

Stack Emissions Evaluation: Combustion of Crude Glycerin and Yellow Grease in an Industrial Fire Tube Boiler

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Preface

The following information reports the results of a stack emissions evaluation demonstration via the utilization of crude glycerin blended with yellow grease as an industrial boiler fuel. Crude glycerin is one of the resulting co-products of biodiesel production. Yellow grease is primarily composed of spent frying grease but can contain other sources of rendered fat. Because it is recognized that no two boilers are alike, the results are limited to one specific boiler set at specific operating parameters during the performance evaluation. It is further recognized that the level of purity of crude glycerin can vary from production site to production site but that the quality of this co-product can be consistent within each established biodiesel production plant. Nevertheless, an alternative boiler fuel necessitates characterization through chemical analysis. The chemical profile is required for regulatory compliance, and it assists the boiler tuners to identify the necessary parameters needed to fire the boiler under unusual conditions. By no means are the reported results an endorsement of crude glycerin as a source, or a partial source, fuel for an industrial boiler. Those interested in using crude glycerin blended as a component boiler fuel should take precautionary measures and must be in total compliance with their state and federal regulatory agencies.

I. INTRODUCTION

Background

Identifying new or alternative uses for glycerin is an identified priority issue for many Minnesota entities including the Agricultural Utilization Research Institute, the Soybean Growers Association, and the biodiesel industry. This is a priority issue because of the overabundance of crude glycerin that is available in current markets. The excess crude glycerin is a result of biodiesel processing. This co-product was once considered a production credit, but for practical purposes, has become otherwise. If a plant encounters difficulty with identifying a market for this material, they may be faced with disposal fees. In Minnesota alone there is over 63 million gallons of biodiesel production capacity that yields approximately 6 million gallons of crude glycerin annually when production capacity is met.

Interest is growing to use crude glycerin to produce energy. One possible alternative is to use this material as a fuel source for industrial boilers. At an industrial level in Minnesota, however, the Minnesota Pollution Control Agency (MPCA) must evaluate emissions from this process prior to approval for use. This is a recognized practice whenever a fuel source is changed in an industrial setting. Compliance must be met by applying for, and obtaining, an emissions permit from the state prior to the regulatory review and actual demonstration. In addition to the permitting requirements, the energy value contained in the crude glycerin directed the project toward using a blend of crude glycerin with another source fuel. In this study, 100% crude glycerin as a boiler fuel source showed little success. Consequently, there is limited information stated in this report to that regard. Instead, results are reported from the emissions via combusting the fuel blend of crude glycerin and yellow grease through a fire-tube boiler.

Project Objective

The primary objective of this project is to determine whether crude glycerin can be used as a source fuel for an industrial boiler. This is determined through fuel characterization, a demonstration, and a regulatory evaluation of the stack emissions when conducting this test. The initial project proposal identified the use of 100% crude glycerin as a fuel source in a Kewanee triple pass 750 Hp fire tube boiler. Due to characterized properties of the crude glycerin, boiler turbulence, and through various attempts by the boiler tuner, it was determined that the boiler could not maintain a flame. The original project objective was withdrawn and it was determined that 100% of this crude glycerin was not a suitable boiler fuel. However, a revised project objective resulted, and the demonstration continued by studying the emissions from the boiler fired with a fuel blend: 10% crude glycerin mixed with 90% yellow grease.

The demonstration site was a Central Bi-Products plant owned and operated by Farmers Union Industries, LLC located in North Redwood, Minnesota. The proposed tests for the emissions performance demonstration are listed in the next section.

Emissions Testing

Method 1 – “Sample and Velocity Traverse for Stationary Sources”

Method 2 – “Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)”

Method 3A – “Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)”

Method 4 – “Determination for Moisture Content in Stack Gases”

Method 5 – “Determination of Particulate Matter Emissions from Stationary Sources”

Method 6C – “Determination of Sulfur Dioxide from Stationary Sources (Instrumental Analyzer Procedure)”

Method 7E – “Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)”

Method 8A – “Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources”

Method 9 – “Visual Determination of the Opacity of Emissions from Stationary Sources”

Method 10 – “Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)”

Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

Method 25A – “Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer”

Method 26 – “Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources – Non-Isokinetic Method”

Method 29 – “Determination of Metals Emissions from Stationary Sources”

Method 202 – “Determination of Condensable Particulate Emissions from Stationary Sources”

II. RESULTS

This section reports the results of the fuel characteristics, operating conditions, monitored parameters of the boiler during the performance demonstration, and a summarized table of the emissions compliance test results. Final information is included in the last segment which identifies the difficulties encountered via this study.

The fuel characteristics listed in Table 1 were not surprising and addition of the yellow grease to the glycerin provided a more promising fuel selection for this demonstration. One of the most detrimental factors for crude glycerin as a source fuel in this boiler is noted in the available energy which was approximately 37% lower than the available energy in yellow grease. The higher ash, moisture, and chlorine contents in the crude glycerin compared to yellow grease are additional inherent concerns. As a result of these differences, obvious efficiencies would be lost through boiler operation.

Table 1. Fuel Characteristics

Test	Method	Units	100% Glycerin	20% Glycerin/ 80% Y.G.	10% Glycerin/ 90% Y.G.	100 % Yellow Grease
Saybolt Viscosity	ASTM D88	SUS, 100°F	205.5	261	243	220
Specific Gravity 60/60	ASTM D1298	@60/60°F	1.2525	0.9761	0.9298	0.8900
Seta Flashpoint	ASTM D3278	°F	> 250	392	391	390
Ash	ASTM D3174	wt %	3.805	0.69	0.43	0.39
Carbon	ASTM D5373	wt %	32.8	65.75	70.33	76.4
Hydrogen	ASTM D5373	wt %	8.56	10.92	11.32	11.6
Nitrogen	ASTM D5373	wt %	< 0.2	<0.2	<0.2	<0.2
Oxygen by Difference	Calculation	wt %	54.55	22.43	17.71	11.40
Total Sulfur	ASTM D4239	wt %	0.085	0.01	0.01	0.005
Calorific Value, cal/g	ASTM D5865	cal/gram	3489	8949	9066	9200
Calorific Value, Btu/lb	ASTM D5865	Btu/lb	6280	16108	16319	16,852
% Water – Karl Fisher	ASTM D1744	wt %	12.55	2.48	1.46	0.09
Total Chlorine	ASTM D808	µg/g	18150	4340	2410	1099
Mercury	EPA 7471	µg/g	< 0.1	<0.02	<0.02	<0.02

Operating Conditions for 10% Crude Glycerin / 90% Yellow Grease Demonstration

Boiler Description: Kewanee 750 Hp triple pass fire tube boiler (est. 1970’s model)
 Gordon Piatt burner installed 2001
 Burner Controls: Honeywell
 Separate modulating motors for gas, air, and liquid fuels
 Computer programmable set points on all modulating motors
 Operating Capacity During Demonstration: 20,000 lb/hr attempted, 18,000 lb/hr obtained
 Fuel Blend: 90% Yellow Grease, 10% Crude Glycerin
 Fuel Consumed During Demonstration: 17,810 lbs
 Monitored Parameters (avg):

Volumetric Flow	
Actual	8,550 acfm
Standard	4,524 dscfm
Gas Temperature	407°F
Moisture Content	10.17 %V/V
Gas Composition	
Carbon Dioxide	11.04 %V/V, dry
Oxygen	6.20 %V/V, dry
Nitrogen	82.75 %V/V, dry
Isokinetic Variation	98.6 %

Listing of Abbreviations:

acfm – actual cubic feet per minute
 dscfm – dry standard cubic foot of dry gas per minute
 gr/dscf – grains per dry standard cubic foot
 lb/hr – pounds per hour
 PM – particulate matter
 ppm,d – parts per million, dry
 ppm,w – parts per million, wet
 V/V – percent by volume

Source: Interpoll Laboratories, Inc.
 Circle Pines, MN

Table 2. Summary of Emission Tests Results

Pollutant	Results
PM10/PM	0.12 gr/dscf ^A 4.93 lb/hr ^A 0.13 gr/dscf ^B 4.95 lb/hr ^B 0.13 gr/dscf ^C 5.00 lb/hr ^C
Opacity	7.25%
Oxides of Nitrogen	108.95 ppm,d 3.56 lb/hr
Carbon Monoxide	2.0 ppm,d 0.04 lb/hr
Sulfur Dioxide	20.39 ppm,d 0.93 lb/hr
VOCs	11.86 ppm,w as carbon 0.11 lb/hr as carbon
Sulfuric Acid Mist	0.10 ppm,d 0.007 lb/hr
Calcium	0.131 lb/hr
Potassium	0.027 lb/hr
Magnesium	0.018 lb/hr
Phosphorus	0.10 lb/hr
Hydrogen Chloride	0.034 lb/hr
Chlorine	0.004 lb/hr
Acrolein	<0.008 lb/hr
Acetaldehyde	<0.008 lb/hr

(A) Filterable particulate matter as determined by U.S. Environmental Agency (EPA) Method 5.

(B) Filterable plus organic condensible particulate matter as determined by EPA Method 5 and Method 202/ Minn. R. 701 1.0726.

(C) Particles with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM10) as determined by EPA Methods 5 and 202.

The reported results are an average of three test points taken at consistent intervals during the stack emissions demonstration. Interpoll Laboratories, Inc. conducted the emissions demonstration and reported that difficulties were not encountered in the field or laboratory evaluation of the samples. It is the testing company's opinion that the reported concentrations and emission rates are accurate and reflect the actual values that existed during the performance evaluation.

Although water and carbon dioxide are typical products of combustion, the regulatory emphasis is on the criteria pollutants that can cause harm to humans and/or the environment. The moisture content in the stack gas is conducted simultaneously with each pollution emission measurement run and the content is used to calculate emissions data. Both carbon dioxide and oxygen content are evaluated to determine the molecular weight of the flue gas and are concurrently run with each pollutant evaluation as well.

In traditional practices such as firing a boiler with natural gas, the regulated pollutants include particulate matter, oxides of nitrogen (NO_x), carbon monoxide, sulfur oxides (SO_x), and volatile organic compounds. Realizing that this demonstration used a non-traditional fuel source directed the pursuit to evaluate the additional emissions listed in Table 2.

It is understood that particulate matter emissions resulting from combustion can include many types of compounds both carbon-containing and non-carbon-containing. With the inclusion of crude glycerin to the source fuel, it is likely that metals and metallic salts contribute to the particulate matter emissions.

The crude glycerin, yellow grease, and the tested fuel blend were similar in their nitrogen content, but whether or not the addition of crude glycerin would contribute to potential increased NO_x emissions is not certain. The flame temperature during boiler operations and the air level within the boiler can contribute to the NO_x emissions as well. Thus, the results posted in the table are reflective of and limited to the established parameters in this demonstration.

Carbon monoxide emissions can be dependent on the burner design. In this case the Gordon Piatt burner allows for flexibility with regard to fuel selection and optimized conditions allowed for the low carbon monoxide emissions.

The sulfur oxides emissions are dependent on the sulfur content of the fuel. The fuel blend sample contained 0.01% sulfur and the major contributing component with regard to sulfur in the fuel blend is crude glycerin.

With respect to boiler emissions, volatile organic compounds are generally recognized as hydrocarbons. The VOC emissions may contain oxygen as well. This generalization is the result of incomplete combustion of traditional boiler fuels such as natural gas. Optimal burner set-up aids in the reduced emissions of VOCs.

The crude glycerin is likely a major contributor to the hydrogen chlorides emissions. By chemical analysis alone, the crude glycerin contained a chlorine content that is over 16 times greater than the content in yellow grease. Thus higher concentrations of the crude glycerin in the boiler fuel will likely increase these emissions unless the chlorine content is reduced. The chlorine content of a boiler fuel can also raise issues with regard to pitting the interior of the boiler or performing unwanted reactions within the boiler chamber.

The acetaldehyde emissions were evaluated with a primary interest in the acrolein content. Incomplete combustion of glycerin can result in formation of this toxin, thus the interest to evaluate it. Although the glycerin contribution was just 10%, the contribution could also be contributed by the yellow grease due to the typical molecular structure of triglycerides.

Difficulties Encountered

A difference in the densities between crude glycerin and yellow grease posed a challenge to maintain a homogenous fuel mixture. It was determined that pump mixing was not sufficient to introduce a consistent fuel mixture into the boiler. Mechanical stirring was identified as a potential resolution to obtain optimized blending conditions for the fuel blend.

Per communication received from staff at the testing site, the burner and jet assembly in the boiler was removed after the demonstration. A complete clean out was necessary due to the accumulated glycerin and yellow grease on the ports that caused a significant build up in the two day test. This delayed typical production processes and assumptions can be made that the incurred implicit costs would negatively affect the use and application of this lower cost fuel blend as a source fuel. Left unchecked, continued boiler operation in this state would lead to severe safety concerns for plant personnel and boiler operations.

III. EMISSIONS COMPARISON

The information reported in Table 3 is for comparative purposes only. Again, it must be stated that emissions are boiler and test and operating parameter dependent. The combustion of yellow grease demonstration occurred in March 2001. The same Kewanee 750 Hp triple pass fire tube boiler was used. Prior to the yellow grease demonstration, the Gordon Piatt burner was installed to allow some flexibility with regard to the fuel selection for the boiler. Although the same company conducted the emissions test, assumptions should not be made that the operating conditions were the same for both demonstrations.

Table 3. Comparison Summary of Emission Tests Results

Pollutant	January 2007 10% Crude Glycerin/ 90% Yellow Grease	March 2001 100% Yellow Grease
PM10/PM	0.12 gr/dscf ^A 4.93 lb/hr ^A 0.13 gr/dscf ^B 4.95 lb/hr ^B 0.13 gr/dscf ^C 5.00 lb/hr ^C	0.028 gr/dscf ^A 1.42 lb/hr ^A 0.026 gr/dscf ^B 1.31 lb/hr ^B 0.026 gr/dscf ^C 1.3 lb/hr ^C
Opacity	7.25%	No available information
Oxides of Nitrogen	108.95 ppm,d 3.56 lb/hr	125.5 ppm,d 5.29 lb/hr
Carbon Monoxide	2.0 ppm,d 0.04 lb/hr	5.4 ppm,d 0.14 lb/hr
Sulfur Dioxide	20.39 ppm,d 0.93 lb/hr	3.05 ppm, d 0.18 lb/hr
VOCs/Hydrocarbons	11.86 ppm,w as carbon 0.11 lb/hr as carbon	0.45 ppm as carbon 0.005 lb/hr as carbon

(A) Filterable particulate matter as determined by U.S. Environmental Agency (EPA) Method 5.

(B) Filterable plus organic condensable PM as determined by EPA Method 5 and Method 202/ Minn. R. 701 1.0726.

(C) Particles with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM10) as determined by EPA Methods 5 and 202.

IV. ECONOMIC EVALUATION

An economical comparison regarding the cost efficiencies of crude glycerin as a source fuel is shown in Table 4. In the current saturated market conditions, crude glycerin is valued at \$0.025 to \$0.05/lb based on 80% purity, FOB U.S. Plant, and yellow grease is valued at \$0.1875/lb (Jacobsen Publishing Company). For crude glycerin, these conditions are expected to be maintained due to the phenomenal growth of the biodiesel industry. Yellow grease prices fluctuate, and just one year ago market prices were reported at \$0.1175/lb.

Table 4. Fuel Cost Comparisons by Btu¹

Product	Avg. Btu/Unit	Units	Millions of Btu	Retail Cost	Cost/Unit	Efficiency	Cost per Million Btu
Coal (bituminous)	11,500	lb	0.0115	\$50/ton	\$0.025	0.5	\$4.35
Electricity	3,413	kWh	0.003413	\$0.06/kWh	\$0.060	0.97	\$18.12
Electricity	3,413	kWh	0.0034	\$0.082/kWh	\$0.082	0.97	\$24.77
Natural Gas	1.028 X 10 ⁶	1,000/ft ³	1.028	\$11.07/1000 ft	\$13.37	0.8	\$13.83
Natural Gas	1.028 X 10 ⁶	1,000/ft ³	1.028	\$7.00/1000 ft	\$7.190	0.8	\$8.74
#2 Fuel Oil	140,000	gal	0.14	\$2.409/gal	\$2.409	0.8	\$21.51
Propane	91,333	gal	0.0913	\$1.48/gal	\$1.480	0.8	\$20.26
Propane	91,333	gal	0.0913	\$1.48/gal	\$1.480	0.65	\$24.93
Crude Glycerin (85%)	6,280	lb	0.00628	\$0.035/lb	\$0.035	0.70	\$7.96
Yellow Grease	16,850	lb	0.01685	\$0.1875/lb	\$0.1875	0.80	\$13.91

¹Calculations by A. Doering, AURI Waseca, MN, Unpublished Data, March 2007

Source Information (Electricity, Natural Gas, Fuel Oil, Propane, Coal): Minnesota Department of Energy Conversion Facts:

One million Btu = 252,000 kilocalories (252 calories)

One Btu of energy will raise one pound of water one degree F

One calorie (252 calories/Btu) will raise one gram of water one degree C

One kilowatt hour = 3,413 Btu (860,076 calories)

One million Btu = 293 kW = 29.9 Boiler Hp = 1,000 lbs Steam = 120 lbs Dry Wood = 7 gals Diesel Oil = 1,000 cu ft Natural Gas

Fuel Facts**:

**Information from Pellet Fuels Institute and Ontario-Ministry of Agriculture, Food & Rural Affairs.

Propane	80% efficient	90,000 Btu/gal
Electric	95% efficient	3,415 Btu/kWh
#2 Oil	80% (+/-)efficient	138,000 Btu/gal
Natural Gas	80% efficient	1MM Btu/therm

The information above lists common fuel sources used for industrial energy requirements. Glycerin or yellow grease is not recognized as a common fuel source but for comparison purposes, they are included in the table. In its purest form, glycerin has a reported calorific value of 19,000 kJ/kg or 8169 Btu/lb (HVAC Toolbox). Assuming a 10.52 factor in the lbs-to-gallon conversion, the gross heat of combustion from pure glycerin can also be reported as 85,938 Btu/gal ($d_{\text{GLYCERIN}} = 1.2613 \text{ g/mL}$). A reduction of this available energy occurs when crude glycerin is evaluated (65%-85% pure), depending on the production process parameters. The

resulting gross heat of combustion for the sample used in the demonstration was reported at 6280 Btu/lb.

A sample of yellow grease consistent with the product used in this demonstration was evaluated for the gross heat of combustion and resulted in 16,850 Btu/lb. An approximate eight lbs-to-gallon factor is used to determine a gross heat of combustion value which yields 134,800 Btu/gal.

The current estimated cost per million Btu for the fuel blend (10% crude glycerin / 90% yellow grease) was calculated at \$13.32. The higher market prices for yellow grease do not make this a competitive fuel in comparison with natural gas costs at the industrial level. At lower market costs for yellow grease such as those reported one year ago (\$0.1175/lb), the fuel blend may appear to be a favorable economical choice to offset production plant energy requirements. However, the fuel blend raises safety concerns when used as a boiler fuel. In addition, implicit costs associated with take-down and clean-up after the boiler has been fired with this fuel blend detrimentally affects the potential cost savings.

V. RECOMMENDATIONS

At first glance, co-firing crude glycerin and yellow grease through a boiler may be an economically favorable option in an industrial setting. This is dependent upon the current market prices for crude glycerin and yellow grease in comparison to traditional boiler fuels. However, particulate matter and coked material build-up inside the boiler require more costly clean-up procedures and excessive downtime. These two detrimental factors along with the fact that crude glycerin did not work as a sole source fuel suggest that it is not a suitable boiler fuel. Blending crude glycerin with another fuel to fire the boiler may work, but again, implicit costs via production losses due to down-time or specialized boiler modifications negatively affect the energy-cost-savings pursuit.

VI. CONCLUSIONS

1. High levels of particulate matter (via the ash analysis), chlorine, and water contents in combination with the low energy value indicated that crude glycerin is not sufficient for consideration as a sole source fuel in an industrial triple pass fire tube boiler application.
2. Even with specialized modifications made to the boiler, the energy value in crude glycerin is inadequate for successful start-up and continuous boiler operation.
3. The high level of residual chlorine contained in the crude glycerin sample is too high for long term boiler operation and can adversely affect internal mechanisms of the boiler.
4. The high level of particulate matter (ash content) contained in the crude glycerin samples is too high for safe boiler operation.
5. In order to maintain a flame in the industrial fire tube boiler, a small amount of crude glycerin (10% V/V) was co-fired with yellow grease (90% V/V).

6. Pump mixing was not adequate to maintain a consistently blended fuel. Differences in the densities of crude glycerin and yellow grease require an advanced mixing mechanism in order to maintain a homogeneous fuel mixture.
7. Higher boiler maintenance costs and excessive clean-up schedules reduce the favorable economical consideration that crude glycerin low market values proffer.
8. Changes in the boiler fuel from that which the boiler was originally designed to burn can reduce boiler efficiency and negatively impact the load.
9. The current estimated cost per million Btu for the fuel blend (10% crude glycerin / 90% yellow grease) was calculated at \$13.32. The higher market prices for yellow grease does not make this a competitive fuel in comparison with natural gas costs at the industrial level.