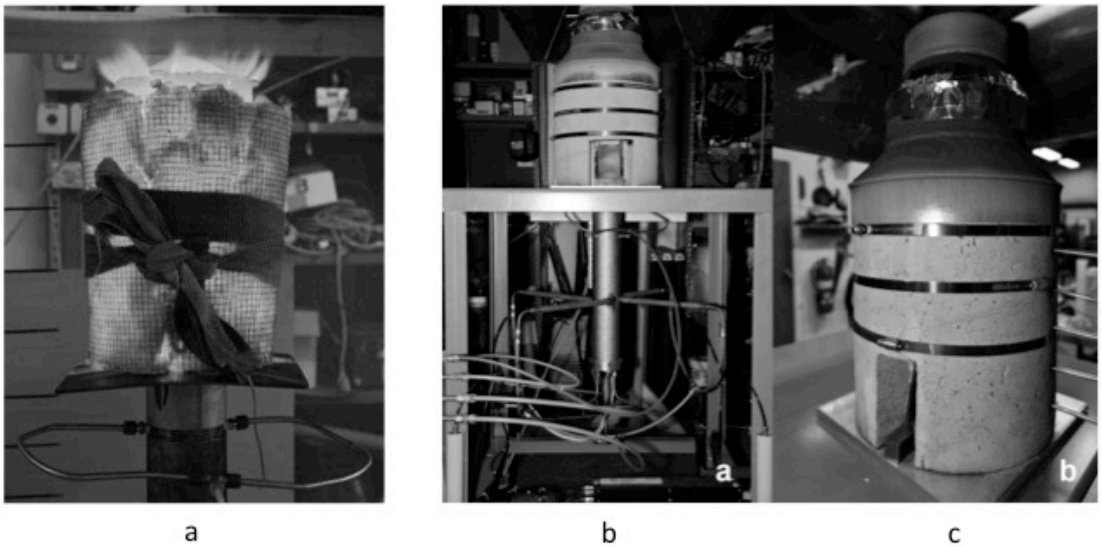


Figure 1: a) Original modified swirl burner, b) improved swirl burner experimental apparatus, c) detailed view of improved combustion chamber

Figure 1 a shows the original burner, composed of a mixing chamber and a metallic combustion chamber wrapped in an insulating blanket. Figure 1 b and c shows the remodeled burner apparatus, with easily accessible mixing chamber and fuel delivery system. Additionally, a new cast refractory combustion chamber was made to provide greater insulation, longer life (the older metallic combustion chambers tended to corrode and deform over time), and access for additional measurements including optical access through a front window and two opposed side windows as well as a bank of thermocouples along the wall of the combustion chamber for temperature profile measurements. Using this system, it is now possible to examine common gas phase emissions, temperature profiles, exhaust gas temperature, and a qualitative analysis of the global flame structure.

As mentioned above, glycerol presents several difficulties to its use as a fuel. The spray burner utilizes a high-swirl stabilized turbulent jet diffusion flame in order to effectively combust glycerol. The difficulties associated with high viscosity fuels include fluid handling and achieving adequate atomization. The burner uses an air-atomizing nozzle specifically designed for high viscosity fuels and is commercially available. The low energy density and high auto-ignition temperature present a coupled problem in which the total heat released and the heat release rate are not sufficient to raise the temperature of the fresh, unburned droplets high enough to sustain combustion if there are significant heat loses or short residence times. This is addressed by utilizing very high swirls and a hot, insulated combustion chamber. The chamber is preheated using a traditional hydrocarbon fuel until steady state is achieved and then the fuel supply is switched to pure glycerol. The high thermal feedback of the hot chamber coupled with the increased residence time and mixing with hot combustion products due to the swirl allow adequate time for the glycerol droplets to evaporate, combust, and release heat back into the system to sustain combustion.

Figure 2 shows the various flow paths within the burner system. The combustion air stream is composed of three flows: axial, tangential, and atomizing. The axial and tangential streams make up the bulk of the total combustion air while the atomizing stream is responsible for creating a fuel spray through the air atomizing nozzle. Axial air enters at the input labeled A and tangential enters at B through four inputs ordered tangentially around the perimeter of the mixing chamber. These two streams mix together and advect upwards, through a venturi and into the combustion chamber. The sudden expansion of the swirling combustion air creates a central low pressure region resulting in a toroidal recirculation zone around the base of the combustion chamber. It is into this recirculation zone that the fuel is sprayed, increasing residence time through entrainment in the recirculation zone as well as mixing with combustion products.

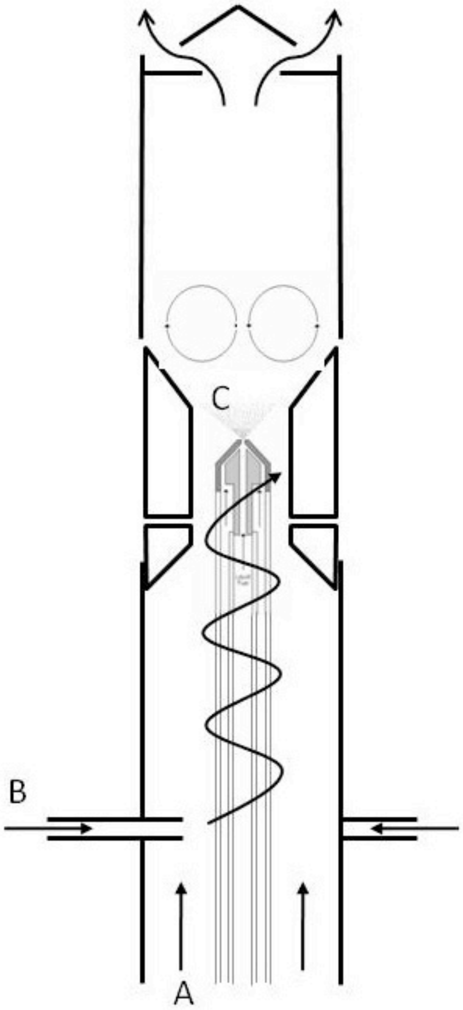
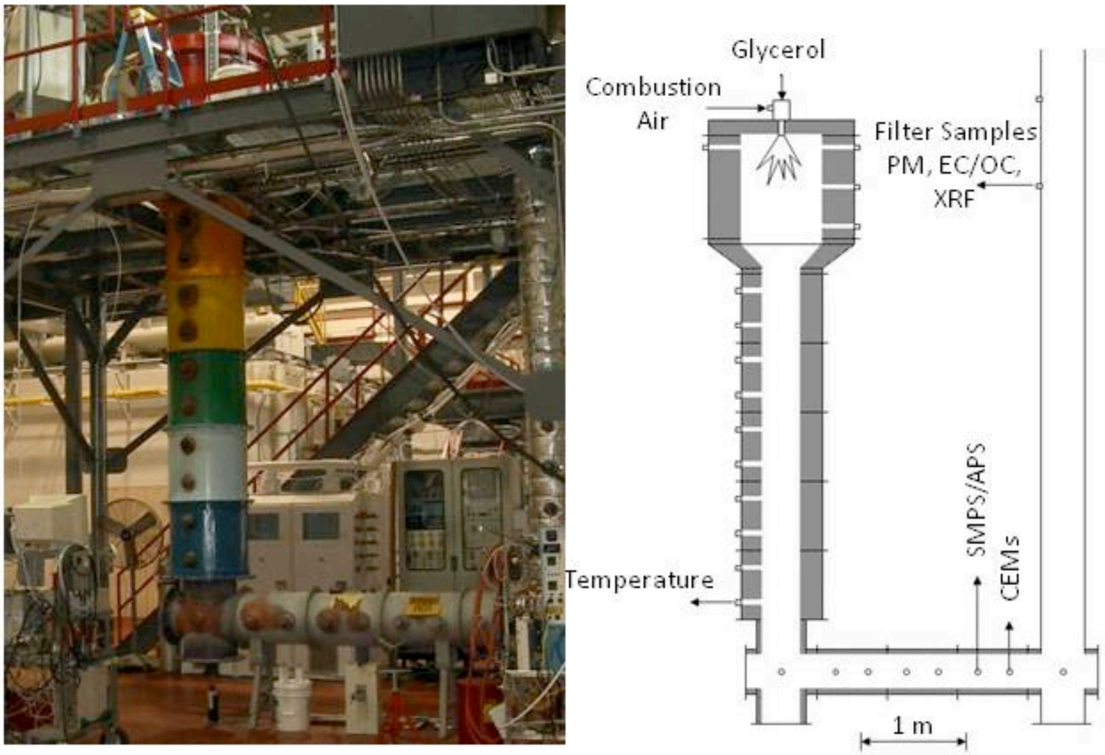


Figure 2: Cross sectional view of flow paths within burner with axial (A), tangential (B), and atomizing (C) air flows

In addition to the newly built experimental apparatus, a refractory furnace was utilized at the Environmental Protection Agency in Research Triangle Park. This furnace is fully instrumented and provides an opportunity to take advantage of the resources available at the EPA, especially with regards to sophisticated organic species measurements, particle size distribution measurements, and larger scales. This furnace is shown in Fig. 3 and the analysis capabilities of this furnace are discussed in greater detail below.

Combustion of natural gas, no. 2 fuel oil, two crude glycerol fuels (methylated and demethylated), and technical grade glycerol was performed in a vertical refractory-lined furnace. This furnace, rated at 82kW, utilized an International Flame Research Foundation (IFRF) movable-block variable-air swirl burner. All experiments were performed at its maximum setting corresponding to a swirl number of ~1.8. Continuous emissions monitors (CEMs) measured exhaust concentrations of O_2, CO_2, CO, NO, NO_2 and total hydrocarbons (THC) similarly to methods described in 40 CFR 60, Appendix A. Temperatures were monitored near the burner and in the stack. PSDs were determined using a TSI Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS). Together, these instruments cover particle diameters from 15nm to 20μm. A stainless steel sampling probe was used to dynamically dilute flue gas to prevent water condensation. Dilution prevented issues related to the effects of liquid water on sample conditioning (particle removal), VOC solubility in the sample containers (SUMMA canisters), and reduced concentrations to levels more appropriate for analysis.



a b

Figure 3: a) Vertical lined refractory furnace , b) sampling locations showing suite of analysis techniques available

Compressed nitrogen was used as the diluent, and was introduced at the probe tip. Furnace and sample NO_x measurements were compared to determine dilution ratios (~70:1 for PSDs, 10-60:1 for VOCs). Three PSDs were averaged for each fuel. Further details are available elsewhere.

Cold Flow Droplet Distribution

Before analyzing combustion properties in the new apparatus, it was important to examine the spray characteristics from the air atomizing nozzle in order to compare the relative droplets sizes and their distributions between the glycerol spray and that made the comparison fuel, diesel. These distributions can be seen in Fig. 4 below.

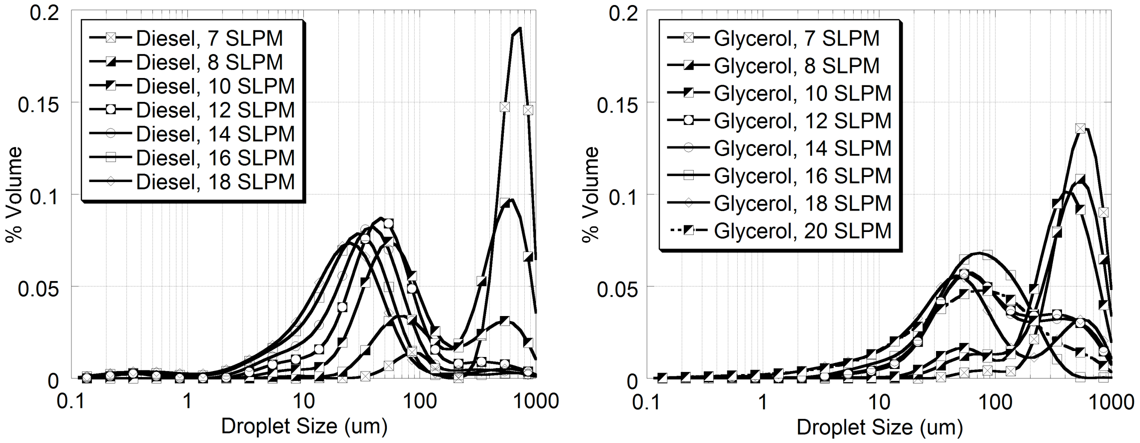


Figure 4: Cold flow droplet size and distribution for diesel (left) and glycerol (right)

Measurements were made using a Malvern Spraytec aerosol and spray droplet size analyzer. The air atomizing nozzle alone was tested in a separate apparatus and measurements were taken over a range of atomizing air flow rates at a distance of 2.5cm from the tip of the nozzle. The diesel and glycerol were sprayed at 25 and 60°C and fuel flow rates of 15 and 31mL/min, respectively. These conditions matched those used in the experiments discussed above. Figure 4 shows the distributions of droplet sizes for diesel and glycerol, respectively, with percent of total volume as a function of droplet size plotted for a series of atomizing air flow rates from 7 to 20SLPM. For both fuels at low atomizing air flow rates, the droplet size distributions are bimodal with peaks centered on 90 and 700μm for diesel and 80 and 600μm for glycerol at 7SLPM. As the atomizing air flow rate was increased, the number of large droplets decreased dramatically and the diesel spray transitioned to a single peak of progressively finer droplets. Diesel atomized using an atomizing air flow rare of 16SLPM resulted in a peak centered on 30μm with 90% of droplets smaller than 58μm and a Sauter Mean Diameter (SMD) of 6μm. The glycerol spray exhibited a similar trend but resulted in overall larger droplets. Glycerol atomized using an atomizing air flow rate of 16SLPM resulted in a peak centered around 70μm with 90% of droplets smaller than 182μm and an SMD of 15μm. Figure 4 shows empirically that the diesel spray creates many more small droplets than the glycerol spray, due to the differences in viscosity (86cP and 1.4cP for 60°C preheated glycerol and 25°C diesel, respectively), surface tension (60.5 and 24.8dyne/cm for glycerol and diesel, respectively), and volumetric flow rate. Due to longer evaporation times and lower Stokes number, glycerol droplets will tend to not follow the gas phase recirculation zones, but rather overcome the negative velocity along the centerline (due to the recirculation zone) or be centrifuged out to the walls of the combustion chamber, ultimately further increasing their evaporation time. Contrastingly, the smaller droplets of the diesel spray will tend to evaporate more quickly and closer to the exit of the nozzle.

Common Emissions Measurements

USP grade glycerol combustion was examined in the prototype refractory burner over a range of swirl numbers and equivalence ratios and compared to operation with propane and No. 2 fuel oil. All three fuels generated either no or negligible ash, as we wanted to avoid ash formation and deposition in these tests and concentrate on flame ignition and stability issues. Propane was chosen as it represents a similar (but non-oxygenated) three-carbon alkane, similar to glycerol. No. 2 fuel oil was chosen to examine and compare atomization using a common liquid fossil fuel. Both propane and No. 2 fuel oil have heating values (46.2 and 42.5MJ/kg, respectively) significantly greater than glycerol. We decided to match the burner load for all three fuels (7kW). This corresponds to fuel feed rates of 28.0, 9.6, and 10.3g/min for USP glycerol, propane, and No. 2 fuel oil, respectively. Glycerol combustion was examined over a wide range of air flows and swirl. Equivalence ratios were evaluated by using a predetermined glycerol flow rate based on desired power output and then airflow was adjusted (both total and swirl) to achieve a stable flame, whereby the flame was entirely contained within the chamber through the full range of swirl. The highest air flow was chosen where the glycerol could burn through the full range of swirl without blowout. Equivalence ratios were determined based on measured air and fuel flows and confirmed from measurements of exhaust O2. Stable and optimum operation was achieved over a range of three air flow rates (210, 227, and 243SLPM) for swirl numbers from 2 to 10. Interestingly, accounting for fuel oxygen, these conditions correspond to low global equivalence ratios (Φ=0.37-0.44). Corresponding air flows and swirl using both propane and No. 2 fuel oil were not possible as the flames tended to blowout. This was due to the flow rate of air through the atomizing nozzle required to atomize the highly viscous glycerol. When the fuel was switched to a less viscous fuel, the high air flow rate through the small orifice created too great a velocity which blew out the propane and diesel flames. Stable operations were achieved at air flow rates of 180 and 202SLPM for propane and 172 and 195SLPM for No. 2 fuel oil for all swirl numbers (2-10) examined. These conditions correspond to global equivalence ratios between 0.48 and 0.65. Lower air flow rates for the glycerol case did produce stable flames for some swirl conditions, but not for the full range, and thus it was difficult to resolve the disparity in the equivalence ratios. The recirculation zone strength will scale with the swirl number. For all swirl numbers investigated here, the flame was stable. The mean exhaust gas temperature decreased with decreasing swirl number, and was fairly insensitive to swirl number at high swirl.

Table 1 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. Interestingly, NOx emissions for the glycerol flames were exceedingly low (7-10ppm, 0% O2) compared to those for the two fossil fuels (110-140ppm, 0% O2). This was true even though O2 levels during glycerol combustion were very high. Except for NOx, these emissions did not have a notable dependence on the swirl number over that range examined. A slight increase in NOx formation with increasing swirl number as would be expected with a more compact flame. 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 2413K, respectively. The adiabatic flame temperature for glycerol is slightly lower, which may contribute to the reduced NOx formation. However, these differences in temperature are not large enough to account for all the disparity. This may indicate that the thermal NOx mechanism is not the dominate mechanism, but NOx formation is rather a combination of thermal and prompt mechanisms, both of which may be suppressed in the glycerol case. It is unlikely that there is any significant contribution of fuel NOx formation due to very low levels of nitrogen in all three fuels. One possibility is that there is greater partial premixing in the glycerol case which may contribute to reduced thermal NOx formation. Appleton and Heywood show that with better atomization, NOx formation is reduced as global equivalence ratios decrease. However, the glycerol case should exhibit lower partial-premixing due to its higher boiling point compared with No. 2 fuel oil. Additionally, propane should exhibit the most premixing due to being a gaseous fuel. Therefore, it seems unlikely that glycerol has greater partial premixing. If large differences in peak flame temperature and partial premixing cannot explain the dramatically different NOx levels, one possible explanation is the very large fuel-bound oxygen content of the glycerol (~52% by mass). Unfortunately, there is no work in the literature with fuels with such high fuel-bound oxygen contents and what effect this may have on NOx formation is not well understood. However, the presence of so much oxygen within the fuel may contribute to a broadening of the flame front, thereby reducing peak temperatures. The presence of so much fuel-bound oxygen may also inhibit the prompt NOx mechanism. The NOx formation is not inhibited by the presence of fuel-bound oxygen in the propane and diesel flames and may proceed through a combination of both prompt and thermal mechanisms, while both mechanisms could be inhibited in the glycerol flame. It was attempted to examine this effect by mixing glycerol with other non-oxygenated fuels. However this effort failed due to the high polarity of glycerol and its immiscibility with most fuels. Further work needs to be done to understand the effect of high fuel oxygen content on NOx emissions.

Table 1: Emissions measured from 7kW swirl burner and 82kW refractory furnace

	7kW Prototype Burner							82kW Furnace	
	USP Glycerol			Propane		No. 2 Fuel Oil		Methylated	De-methylated
Load (kW)	7.3	7.3	7.3	7.4	7.4	7.3	7.3	80.5	53.9
Φ[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
NOx (ppm)	3.0	3.5	3.6	60.2	62.8	74.7	62.5	146.5	118.3
NOx 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. (°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 O_2 in the exhaust.

[b] Temperature measured at the throat of the exhaust for the 7kW prototype burner and at the exit of the 82kW refractory-lined furnace.

[c] Adiabatic flame temperature calculated at stoichiometric ratios listed above.

Both methylated and demethylated crude glycerol fuels burned reasonably well in the refractory-lined furnace without fossil fuel co-firing. In fact, the warmed demethylated glycerol fed more consistently through the air atomizer than the methylated fuel which, due to its lower viscosity, required larger amounts of fuel and atomizing air to produce a stable spray. This difference in viscosity accounts for the higher load and excess air reported in Table 1 for this fuel. The required high fuel feed rates (due to low heating values) produced long flames which were shortened by maximizing the IFRF burner swirl (1.8). Interestingly, the refractory-lined furnace uses a UV-based flame safety system, and although both fuels produced stable flames (base on visual observations) the UV detector had difficulties establishing a stable signal. Eventually, a flame rod was substituted and stable flame signals were established. The equivalence ratios were determined based on exhaust O2.

Table 1 presents the results of the gas-phase emission measurements averaged over the course of three replicate experiments. These results indicate that glycerol combustion in a refractory-lined furnace produced gas phase emissions comparable to previous experiences with fossil fuels (natural gas and No. 2 fuel oil). Unfortunately, accurate CO emissions could not be determined due to instrument malfunction. However, both total hydrocarbon concentrations as well as total carbon (TC) concentrations in the fly ash were consistently low and typical of emissions indicating reasonably complete combustion. Oxygen levels were slightly elevated, but this was a consequence of maintaining proper fuel atomization and the high inherent oxygen contents of the glycerol fuels. Concentrations of NOx (~150-240ppm, 0% O2) were typical of the relatively high combustion temperatures and low fuel nitrogen contents. The data suggest that the demethylated glycerol produced slightly less NOx than the methylated fuel. It is notable that the prototype burner produces NOx emissions significantly lower (~6ppm, 0% O2) than those measured in the refractory-lined furnace. This difference in NOx emissions may be related to the variation in swirl (1.8 compared to 2-10), but is most likely related to the longer residence times in the refractory-lined furnace. The prototype burner was able to maintain stable glycerol flames at global equivalence ratios beyond the operating range for the other fuels examined (propane and diesel). It should be noted, however, that the crude glycerol fuels examined in the refractory-lined furnace were not the same as the USP glycerol examined in the prototype burner. The presence of MONG and other process by-products in the crude glycerol fuels reduces the fuel oxygen and may well affect NOx formation. Because of the large differences in fluid dynamics, swirls, and residence times between the two experimental systems, it is difficult to compare NOx emissions. However, comparisons within their individual systems is valid and of interest.

Analysis of Global Flame Structure in Prototype Burner

Photographs were taken of the flame's natural luminosity while varying atomizing air flow rate to access global flame structure features. These photos can be seen in Fig. 5, where the upper set of photos is of the diesel flame while the lower set is of the glycerol flame. In both sets of images, atomizing air flow rate increases from left to right while the swirl number, power, and total air flow rate (210SLPM) are held constant throughout. Global equivalence ratio was held at 0.67 and 0.22 for diesel and glycerol, respectively. While the power is held constant, it is import to remember that the large disparity in energy densities requires approximately three times the mass flow rate of fuel through the nozzle for glycerol compared to diesel. Exposure times and aperture values were held constant throughout all the images and neutral density filters were used with the diesel images to avoid detector saturation.

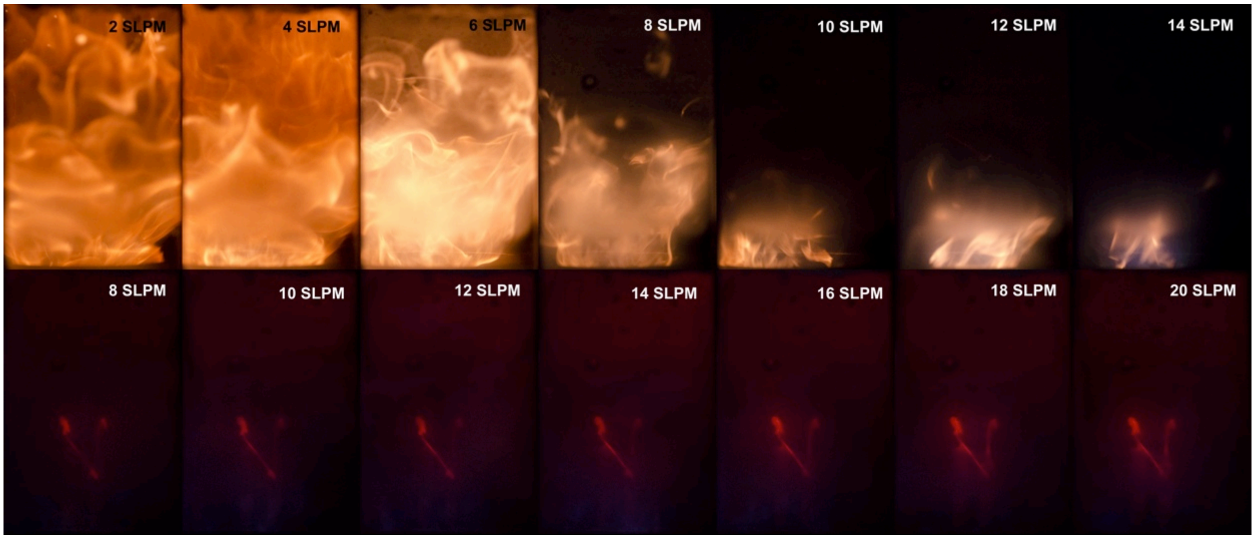


Figure 5: Photographs showing natural luminosity for diesel (upper) and glycerol (lower) flame with increasing atomizing air flow rate

It is immediately apparent that the glycerol flame is far less luminous than the diesel flame, indicating that glycerol has a much lower propensity to form soot than diesel due to its high degree of oxygenation. A second observation is that changes in atomizing air flow rate have a significant impact on the structure of the flame. It is interesting to note that it was possible to increase atomizing air flow rate in the glycerol flame significantly higher than 20SLPM, much higher than it was possible to spray the diesel. At the low end of atomizing air flow rate for both fuels, the flame is very wrinkled and large droplets of liquid fuel are occasionally observed far from the nozzle. Lower than 5SLPM, the diesel flame completely fills the field of view while increasing atomizing air flow rate causes the flame to become more compact. For both fuels at high atomizing air flow rate, the flame is extremely compact and very blue, indicating significantly reduced soot formation. There appears to be a transition in flame shape around 7SLPM for the diesel flame and around 12SLPM for the glycerol where the flame transitions from a large, wrinkled flame with significant interaction with the recirculation zone to a compact, much less luminous flame. This transition can be attributed to observations made by Chen *et al.* when examining the influence of the fuel jet momentum on the recirculation zone of swirling flames. It is clear from these images that when the fuel jet momentum becomes sufficiently large, the fuel jet is able to overcome the reversed flow along the centerline and the flame is not contained within the recirculation zone. This transition is clear in the 8SLPM image in Fig. 5 for the diesel case, and while harder to see, the same has been observed for the glycerol spray.

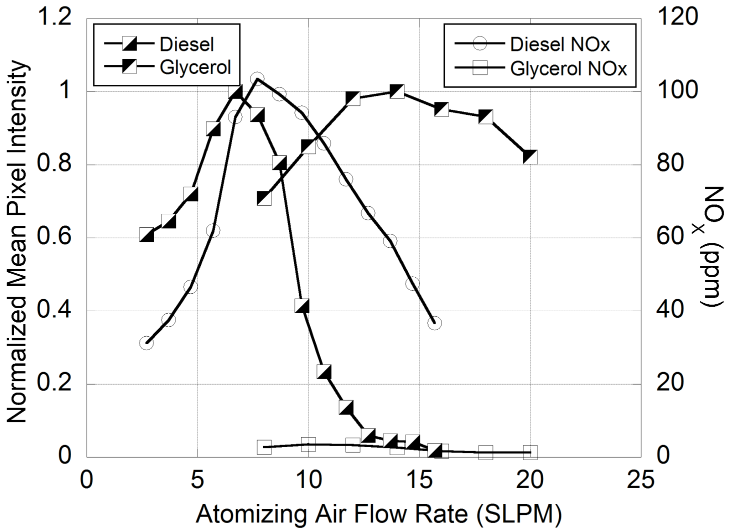


Figure 6: Normalized mean pixel intensity for natural luminosity and NOx formation as a function of atomizing air flow rate

Figure 6 shows average intensities of the images in Fig. 5 and the measured NOx level as a function of atomizing air flow rate. Pixel intensity values are normalized by the maximum average value for each fuel. Diesel luminosity peaks around 7SLPM while glycerol luminosity peaks around 12SLPM, which is consistent with a change in the flame shape as described above. For diesel, peak NOx occurs around 8SLPM and appears to mirror the same trends as the soot intensity inferred from the luminosity, but offset to a slightly higher atomizing air flow rate. It is reasonable that peak NOx would be offset from peak flame luminosity due to the large soot volume fraction increasing radiative losses and lowering peak temperatures. Glycerol peak luminosity and peak NOx occur near the same value, as would be expected with so little soot formation and the resulting radiative losses being relatively insignificant.

Volatile Organic Compound Measurements

Acrolein and other VOC measurements was accomplished in the refractory furnace through collection of diluted flue gases in SUMMA canisters followed by analysis by Gas Chromatography-Mass Spectrometry (GC-MS) following EPA method TO-15. All samples were collected in 6L SUMMA passivated canisters. Prior to sample collection, canisters were cleaned in an oven at 373K by evacuating them to 0.13kPa with a molecular drag pump and then filling them with humidified nitrogen to 138kPa. This cycle was completed five times before the canisters were brought down to their final pressure of 1.33Pa. Canisters were cleaned in batches of 12 and canister cleanliness was assessed by batch blanks. The acceptance criterion was 0.2ppbv for VOC species on the TO-15 analyte list.

Dynamically diluted VOC sampling was performed using an in-stack dilution probe. An acrolein/air mixture, used for spiking, was generated using a Valco Instruments Co. Inc. (VICI) dynacalibrator permeation oven. Certified VICI acrolein permeation tubes were heated to 308K to emit 550ng of acrolein per minute (rate confirmed by weight change). Maximum dilution flows on the VICI oven allowed the production of an air sample containing 100ppbv acrolein. Spiked canisters were humidified and filled with 0.5sL of spike gas before sampling. Furnace stack samples were collected from dual sampling trains over a span of 20min per sample. Samples were pulled through quart filters, heated to 378K, to prevent particulate matter from entering the canisters. Each of three pairs of samples for glycerol fuels and two pairs for natural gas contained one pre-spiked and one non-spiked SUMMA canister. Comparison of simultaneously sampled cans allows spike recovery rates to be calculated. One additional SUMMA canister for each fuel was spiked. This field spike was present near the furnace during experimentation, and then filled with nitrogen following the experiments. All canisters were filled to a total volume of 5sL, determined by pressure. Experimental conditions are shown in Table 2.

Table 2: Summary of experimental conditions for VOC sampling

		Volatile organic compounds			
	Units	Natural gas	Methylated Glycerol	Demethylated glycerol	Technical glycerol
Fuel flow	LPM	108	0.104	0.142	0.272
Air flow	sLPM	1560	863	1144	1312
Stoich. ratio		0.79	0.65	0.81	0.73
Load	kW	67.0	38.8	62.0	100.6
Stack temp.	K	791	713	878	1024
Burner temp.	K	1345	1267	1339	1318
O_2	%	4.8	7.6	4.2	5.4
CO_2	%	9.6	9.2	13.7	14.8
CO	ppmv	21	31	322	17
NO_x	ppmv	112	45	119	84
NO_x at 0% O_2	ppmv	145	70	149	112
THC	ppmv	9.7	9.7	9.1	17.3

Canister samples were analyzed for VOCs according to U.S EPA Compendium Method TO-15. Samples were preconcentrated with a headspace preconcentrator (Entech Instruments Inc., model 7150) interfaced to an Agilent model 6890 GC and model 5973N MS. The preconcentrator was used to pull a metered volume of sample air (including internal standards) from the canisters, cryogenically concentrate the VOCs, and then transfer the analytes to the GC-MS for analysis. A Restek fused silica capillary column (Rtx®-1, 60m x0.32mm x1.00µm) was used with the GC oven held at 308K for 5min; then ramped at 5K/min to 403K; then ramped to a final temperature of 523K with a 3min hold. Column flow was held constant at 2.0mL/min. The MS source was set to 503K; the MS quad was set to 423K; and selected ion monitoring was utilized for low ppbv detection limits. The entire headspace preconcentrator and GC-MS system was calibrated with a 5-point calibration curve (2.00, 1.00, 0.50, 0.25, and 0.12ppbv) for 82 target organic analytes. Internal standard calibrations were performed using bromochloromethane, 1,4-difluorbenzene, and chlorobenzene-d5. The calibration mixtures were prepared by blending/diluting three commercially prepared mixtures.

Table 3 presents the measured concentrations of VOCs determined by GC-MS analysis of stack samples collected in non-spiked SUMMA canisters. Averages and standard errors are presented for natural gas, methylated, demethylated, and technical glycerol fuels. Concentrations, in ppbv, have been dilution and blank corrected, and species are presented in elution order. One non-spiked canister from both the demethylated and technical glycerol sets was discarded, as the presence of some compounds was detected in abnormally high concentrations. The spiked samples corresponding to the discarded samples had concentrations consistent with the remaining canisters, indicating the abnormality was not in stack emissions. Dilution ratios and preconcentrator injection volumes, which were chosen to keep acrolein concentrations within the GC-MS calibration range, varied by sample. As a result, most other compounds detected were in concentrations below the calibration range, and detection limits for each sample varied. Acrolein emissions ranged between 13 and 39ppbv. Recoveries of known quantities of acrolein (~10ppbv) spiked into selected SUMMA canisters were 172%, 96%, 142% and 140% for natural gas, methylated, demethylated, and technical glycerols, respectively. This variability is thought to be relatively minor and likely the result of spiking inconsistency. Recoveries in field spikes were found to be comparable to recoveries from other canisters spiked at the same time. Additionally, the acrolein spike concentration was chosen before knowing the actual concentrations of acrolein in the emissions. As a result, spike concentrations were higher than diluted stack concentrations. Interestingly, acrolein emissions for crude and technical glycerol were comparable to emissions from natural gas. The conclusions to be drawn are that while actual acrolein emissions from glycerol combustion may differ by a factor of two or three from those measured here, they are still likely to be extremely low, and comparable to those of natural gas. Acrolein emissions from glycerol combustion does not seem to be a major issue of concern, and this is consistent with the stable flames and good fuel burnout observed.

With the exception of ethanol, acetone, and isopropyl alcohol, no other VOC was measured in concentrations higher than 100ppbv. Natural gas and technical glycerol typically produced the lowest and highest VOC concentrations, respectively. However, VOC emission concentrations for all the glycerol fuels were often comparable, and at most, no more than 30 times those of natural gas. It is interesting to note the presence of a number of halogenated VOCs in very low concentrations. These were present in the natural gas emissions and typically in higher concentrations in the glycerol emissions. While extremely low, these measurements are above blank levels and believed to be real. Table 1 indicates that significant quantities of chlorine (100-500ppm) are present in all the glycerol fuels, and this is thought to be the source of the halogen.

Table 3: Acrolein and other VOCs (ppbv)

	Natural gas		Methylated glycerol		Demethylated glycerol		Technical glycerol	
	Average	Standard error	Average	Standard error	Average	Standard error	Average	Standard error
Dichlorodifluoromethane	0.7[ef]	-	2.4[e]	0.5	8.9[ef]	-	ND	-
Dichlorotetrafluoroethane	3.7	0.6	22.7[f]	17.2	52.8[f]	27.0	44.8[f]	17.8
Ethanol	101.5	14.5	191.7[f]	131.1	173.0	9.8	260.7	16.0
Acetonitrile	5.9	2.8	45.5	36.5	<37.8[d]	-	ND	-
Acrolein	13.3	1.8	16.5[e]	9.2	<18.9[d]	-	20.7[ef]	-
Acetone	173.6	1.2	190.2[e]	117.4	<31.0[de]	-	42.1[e]	-
Trichlorofluoromethane	2.5	0.0	2.4[e]	1.2	7.5[ef]	2.6	<12.7[d]	-
Isopropyl alcohol	60.5	11.4	99.7[e]	73.6	<37.8[d]	-	46.5[e]	-
Acrylonitrile	33.5	0.1	36.7[f]	13.7	31.0[f]	2.7	54.1[f]	16.2
Tert-butanol	2.5	0.1	8.3[e]	-	ND	-	ND	-
Methylene chloride	2.1[f]	0.4	7.2[e]	3.9	<6.3[d]	-	<12.9[d]	-
3-chloro-1-propene	0.6[f]	0.0	3.3[ef]	2.4	11.2[ef]	-	6.8[ef]	-
1,1,2-trichloro-1,2,2-trifluoroethane	1.2[f]	0.0	1.2[ef]	0.6	6.7[ef]	-	6.8[ef]	-
trans-1,2-dichloroethene	ND	-	8.1[ef]	1.7	ND	-	ND	-
Vinyl acetate	3.2	0.4	8.5[e]	3.0	ND	-	<8.2[de]	-
2-butanone	14.0	1.4	20.6[e]	15.1	<31.0[de]	-	<33.6[de]	-
Ethyl acetate	0.5[f]	0.0	0.5[ef]	0.2	6.8[ef]	-	7.2[ef]	-
Tetrahydrofuran	3.1	0.1	10.4[f]	6.6	13.3[f]	0.8	21.4[f]	7.9
Ethyl tert-butyl ether	0.5[f]	0.1	ND	-	4.8[ef]	-	11.6[ef]	-
1,1,1-trichloroethane	0.6[f]	0.0	0.6[ef]	0.3	8.4[f]	0.8	13.5[f]	5.3
Benzene	1.3[f]	0.4	1.0[ef]	0.5	6.7[ef]	-	<9.1[d]	-
Carbon tetrachloride	2.2	0.2	10.8[f]	8.8	19.6[f]	4.4	25.6[f]	9.8
1,4-dioxane	1.4[f]	0.9	4.1[f]	2.4	4.5[f]	0.4	7.9[f]	3.1
4-methy-2-pentanone	1.2[f]	0.2	2.0[ef]	1.5	7.8[ef]	-	13.8[f]	5.0
1,1,2-trichloroethane	0.9[f]	-	1.4[ef]	-	18.3[ef]	-	ND	-
Toluene	1.7[f]	0.0	4.8[ef]	3.7	1.6[ef]	-	7.2[e]	0.7
2-hexanone	2.6	0.4	3.7[ef]	2.6	ND	-	20.0[ef]	-
1,2-dibromoethane	0.3[f]	-	ND	-	5.6[f]	0.6	9.0[f]	3.6
Ethylbenzene	0.4[f]	0.0	0.9[ef]	0.6	2.6[ef]	-	5.4[f]	1.2
m-xylene	0.7[f]	0.1	1.7[ef]	1.0	3.8[f]	1.0	12.1[f]	2.4
Bromoform	0.7[f]	0.0	9.3[f]	8.5	13.6[f]	1.4	21.8[f]	8.6
Styrene	0.4[f]	0.0	4.2[f]	3.7	6.1[f]	0.6	9.9[f]	3.7
o-xylene	0.5[f]	0.0	1.1[ef]	0.7	2.8[f]	0.8	8.3[f]	1.7

[a] Non-detect (ND) indicates no response in GC-MS analysis.

[b] The following compounds were detected in average concentrations less than 5ppbv in all fuels: propylene, chloromethane, 1,3-butadiene, 1,1-dichloroethene, carbon disulfide, 1,1-dichloroethane, methyl-t-butyl-ether, 2-chloroprene, cis-1,2-dichloroethene, n-hexane, chloroform, 1,2-dichloroethane, 1,2-dichloropropane, bromodichloromethane, trichloroethene, isooctane, methyl methacrylate, heptane, dibromochloromethane, tetrachloroethene, chlorobenzene, p-xylene, 1,1,2,2-tetrachloroethane, naphthalene.

[c] The following compounds were ND in all samples: vinyl chloride, bromomethane, chloroethane, vinyl bromide, cyclohexane, tert amyl methyl ether, cis-1,3-dichloropropene, trans-1,3-dichloropropene, 1,1,1,2-tetrachloroethane, bromofluorobenzene, cumene, chlorotoluenes, n-propylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, tert-butyl benzene, 1-ethyl-4-methyl benzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, sec-butyl benzene, 1,2-dichlorobenzene, o-cymene, n-butyl benzene, 1,2,4-trichlorobenzene, hexachlorobutadiene.

[d] Below Detection Limits (BDL). Detection limit defined by multiplying the Student's t-value (3.143 for six degrees of freedom) by the standard deviation of seven replicate analyses of a low level calibration standard (50 pptv). Table values adjusted for dilution.

[e] One or more samples were BDL or ND.

fOne or more samples were below the lowest calibration point but above detection limits.

NOx Emissions in Prototype Burner

NOx emissions were measured as a function of global equivalence ratio in the prototype burner and are shown in Fig. 7. For these measurements, the power and the swirl number were held constant as the total air flow rate was varied. A constant swirl number was achieved by varying the axial and tangential flow rates independently while keeping the relative proportions constant. NOx was measured at a constant atomizing air flow rate to remove the droplet size dependence. The glycerol global equivalence ratio was varied from 0.16 to 0.34 (atomizing air flow rate of 8, 14, and 20SLPM) while the diesel global equivalence ratio was varied from 0.56 to 0.86 (atomizing air flow rate of 4, 8, and14 SLPM). Recall that the large difference in global equivalence ratio between the two fuels is due to the high $Y_{O,FB}$ in the glycerol. It was not possible to operate at similar global equivalence ratio because a stable flame could not be achieved at atomizing air flow rates less than 7SLPM in the glycerol case or at flow rates greater than 16SLPM in the diesel case.

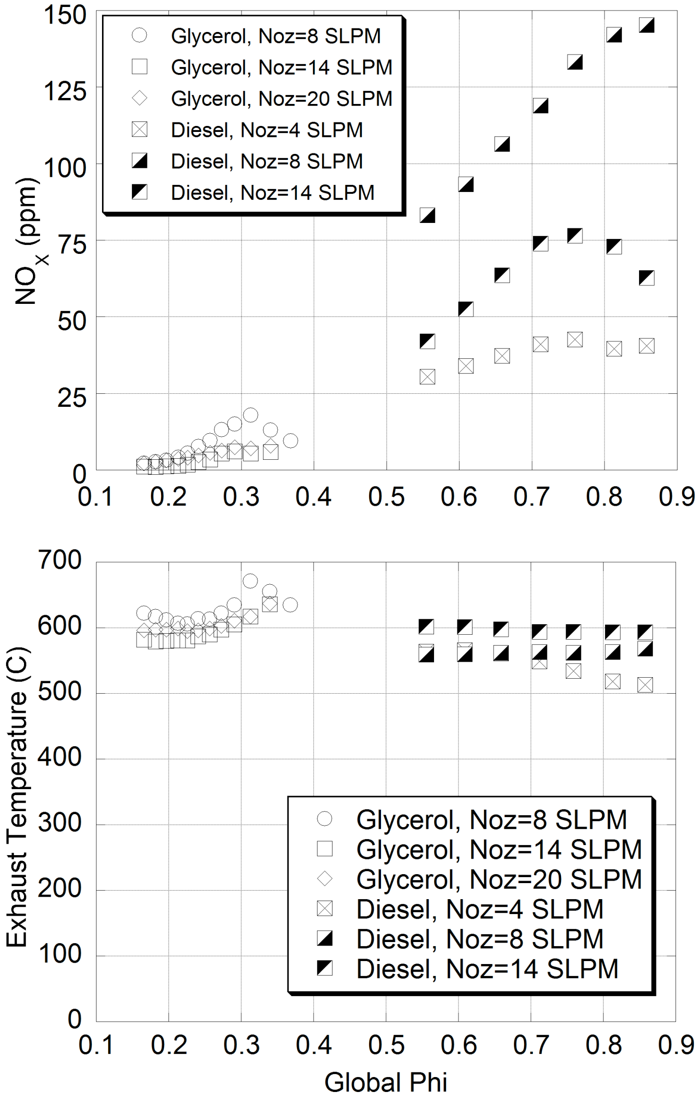


Figure 7: a) NOx emissions and b) exhaust gas temperature measured as a function of global equivalence ratio

Figure 7a shows the very significant difference in NOx levels for the two fuels. As was observed in previous work, NOx emissions in glycerol combustion can be up to an order of magnitude lower in some cases. Increases in NOx emissions with increasing global equivalence ratio are consistent with the dilution effect on temperature. It is interesting to note that the highest levels of NOx were measured at an atomizing air flow rate of 8SLPM for both fuels. Recalling Fig. 4, at 8SLPM much of the fuel is composed of large droplets D>300 μm with a smaller portion of D<100 μm sized droplets. The ideal droplet size distribution for flame stability in this geometry is not necessarily composed solely of small droplets however, but rather a combination of small droplets to anchor the flame and larger droplets to evaporate more gradually. In Fig. 7a, the NOx versus global equivalence ratio trend for both fuels appear to line up, suggesting that if it were possible to burn glycerol at higher equivalence ratio or diesel at lower global equivalence ratio, NOx emissions from the two fuels might be more comparable. This is a topic of current research where blends of fuels are used to span the gap in global equivalence ratio between glycerol and diesel. This is made difficult due to differences in polarity between glycerol and diesel (glycerol being highly polar) making the two fuel immiscible. However, in this burner geometry, attempting to increase the glycerol-air global equivalence ratio to greater than 0.4 resulted in the burner becoming unsteady and the flame extinguishing. Figure 7b shows the exhaust gas temperature (EGT), measured downstream of the exit of the combustion chamber to allow for adequate mixing. As would be expected with a constant power, the exhaust gas temperature is nearly constant between each series. It is also important to observe that calculated adiabatic flame temperatures for glycerol and diesel (approximated as dodecane) are 2201 and 2413K, respectively, a difference not great enough to account for an order of magnitude difference in NOx.

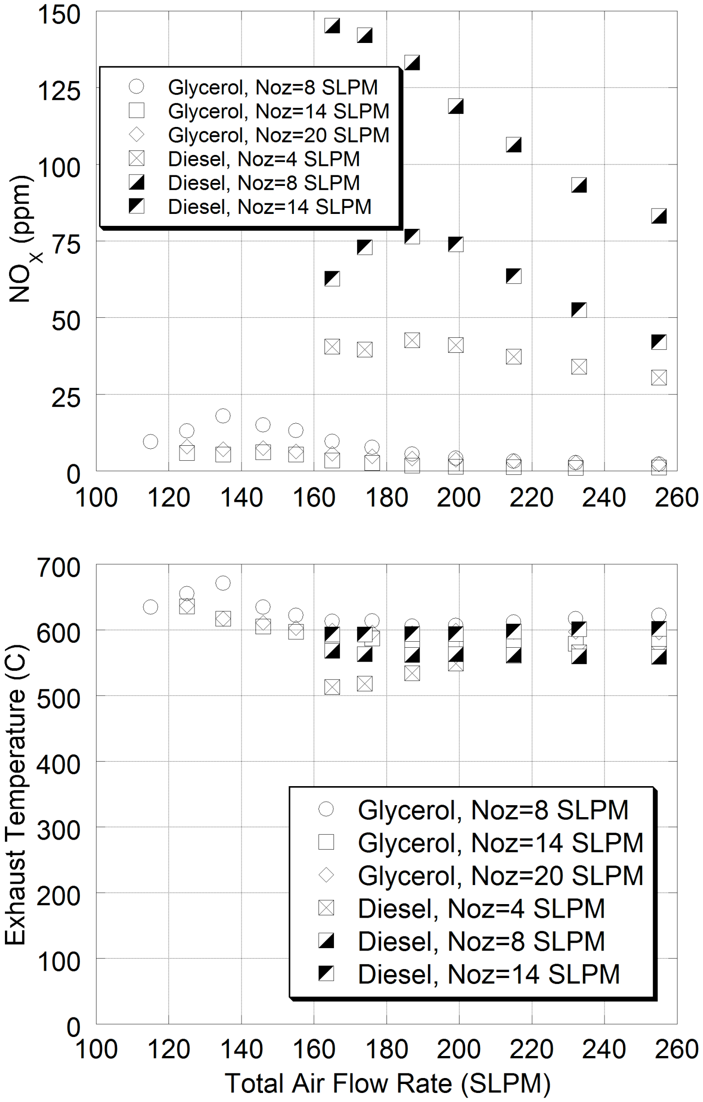


Figure 8: a) NOx emissions and b) exhaust gas temperature rescaled as a function of total air flow rate

Because $Y_{O,FB}$ is so high for glycerol and this is not a premixed flame, it is important to look beyond the global equivalence ratio. Figure 8 rescales Fig. 7 and plots NOx and EGT versus total air flow rate, rather than global equivalence ratio, and shows that at similar operating conditions, NOx formation from glycerol is significantly lower. Recall that power and swirl were held constant throughout the experiment; the only parameter changing was the total combustion air flow rate.

NOx measurements were also made for several different global equivalence ratios over a large range of atomizing air flow rate, including operating conditions for the images above. These measurements are shown in Fig. 9 along with the exhaust gas temperature measured downstream of the exit of the combustion chamber. Power and swirl number were again held constant throughout. Figure 9a shows the large disparity in NOx formation for glycerol compared with diesel as was observed previously. NOx formation peaks around 8 and 10SLPM for diesel and glycerol, respectively. Figure 9b shows the glycerol NOx measurements rescaled. As expected, the measured peak NOx value increases as global equivalence ratio decreases due to the dilution effect. However, at the high and low end of the operational range of the atomizing air flow rate, the NOx emissions for each fuel converges to a single value for each fuel, despite the differences in global equivalence ratio. The reduction in NOx emission with increasing atomizing air flow rate is due to the corresponding decrease in droplet size as discussed earlier. The smaller droplets result in faster evaporation and greater partial premixing with more fuel being burned at off-stoichiometric conditions resulting in reduced NOx formation. The reduction in NOx near the low end of the atomizing air flow rate range corresponds to a growing proportion of the spray as large droplets, which result in a lower heat release rate and ultimately lower peak temperatures although similar exhaust gas temperature. It is also likely that, particularly for extremely large glycerol droplets, reduced evaporation rates coupled with shorter residence times (due to lower entrainment in the recirculation zone characterized by lower Stokes numbers) could result in less than complete combustion by the time the droplet reaches the exit of the combustion chamber. This could also help to explain the decrease in NOx formation seen in Fig. 7 for the 8SLPM atomizing air flow rate series at high global equivalence ratio and corresponding low total air flow rate. According to Chen et al, decreasing the vortex momentum (in this case by decreasing the total air flow rate) decreases vortex strength and allowing a transition in flame structure as discussed above. Despite significant differences in the NOx emissions, not only between fuels but with varying atomizing air flow rate, it is interesting to note that the measured EGT remains nearly constant.

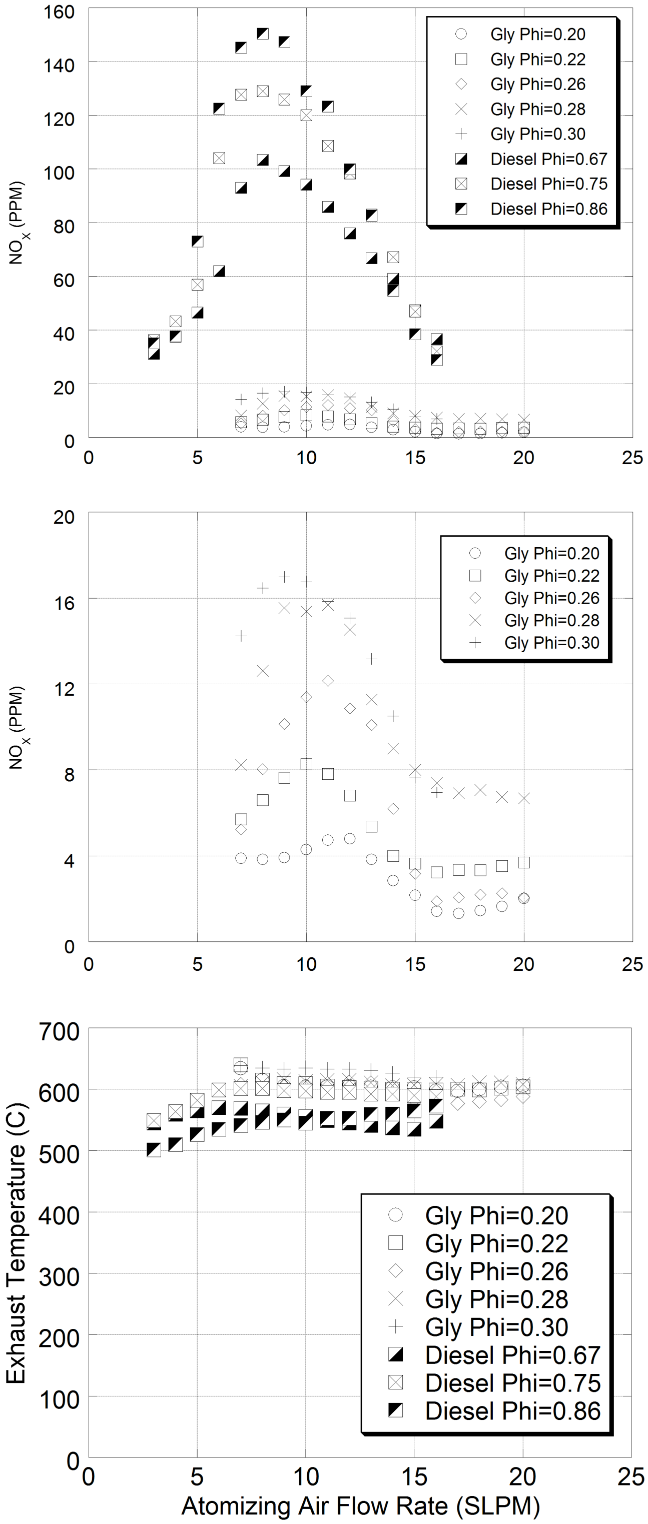


Figure 9: a) NOx formation, b) rescaled NOx formation, and c) exhaust gas temperatures for changes in atomizing air flow rate

Analysis of Fly Ash Size and Composition

Mass concentrations of fly ash determined gravimetrically indicate average emissions of 3380 and 2200mg/m3 for the demethylated and methylated glycerol fuels, respectively. These are very high values and are consistent with the high ash concentrations of these fuels. These values can be compared to concentrations of ~90mg/m3 measured in the same combustor burning a No.6 fuel oil with an ash content of 0.1%. In fact, concentrations of 3000mg/m3 approach those for coal combustion before particulate control. Particle size distributions measured from emissions of the two fuels indicated a large distinct accumulation mode (~100-110nm) suggesting vaporization, nucleation, and coagulation of a significant amount of ash. These results are consistent with the very high alkali metal content of the fuels. These data also indicate the presence of a substantial coarse mode (>5μm), especially for the demethylated fuel.

Table 4: Elemental composition of fly ash

	Methylated	Demethylated
C	4.88	2.74
OC	1.31	0.53
EC	3.56	2.21
O	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
K	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

Table 4 presents a summary of the elemental analyses 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 analyses 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 bio-fuels. Between the unburned carbon and the inorganic elements measured, the majority of the particulate mass composition is identified.

In an effort to further characterize the carbon speciation, similar filter media was spiked with sodium carbonate and sodium bicarbonate. TOT analyses of these samples demonstrated that the resulting thermogram interprets carbonates as mixtures of organic and elemental carbon. Further analysis using Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) verified the possible presence of sodium carbonate in the fly ash samples, as evident by IR responses near 700, 870, and 1450cm-1. Equilibrium calculations were also performed using HSC Chemistry to determine thermodynamically stable species. These calculations were performed for methylated and demethylated glycerol corresponding to system concentrations of fuel and 20% excess air. A total of 85 species, comprised of C, H, N, O, Na, P, S, Cl, and Ca, were considered. Kinetic and mixing limitations are not considered, so equilibrium results need be used with care. Figure 10 presents Na equilibrium predictions for 1atm and system temperatures from 300 to 2500K. At temperatures below a predicted 1700K Na dew point, equilibrium suggests stable condensed-phase mixtures of sodium sulfate (Na2SO4), sodium phosphate (Na3PO4), and sodium carbonate (Na2CO3). These predictions qualitatively agree with the previous XRF and the FTIR-ATR results, suggesting that Na2CO3 is the primary source of carbon in the fly ash and that negligible amounts of unburned carbon are present.

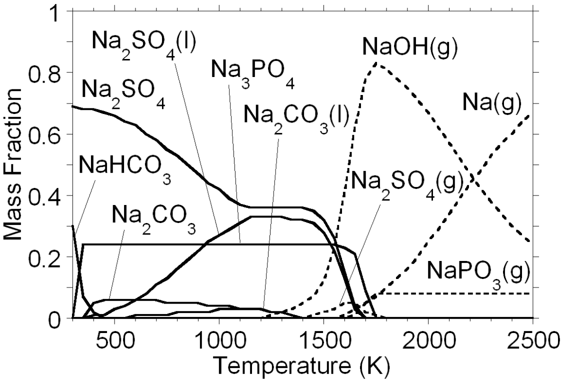


Figure 10: Na equilibrium predictions

Figure 11a presents the averaged measured volume PSDs (with standard errors) for each fuel. The measured PSDs are unimodal indicating well-defined accumulation modes, with mean volume diameters of 0.7 and 0.3μm for the methylated and demethylated glycerol fuels, respectively. There was no evidence of a coarse mode for either fuel. These results indicate that the ash, composed predominantly of alkali and alkaline earth elements, are extensively vaporized during combustion. Once vaporized, the ash species undergo homogeneous nucleation and particle growth via coagulation and condensation processes. The large mean particle diameters indicate extensive particle growth corresponding to very large particle number concentrations. Number concentrations measured at the sampling location were 3.3x108 and 1.6x108#/cm3 for the methylated and demethylated fuels, respectively. It should be noted that significant ash is lost to the furnace walls as evident by the persistence of a large accumulation mode

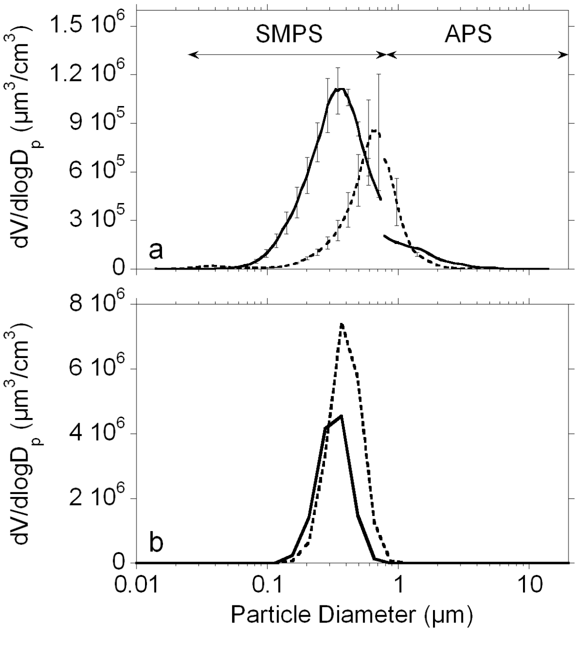


Figure 11: a)Measured particle size distribution and b) multicomponent aerosol simulation for particle coagulation estimation of particle size distribution

measurable during natural gas combustion many weeks after the glycerol experiments. In fact, this furnace contamination made it impossible to close ash mass balances, and indicates that crude glycerol combustion in boilers is not likely until new catalyst options are employed.

Particle coagulation was modeled using the multicomponent aerosol simulation (MAEROS) code to determine the extent that this mechanism could be used to describe aerosol growth. System inputs included an assumed particle density of 2.2g/cm3 and mass concentrations of 5050 and 3310mg/m3 corresponding to the calculated ash concentrations for methylated and demethylated fuels, respectively. Residence times from the burner to sampling location, based on fuel and air flows and a linear temperature profile, were calculated to be 3.9 and 3.3s for the methylated and demethylated fuels, respectively. Figure 11b presents the results of these MAEROS calculations for both glycerol fuels. Comparisons with Fig. 11a suggest reasonable agreement between the model predictions and the data. The model predictions suggest higher volume concentrations with slightly smaller mean diameters. These differences are likely the result of significant mass losses to the furnace walls and the added contribution of ash condensation on existing particles.

Commercialization Strategy

Outline:

I. Commercialization Plan
II. Commercialization Team Members – Roles & Responsibilities
III. Financing Options
IV. Economic Modeling
V. Competitive Assessment
VI. Pilot Demonstration
VII. Commercial Systems

Commercialization Plan

Moving forward from Phase II of the Department of Energy (DOE) Industrial Energy Efficiency Grant Challenge Grant will require a scale-up of the patent pending technology and more robust testing. Therefore, the Applied Combustion Technologies (ACT) team has defined a 30-month follow-on phase, termed the "pre-pilot demonstration" phase. It is during this phase that the team intends to build a ~200 kW system as representative as possible to a commercial design and conduct extensive testing. The size of the system is driven by the desire to make a significant jump in scale from the 20 kW prototype system (see Fig. 12), but not out of the norm for combustion systems development. A 10X increase in output power is technically and programmatically sound. This would also allow for another 10X jump in scale later to reach a commercial size of roughly 2 – 3 MW.

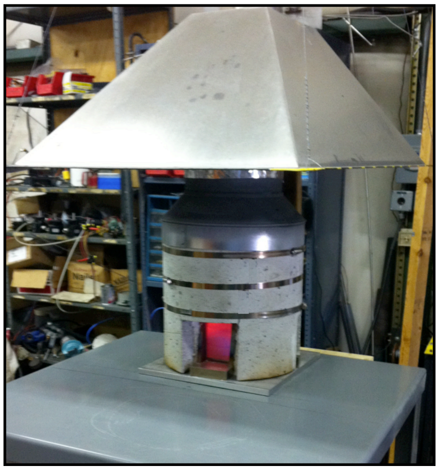


Figure 12: Laboratory scale burner

Figure 13 depicts the 30-month pre-pilot demonstration phase in detail. It is broken into four distinct periods, plus a three-month pad at the end for project margin. The first period, "design," includes four months for solidifying system requirements, conducting multiple design reviews, and developing parts lists and sourcing channels. The second period, "assembly, integration, and test," begins with infrastructure preparation and continues into procuring and fabricating parts (as necessary), assembling everything together, and finally conducting a series of checkout tests to ensure the burner is ready to enter the main test period. This second period is envisioned to last approximately eight months.

The third period, "pre-pilot demonstration testing," is the most critical portion of the project and is planned to last for one year at North Carolina State University (NCSU). In this period the team plans to conduct a series of tests to checkout the burner both stand-alone and while integrated with a burner representative of the potential customer market (likely a water-tube package boiler defined by Alcoa, REG, or another industrial partner). These tests will be detailed and rigorous, including: 1) testing various types and sources of crude glycerol, 2) running tests over long periods of time to determine issues with duration and parts wear-and-tear, 3) emissions characterization, 4) operational procedures development and refinement, and 5) start-up and shut-down procedures. These tests will be done first with the burner alone, then

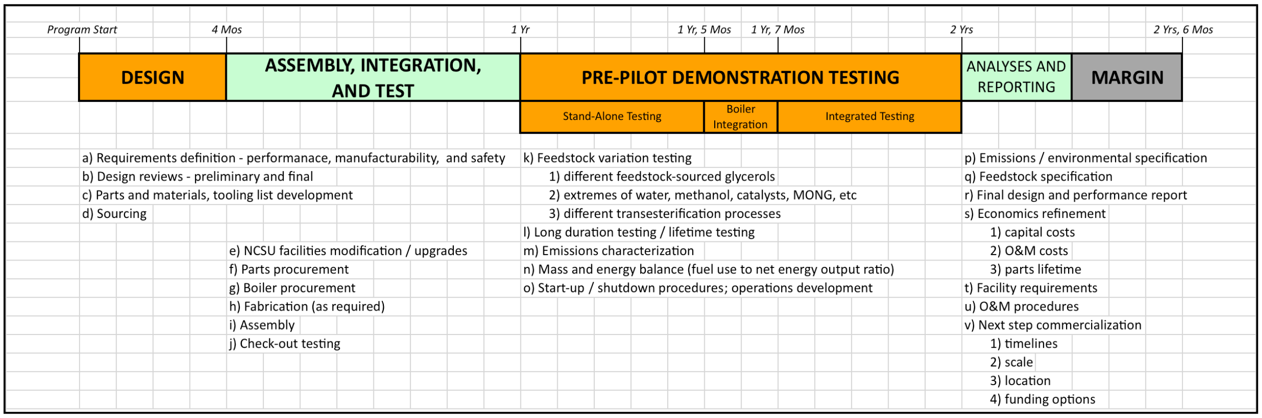


Figure 13: 30-month pre-pilot demonstration phase

with a burner-boiler end-to-end architecture representative of a steam generation system. The intent is to procure a commercial boiler and adapt it to be fed by the crude glycerol burner – all while as close as possible to the eventual commercial design.

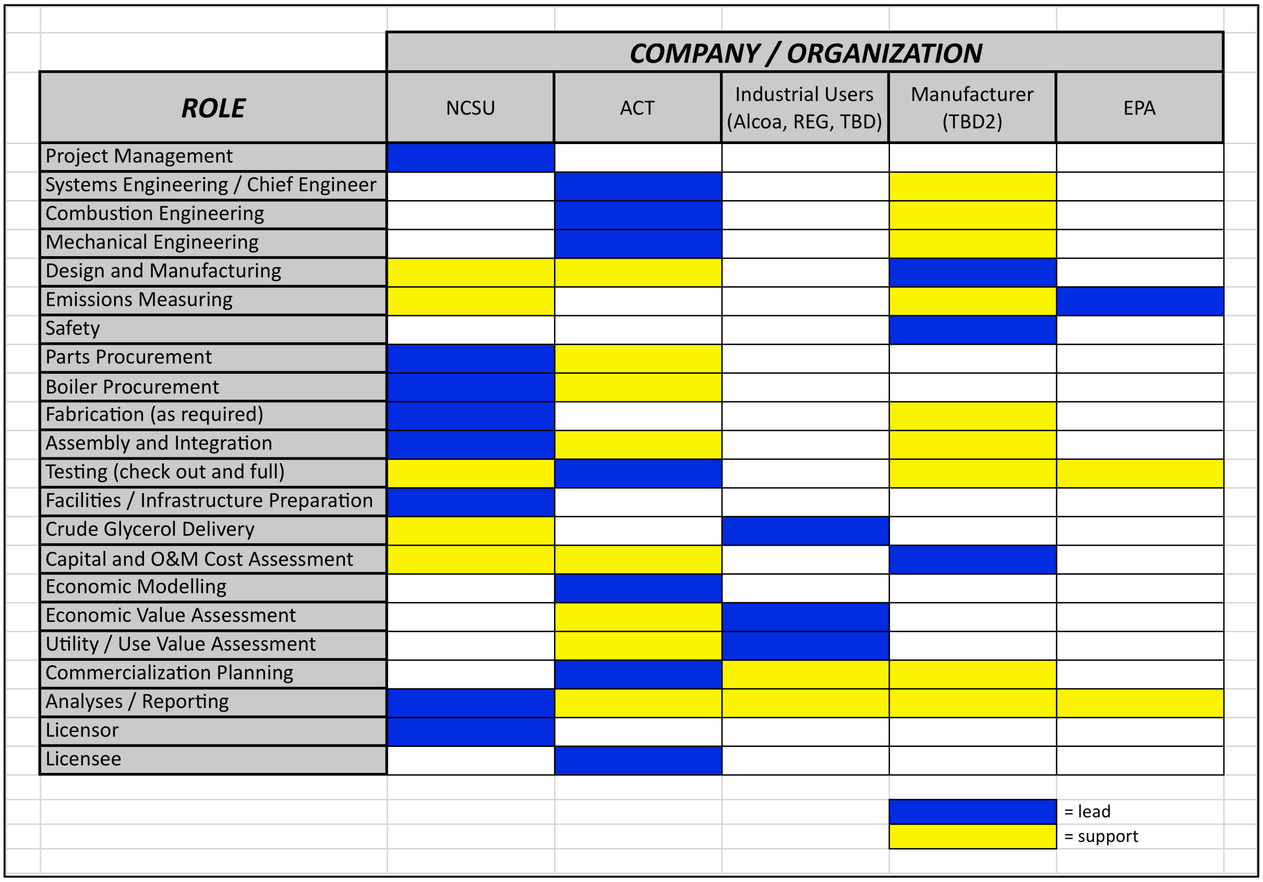
The last period, "analyses and reporting," constitutes the activities to assess and document the results of the project and a go-forward plan. The specifics of these activities are detailed in the figure. These tasks are expected to last three months. An additional three months are added to the end of the project to allow a margin for contingency or for more testing if desired.

While the intent is to conduct the pre-pilot demonstration at NCSU, this is not necessarily required. It is quite possible to do the development and testing at another facility, as long as the infrastructure and technical expertise is available.

Commercialization Team Members – Roles & Responsibilities

Figure 14 provides a depiction of the roles and responsibilities of the team members during the pre-pilot demonstration phase. The figure shows five principal contributors to the program: NCSU, ACT, Industrial Users, a Manufacturer and the Environmental Protection Agency (EPA). In the table blue is used to indicate an entity that will be leading an activity, while yellow is used to depict a supporting role. This list includes a number of new entities to the program, brought onto the effort to help accelerate commercial introduction of the burner. NCSU will act, similar to Phase II of the DOE grant, as the prime contractor and project lead. They will be responsible for management of the program, procuring and fabricating (as needed) parts to build the burner, procuring the boiler, conducting assembly and integration of the system, and leadership for the preparation of all analyses and reports. NCSU will also provide the facilities and infrastructure for the pre-pilot system in Raleigh, NC.

Applied Combustion Technologies (www.actresource.com), as the commercial licensee to the intellectual property, will take on a greatly expanded role during the pre-pilot demonstration. Similar to the current Phase II effort, they will continue to have primary leadership for economic modeling and commercialization planning, to include all efforts to attract strategic and financial partners, as well as end customers. Moreover, in this next phase they will also be responsible for a number of engineering tasks (systems, combustion, and mechanical) in addition to taking over responsibility for the testing program. It is ACT's intention to hire several engineers, most likely



	COMPANY / ORGANIZATION				
ROLE	NCSU	ACT	Industrial Users (Alcoa, REG, TBD)	Manufacturer (TBD2)	EPA
Project Management	🟦				
Systems Engineering / Chief Engineer		🟦		🟨	
Combustion Engineering		🟦		🟨	
Mechanical Engineering		🟦		🟨	
Design and Manufacturing	🟨	🟨		🟦	
Emissions Measuring	🟨			🟨	🟦
Safety				🟦	
Parts Procurement	🟦	🟨			
Boiler Procurement	🟦	🟨			
Fabrication (as required)	🟦			🟨	
Assembly and Integration	🟦	🟨		🟨	
Testing (check out and full)	🟨	🟦		🟨	🟨
Facilities / Infrastructure Preparation	🟦				
Crude Glycerol Delivery	🟨		🟦		
Capital and O&M Cost Assessment	🟨	🟨		🟦	
Economic Modelling		🟦			
Economic Value Assessment		🟨	🟦		
Utility / Use Value Assessment		🟨	🟦		
Commercialization Planning		🟦	🟨	🟨	
Analyses / Reporting	🟦	🟨	🟨	🟨	🟨
Licensor	🟦				
Licensee		🟦			

🟦 = lead
🟨 = support

Figure 14: Detailed description of project roles and responsibilities

former NCSU personnel and others familiar with the technology, into the company. ACT has already started discussions with several high-caliber candidates. If required, ACT could also take over prime contractor responsibility from NCSU.

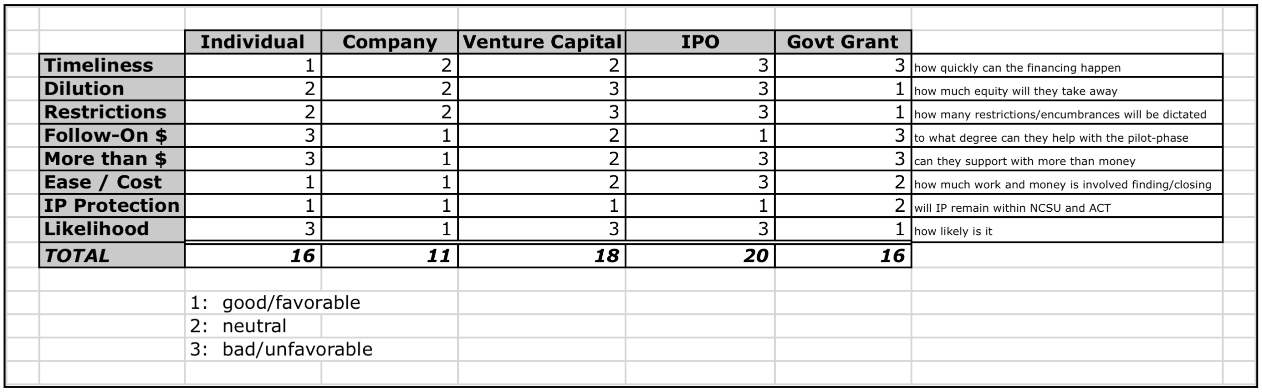
The "Industrial Users" category is intended to represent a broad class of potential end customers who would benefit from a crude glycerol burner introduced into their industrial operations. These customers represent some of the largest consumers of natural gas in the U.S. and also significant contributors to CO_2 emissions. Alcoa (www.alcoa.com), the world's largest aluminum manufacturer, may continue on as a partner expanding their role to identify and assess a facility to host the pilot plant. This would include a detailed assessment of the value for such a system, including the economics. They would also be responsible for assessing the infrastructure, integration, and permitting requirements for a pilot demonstration unit, as well as the operational impacts during installation and integration into their plant.

During Phase II of the grant ACT has received a commitment from the Renewable Energy Group (REG) (www.regfuel.com) to join the development effort in the next phase. As the largest biodiesel company in the U.S., ACT is excited to have REG join the team. REG would assume a role similar in nature to that of Alcoa. REG is a significant consumer of natural gas in their facilities for the heating required to produce biodiesel. Furthermore, REG's transesterification process produces large amounts of crude glycerol. Therefore, a glycerol burner in a REG facility would offer a closed-loop energy process and also eliminate their need to store and transport glycerol out of their plants. Lastly, it protects REG from the volatility of crude glycerol pricing (they currently sell their glycerol in the marketplace), allowing for more stability in the prediction of their operating income. Similar to Alcoa and REG, ACT is continuing to seek out additional industrial partners to join the project. Integrity Biofuels LLC (www.integritybiofuels.com) out of Indiana has expressed a keen interest in the use of a burner in their biodiesel plant – feeding a boiler for steam generation and mitigating their dependence on natural gas. ACT is also targeting glass and cement manufacturers.

Another major contributor to a future program phase is labeled “Manufacturer” in Figure 2. The team currently does not have a manufacturer supporting Phase II and felt it was critical going forward. As was discussed earlier, it is the intention of the 200 kW burner used in the pre-pilot demonstration to be as close as possible to the eventual commercial design. Therefore, having a company with a solid pedigree in the design, fabrication, sales, and support of liquid burners is critical. This company would be responsible for taking the Phase II burner design and making modifications and improvements for the 200 kW system. These improvements would take into account such things as performance, manufacturability, safety, operations and maintenance, and capital and operations costs. ACT is now in the process of contacting a select set of manufacturers in the U.S. It is very likely that this manufacturer will ultimately be a strategic/financial partner, as opposed to an “arms length” vendor in the project.

The last participant in the next phase, the EPA, is also a new teammate. While NCSU has previously consulted with the EPA on the glycerol burner and conducted some preliminary testing, the team felt it was important to carve out a formal and broader role for the EPA going forward. In the next phase the EPA would be responsible for designing the emissions testing program, conducting the emissions testing, and writing up their findings. It is expected the EPA will work very closely with all the other teammates.

Financing Options



	Individual	Company	Venture Capital	IPO	Govt Grant	
Timeliness	1	2	2	3	3	how quickly can the financing happen
Dilution	2	2	3	3	1	how much equity will they take away
Restrictions	2	2	3	3	1	how many restrictions/encumbrances will be dictated
Follow-On $	3	1	2	1	3	to what degree can they help with the pilot-phase
More than $	3	1	2	3	3	can they support with more than money
Ease / Cost	1	1	2	3	2	how much work and money is involved finding/closing
IP Protection	1	1	1	1	2	will IP remain within NCSU and ACT
Likelihood	3	1	3	3	1	how likely is it
TOTAL	***16***	***11***	***18***	***20***	***16***	

1: good/favorable
2: neutral
3: bad/unfavorable

Figure 15: Evaluation of potential financing options

Going forward into the pre-pilot demonstration phase will require on the order of $2.5M - $3M in funding for the 30 month project. This represents a rough approximation based on the lessons learned from DOE Phase II, the size of burner to be developed, the integration of the burner to a boiler, and the roles of the various teammates. However, by far the largest element of cost is driven by the one full year of pre-pilot unit testing. It is critical that a rigorous set of tests be conducted over an extended period of time per Figure 13. This effort will be labor intensive in conducting the testing, measuring the performance, making necessary adjustments, and documenting the results. As shown in Figure 14, engineers from all teammates except the "Industrial Users" will actively participate in the testing. It may be possible to reduce the effort in this area, however, the team currently feels this is a prudent path forward.

The funding for this phase could come from various sources. To date the development has been funded by private companies and the DOE Phase II grant. As depicted in Figure 15, the source of the necessary pre-pilot funding could be from one or more paths and each alternative has its pros and cons. The figure shows the potential sources of funding, to include: individual investors, private or public companies, venture capitalists (or private equity), an initial public offering by ACT, or from additional federal government grants. These options were evaluated based on eight key criteria and scored for each, with one being the most attractive and three being the least attractive. The criteria encompass the most important things to consider when a small company intends to raise financing to mature a technology. While ACT attempted to conduct the scoring based on the company's experience in the marketplace and through studying independent opinions for financing options, there is nevertheless a fair amount of subjectivity in the scoring.

The results show "company" financing as the most appealing option going forward, followed by "individual" and "government" financing. These results have been driving ACT's actions in the marketplace. As part of the effort to secure teammates for the next phase, ACT has also been engaging these companies about opportunities to become more than just a development participant. Particularly appealing to ACT is the potential to bring on a commercial burner manufacturer as a strategic partner – where they provide the financing in return for some combination of equity in ACT and/or the rights to be the exclusive manufacturer, distributor and maintainer of future commercial systems.

While "government" financing scored second, the team is extremely hopeful that the DOE will release a Phase III of the current program. The team has accomplished (or will shortly) all of the technical and performance objectives outlined in Phase II. This, coupled with a strong and compelling team for Phase III (licensee, multiple "big name" commercial users, a key manufacturer, and the EPA) and positive market economics make an attractive candidate for a Phase III award justification.

Economic Modeling

ACT has built an economic model to assess the long-term commercial viability of the crude glycerol burner technology. The team originally intended to construct a bottoms-up estimate of the capital and operations and maintenance (O&M) costs of the system, then use those estimates to determine the attractiveness of the technology. However, given the fact that the design for a full-scale system has not been completed, an alternative approach to the modeling has been undertaken and provides for a reasonable approximation to the bottoms-up estimate. It is expected that in the pre-pilot demonstration activity a detailed system design for a full-scale architecture will be completed, at that point allowing for a bottoms-up assessment. This was shown as Task S in Figure 1.

The basic premise to this approach is that a commercial crude glycerol burner based on the intellectual property (IP) under development will be very close in capital and O&M costs to traditional fuel oil or natural gas burners used today. This is a reasonable assumption given that:

- The burner uses no exotic materials, most parts are similar to burners in the market today.
- The burner size is similar to traditional systems, so the volume of materials used is roughly equivalent.
- The relative design complexity is only modestly more complex than traditional systems. The team chose to account for this by slightly increasing the capital costs relative to competing systems (specifics described later).
- It is expected that the operations of the burner will be no more or no less complex than traditional burners.

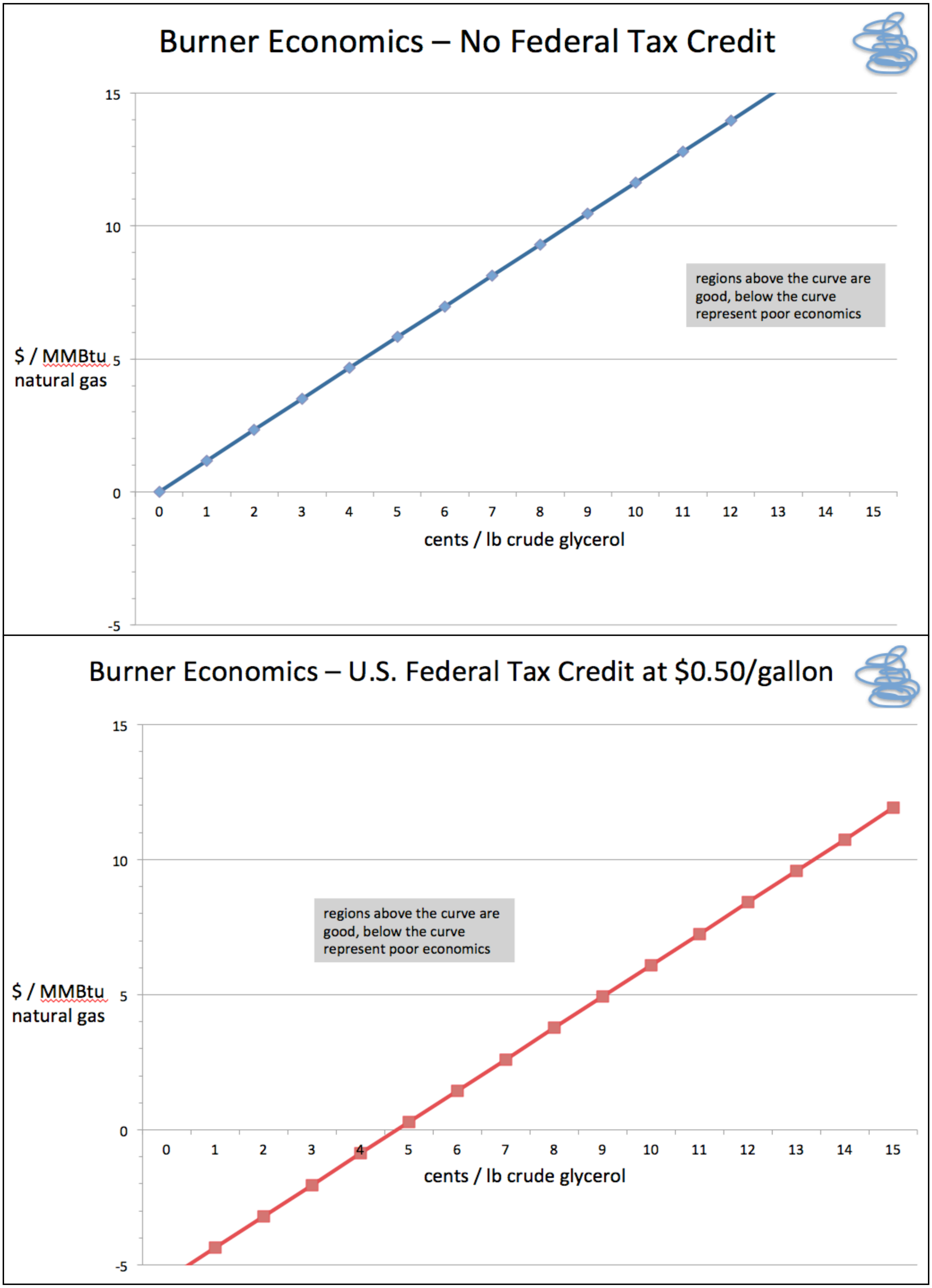
In he next phase the Manufacturing partner will validate the above assumptions. Given all this, *the economics become a comparison of the relative energy content per dollar of crude glycerol versus competing fuels (on a $/MMBtu basis)*. Because natural gas is the dominant fuel used today in the industrial marketplace for process heating applications, the team chose to conduct the analysis with natural gas as the competing fuel. A few key assumptions include:

- To account for the slight increase in complexity for the glycerol-based burner, it was assumed that a commercial 2 MW crude glycerol-based boiler application would cost ~$10k more in capital costs compared to a similar natural gas fired system. This increase in cost was amortized over a 20 year burner lifetime assumption.
- O&M costs for a crude glycerol versus natural gas system are equivalent.

Crude glycerol energy content is ~20 MJ/kg. While pure glycerol is 16 MJ/kg, the team has analyzed a large number of crude glycerol samples from various biodiesel plants across the U.S. and discovered that a 25% increase in energy density compared to pure glycerol is common. This is driven partially by the residual methanol often left in the glycerol and mostly from Matter Organic Non-Glycerol (MONG). MONG is generally comprised of free fatty acids (FFA), soaps, unreacted Mono-, Di-, and Tri-glycerides, and unreclaimed fatty acid methyl esters (FAME).

The results are shown next in two graphics. Figure 16a shows the economics assuming no federal tax credit for burning a renewable feedstock like glycerol. On the “y axis” is the cost of natural gas for an industrial user in $/MMBtu and on the “x axis” is the delivered cost of crude glycerol in cents/pound for that same user. The line represents the equivalency point for each fuel. That is, for an industrial process heating application (like a 2 MW steam boiler) the end user would not benefit or lose from using the glycerol burner if both fuel prices were on the line. On the other hand, regions above the line make the economics attractive for using the crude glycerol burner and regions below the line are not beneficial. For example, if natural gas prices were $5/MMBtu, then having access to crude glycerol at $0.04/pound or less would make the glycerol burner financially attractive.

Figure 16b depicts the potential benefits gained by capitalizing on the (pending) legislation to provide a $0.50/gallon tax credit for renewable fuel usage. This tax benefit was assumed to be a dollar-for-dollar benefit to the bottom line. In essence, this shifts the curve to the right roughly $0.05/pound of glycerol. Using the same example as earlier, in this case at $5/MMBtu of natural gas, an industrial user could now afford to pay up to $0.09/pound for crude glycerol and still gain an economic benefit relative to a natural gas fired system.


Burner Economics – No Federal Tax Credit

regions above the curve are good, below the curve represent poor economics

Burner Economics – U.S. Federal Tax Credit at $0.50/gallon

regions above the curve are good, below the curve represent poor economics

Figure 16: Economic analysis of the energy cost of glycerol compared to natural gas both a) without and b) with an applied federal tax credit

The economic analyses demonstrates that the commercial viability (from a financial stand-point) of the crude glycerol burner technology is dependent upon the cost of securing crude glycerol versus that of competing fossil-derived fuels like natural gas or fuel oil. While it is virtually impossible to predict the future of prices, there are a number of general observations that can be drawn. First, the natural gas market in the U.S. is currently depressed and prices are at decade lows. However, many experts predict that the current oversupply situation will be short-lived as demand for the cheap fuel picks up as the recession passes and alternative electricity generation sources that were envisioned to come on-line over the next couple of decades experience delays. In particular, it is quite reasonable to assume that new nuclear plants will not be constructed in the U.S. for the foreseeable future due to the 2011 incident in Japan.

A second observation is in regards to crude glycerol pricing. The crude glycerol market is quite volatile and highly dependent on the physical location of the crude glycerol, its respective quality, and the current supply/demand market dynamics. For example, there are remotely located biodiesel plants in the U.S. without access to "market makers" for crude glycerol that are selling their glycerol for 1 – 2 cents/pound, and sometimes even paying to have it shipped away. On the other hand, there have been plants in more central locations and with good market conditions that are getting a much higher premium. For example, the Renewable Energy Group (REG), the largest biodiesel producer in the U.S., is currently getting 5 – 8 cents/pound at their Midwest plants as of mid-2011. These price differentials are also strongly correlated to the quality of the crude glycerol generated. Lastly, in regards to market dynamics, it is not unreasonable to assume that with increasing federal/state mandates for biodiesel production and rising crude oil prices (as of December 2011 over $100/barrel) that the supply of biodiesel produced in the U.S. will continue to rise – in concert driving the supply of crude glycerol up and respective pricing down if demand were to stay constant. In fact, from REG's recent filing to go public they state:

> *On July 1, 2010, RFS2 became effective, requiring that Obligated Parties use 800 million gallons of biomass-based diesel in 2011, and 1.0 billion gallons in 2012. Recently the EPA, proposed that 1.28 billion gallons be used in 2013. Biodiesel is currently the only commercially significant RFS2-compliant biomass-based diesel fuel produced in the United States. In the first five months of 2011, 297 million gallons of biodiesel were produced in the United States, while 311 million gallons were produced in all of 2010.*

As ACT begins to plan for Phase III of the grant and commercial introduction of the technology, one strategy being considered is to target industrial users in geographic locations where crude glycerol prices are attractive. This would entail finding those remote and "stranded" sources of crude glycerol. Since the biodiesel industry has been emphasizing the placement of plants near the sources of feedstock to reduce transportation costs, there are lots of opportunities to find such glycerol sources throughout the U.S.

A third observation is related to the importance of a whole serious of other benefits not accounted for in the earlier analyses. Some of these benefits could by themselves be game-changers for technologies such as the glycerol burner. A few such examples include:

1. reduced carbon emissions allowing for cap and trade credits
2. public relations and community benefits by being "green"
3. state tax credits

4. for biodiesel producers using this technology – reduced glycerol storage requirements and energy price stability
5. special debt financing arrangements as a consequence of using a renewable feedstock

The last conclusion is related to the relative unimportance of the capital cost assumption for the crude glycerol burner. The team assumed a 2 MW glycerol burner would cost a total of $10k more than a competing natural gas burner, amortized over 20 years. This translated to a mere 8/10th of one cent impact to natural gas prices – meaning an industrial user could afford to pay $0.008/MMBtu (for natural gas) more with a natural gas system and still be breakeven with a crude glycerol system. Even if the $10k capital cost assumption were a magnitude of order wrong, it would still have a very small impact on the economics. The economics are mostly driven by the cost for crude glycerol relative to competing fossil-derived fuel alternatives.

Competitive Assessment

Natural Gas and Traditional Fuel Oil Burners

The market is currently dominated by natural gas and fuel oil burners. As long as these energy sources stay at their current pricing (almost historical lows as of November 2011), it will be difficult for a system based on crude glycerol it achieve any meaningful market penetration. Replacing or retrofitting existing systems will be extremely challenging. The best option will be to target new installations. A burner that has the capability to utilize both natural gas/fuel oil and crude glycerol may be quite attractive. However, in the end it will still depend on the economics and the customers' view of risks.

There are a handful of companies promoting the use of their existing waste oil burners for glycerol applications. Generally these companies discuss the capability to co-fire their boilers or heaters with a mixture of a traditional fuel plus glycerol. It is believed that fuel mixing is required and these systems cannot operate on crude glycerol alone. The overall output efficiencies are also likely diminished. One such company is:

AgSolutions, LLC
5361 Highway 54
Owensboro, KY 42303
(866) 605-4328
www.agsolutionsllc.com

They claim to have sold their boiler systems to several biodiesel producers for both process and space heating applications. One such site may be a 10 MMgpy plant in Gladstone, MI. Various sized boilers have been delivered and connected to tanks with heated jackets, tanks with internal coils, and to plate and frame heat exchangers. The boilers they offer are sized from 105k – 500k BTU/hr (40 – 150 kW). Fuels being used include motor oils, transmission fluids, hydraulic fluids, vegetable oils, and glycerol generated from the plant's biodiesel production. Given all this, it is not clear from on-line research how successful these operations have proven.

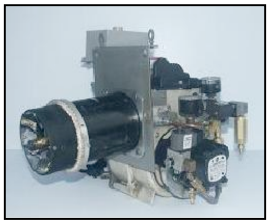
Electric Heaters

In general, electricity costs have made it financially unattractive to use electric heaters in large-scale industrial applications. In addition, there are challenges associated with scale to generate the required output power for most industrial needs.

Competing Crude Glycerol Burners

Only a handful of companies claim to have similar technologies to the system built by NCSU. One such company is:

AlterHeat Company, LLC
7589 Race Road
North Ridgeville, OH 44039
(440) 353-0650
www.glycerinburners.com



The "MK Glycerin Burner" is being actively sold as a commercial item by AlterHeat Company, LLC. Key points include:

- CEO, Ray Masin, has 25 years of experience in liquid and gas combustion systems.
- Claims to be the only burner on the market capable of burning crude glycerol "as is." No co-burning is required. Although, the viscosity of the incoming fuel must not be higher than 220 SSU and it should be filtered to a minimum of 149 Mi (Micron) with a 100 mesh strainer screen.
- Appears to be offering systems with output power of 0.35 – 1.2 MW.
- Company is targeting both the residential and industrial heating market.
- No indications are provided if any units have been sold. Would assume this means they have not sold any.
- Appears that information on the web site is dated back a couple of years.
- Patents in the US and international markets are "pending."
- Says the units are built from scratch since current waste oil burners won't work – they need a costly combustion enhancer that just makes it too expensive and inefficient. Built upon the reliable Beckett AF burner chassis, but that is the only similarity with other systems.
- Company may offer a scrubber at some point in time.
- Comes with a one year warranty on the burner.

- Regarding acrolein, company claims to be operating substantially above acrolein formation levels of 200 – 300° C. Although, it doesn't appear any test have been conducted to verify the aldehyde content in the emissions from the units.
- The ashes in the emissions (looks like "white smoke") are sodium pyrophosphate white, tan or light green color, hydroscopic, water soluble, lightly alcaloid and turn black when wet.

Key technical attributes of the burner include:

- Patented nozzle provides extremely uniform atomization of fuels.
- 190 psi, high pressure atomization.
- No preheating of the assembly is required.
- Patented water purge system.
- Unique air flow design eliminates the need for a flame retention head.
- Average of 1649° C flame temperature.
- Requires a 5 – 10% combustion enhancer (methyl alcohol) at start-up for roughly one minute, then shut off.
- Requires compressed air at 5 psi.
- Burner weighs approximately 60 lbs.
- Dimensions:
  - Height 11 1/2" (29 cm)
  - Width 12 7/8" (32.6 cm)

A detailed brochure is available on the company's web site at:

www.glycerinburners.com/pdf/MK_GLYCERIN_BURNER-Specifications.pdf

Another competing system is:

The University of Alabama
Professor Ajay Agrawal
Tuscaloosa, AL
Aagrawal@eng.ua.edu
www1.eere.energy.gov/industry/fuelflexibility/pdfs/fuel-flex_burner.pdf

This is a development stage technology being developed by the University of Alabama in concert with an industrial partner – Wise-Alloys, an aluminum processing company. The university won a grant from the DOE/EERE's Industrial Technologies Program. According to the DOE, this project was funded by the American Recovery and Reinvestment Act (ARRA) program and is on the order of three years in length. It is expected that this grant will come to an end very shortly. It is not known the degree of progress that was accomplished. As of late November 2011, ACT has a call into Wise-Alloys to discuss this technology and their requirements for similar systems going forward.

According to the literature, this project is aimed at developing a *fuel-flexible, low-emissions burner capable of using various biomass-derived liquid fuels*. These fuels include glycerin and fatty acids. The goal is to offset natural gas consumption in industrial applications and reduce carbon footprints. The project will explore two newly developed combustion techniques to atomize crude glycerol: porous inert media combustion and a flow-blurring injector. Four R&D stages for the project were defined, varying from design studies to the fabrication of a pilot-scale system.

Pilot Demonstration

Following the pre-pilot demonstration, the team intends to build, install, and operate a ~2 MW system at a location identified by one of the Industrial Partners. This would therefore represent another [similar to the pre-pilot demonstration stage] scale-up in output power of 10X, not unreasonable in the development of combustion systems. Alcoa has expressed interest in the possibility of hosting a demonstration at their facility in either Colorado or Texas. ACT expects that other industrial teammates will also make similar requests and all of these will have to be evaluated going forward. This effort would likely be led by ACT or their manufacturing partner.

Since the planning for this demonstration is still in the early phases, the specific size of the burner, costs, choice of what it will be integrated into (most likely a boiler), financing, among many other parameters are not yet known. For example, the system could be designed to operate on both crude glycerol or natural gas. In that manner, dependent upon supply/demand and pricing of both crude glycerol and natural gas the burner could be operated using the most economical fuel source. In addition, the ~2 MW size needs to be vetted by assessing the most likely set of users going forward. It is the team's intention that the burner used for the pilot demonstration be as close as possible to the final size and configuration as that expected for commercial systems. All of these decisions, among others, will be determined in the "next step commercialization" tasks per Figure 13.

The purpose of the pilot demonstration will be to operate the commercial-like system for an extended period of time in an environment as close as possible to real operations. In this manner a definitive assessment can be made on the merits of the system and a set of final "tweaks" can be performed. It is the intention of ACT to exit the pilot demonstration phase with a system that is ready to be built and sold in large volume.

Commercial Systems

ACT, as the licensee of the IP, does not intend to enter the combustion manufacturing, sales, distribution, and servicing industry. Instead, upon completion of the pilot demonstration it would be ACT's desire to license/assign the IP to the manufacturing partner or some other 3rd party company that has the highest probability of success in introducing and selling these systems into the marketplace.

Accomplishments

Publications:

Glycerol Combustion and Emissions – Proceedings of the Combustion Institute 33 (2011), 2717-2724

NOx Emissions from High Swirl Turbulent Spray Flames with Highly Oxygenated Fuels – Submitted to the Proceedings of the Combustion Institute 34, January 2012

Crude Glycerol Combustion: Particulate, Acrolein, and Other Volatile Organic Emissions – Submitted to the Proceedings of the Combustion Intitute 34, January 2012

Conference Papers:

An Experimental Study on the Effect of Fuel-Bound Oxygen on NOx Production in Glycerol Combustion - 7th US National Technical Meeting of the Combustion Institute hosted by the Georgia Institute of Technology in Atlanta, GA, March 2011

An Experimental Study on Unburned Hydrocarbon Emissions in Glycerol Combustion Utilizing GC/TCD/FID - Eastern States Section of the Combustion Institute Fall 2011 Technical Meeting hosted by the University of Connecticut in Storrs, CT, October 2011

Acrolein and Other Volatile Organic Emissions from the Combustion of Crude Glycerol - Eastern States Section of the Combustion Institute Fall 2011 Technical Meeting hosted by the University of Connecticut in Storrs, CT, October 2011

Website Development:

Applied Combustion Technologies (www.actresource.com)

Conclusions

The primary objectives of this work can be summed into two major categories. Firstly, the fundamentals of the combustion of glycerol (in both a refined and unrefined form) were to be investigated, with emphasis of the development of a system capable of reliably and repeatedly combusting glycerol as well as an analysis of the emissions produced during glycerol combustion. Focus was placed on quantifying common emissions in comparison to more traditional fuels and this work showed that the burner developed was able to completely combust glycerol within a relatively wide range of operating conditions. Additionally, focus was placed on examining specific emissions in more detail, namely interesting NOx emissions observed in initial trials, acrolein and other volatile organic emissions, and particulate and ash emissions. This work showed that the combustion of crude glycerol could result in significantly reduced NOx emissions as a function of the high fuel bound oxygen content within the glycerol fuel. It also showed that when burned properly, the combustion of crude glycerol did not result in excessive emissions of acrolein or any other VOC compared to the combustion from more traditional fuels. Lastly however, this work has shown that in any practical application in which glycerol is being burned, it will be necessary to explore ash mitigation techniques due to the very high particulate matter concentrations produced during glycerol combustion. These emissions are comparable to unfiltered coal combustion and are directly tied to the biodiesel production method.

The second focus of this work was directed to developing a commercialization strategy for the use of glycerol as a fuel replacement. This strategy has identified a 30-month plan for the scaling up of the laboratory scale burner into a pre-pilot scale system. Additionally, financing options were explored and an assessment was made of the economics of replacing a traditional fuel (namely natural gas) with crude glycerol from biodiesel production. This analysis showed that the cost of replacing natural gas with crude glycerol requires a strong function of the market price per unit of energy for the traditional fuel. However, the economics can be improved through the inclusion of a federal tax credit for the use of a renewable fuel. The conclusion of this analysis also shows that the ideal customer for energy replacement via crude glycerol is biodiesel producers who are located in remote regions, where the cost of energy is higher and the cost of crude glycerol is lowest. Lastly, the commercialization strategy analyzed competing technologies, namely traditional natural gas and electric heaters, as well as competing glycerol burners, and concludes with a discussion of the requirements for a pilot demonstration.