



Environmental Technology Verification

Verification Testing of
Emissions from the
Combustion of
A-55[®] Clean Fuels
in a Firetube Boiler

ET ✓ ET ✓ ET ✓

EPA Review Notice

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

Verification Testing of Emissions from the Combustion of A-55[®] Clean Fuels in a Firetube Boiler

by:

C. Andrew Miller
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Research Triangle Park, NC 27711

EPA Cooperative Research and Development Agreement 0138-97
with
A-55 Limited Partnership
5270 Neil Road
Reno, NV 89502

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

Abstract

Two emulsified fuels and one non-emulsified fuel were tested in a small (2.5×10^6 Btu/hr [732 kW]) firetube package boiler to determine emissions of carbon monoxide (CO), nitrogen oxide (NO), particulate matter (PM), and total hydrocarbons (THC), and to calculate the thermal efficiency of the boiler using each of the fuels. Changes in emissions and thermal efficiency when using the emulsified fuels were compared to the base fuels from which they were produced, or that they would replace in normal usage. The fuels tested were a standard #2 fuel oil, the same #2 oil emulsified with 30% water by volume, and a fuel naphtha emulsified with 30% water by volume. The oil/water emulsions were produced by A-55 Limited Partnership of Reno, Nevada, and were tested at EPA's National Risk Management Research Laboratory, Air Pollution Prevention and Control Division in Research Triangle Park, NC, under EPA's Environmental Technology Verification (ETV) Program. Each of the fuels was tested at three different boiler loads.

NO emission concentrations from combustion of the emulsified #2 oil decreased 15 to 34% compared to the #2 oil at the same loads. For the emulsified naphtha, NO emissions decreased 33 to 51% compared to the #2 oil. Reductions in NO emission factors (in lb/10⁶ Btu [kg/kJ]) ranged from 22 to 37% for the emulsified #2 oil and from 37 to 54% for the emulsified naphtha, compared to the #2 oil emission factors. CO and PM emissions from all the fuels were very low, with CO emissions less than 8 ppm (at 3% O₂) in all cases, and PM emissions less than 5 mg/dscm in all cases (except for the initial test run, for which higher PM emissions were suspected as being the result of entrainment of particles previously on the boiler tubes). THC emission concentrations were typically less than 1 ppm for all cases.

Thermal efficiency typically was lower for the emulsified fuels than for the non-emulsified fuel, with a drop of 2.5 percentage points for the emulsified #2 fuel and 3.4 percentage points for the emulsified naphtha, compared to the #2 oil.

Preface

The U.S. Environmental Protection Agency (EPA) established the Environmental Technology Verification (ETV) program as a means to accelerate the commercialization of environmental technology through objective verification and reporting of technology performance. The ETV program approach is to evaluate technologies and report their performance characteristics, without considering regulatory compliance requirements, ranking of performance, labelling as acceptable or unacceptable, or determining “best available technology.” This straightforward reporting of technology performance is intended only to provide objective and quality-assured data for potential technology users.

The ETV program is currently in its initial phase of determining the most effective approaches to technology verification. Two of the verification approaches being evaluated are to arrange for independent verification entities to conduct testing following standard test protocols developed for the ETV program according to EPA requirements, or to have EPA conduct the testing directly using a specified or developed protocol. Although the majority of verification testing is planned to be conducted by independent verification entities, EPA’s Office of Research and Development has both substantial equipment and expertise to perform a number of verification tests at EPA’s facilities. Such “in-house” tests can be done when the testing is in line with the mission and resources of the organization within EPA best suited to conduct the tests.

In the Spring of 1997, EPA’s Air Pollution Technology Branch (APTB) of the National Risk Management Research Laboratory’s Air Pollution Prevention and Control Division (APPCD) was asked to conduct a series of verification tests on emulsified fuel oils. APTB has operated combustion equipment for study of pollution formation and control for over 20 years and was able to provide the expertise and equipment necessary to conduct the requested tests. A cooperative research and development agreement was negotiated with A-55 Limited Partnership to conduct the tests and testing was conducted in the Summer and Fall of 1997.

Acknowledgments

Substantial assistance in preparing for testing, reviewing test data, and verifying quality assurance was given by Richard Shores of the Technical Services Branch of APPCD. Robert Russell of A-55 Limited Partnership provided considerable help in reviewing data. Dahman Touati and Charlie King of ARCADIS Geraghty & Miller (formerly Acurex Environmental Corporation) provided the vast majority of technical support in conducting these tests.

Contents

Abstract	ii
Preface	iii
Acknowledgments	iv
List of Figures	vii
List of Tables	viii
Nomenclature and Symbols	ix
Chapter 1 Introduction	1
EPA Environmental Technology Verification Program	1
Emulsified Fuel Oils	1
ETV Testing of A-55® Clean Fuels	2
Limitations of Results	2
Chapter 2 Equipment and Test Approach	4
North American Firetube Boiler	4
Emissions Measurement Instrumentation	4
NO/NO _x Analyzer	5
O ₂ Analyzer	5
CO and CO ₂ Analyzers	5
THC Analyzer	6
Data Acquisition System	6
Extractive Sampling Methods	7
Total Particulate	7
Scanning Mobility Particle Sizer	7
Cascade Impactor	7
Thermal Efficiency Instrumentation	7
Measurement Method	7
Instrumentation	8
Test Matrix	8
Fuel Composition	10
Chapter 3 Thermal Efficiency Determination	13
Heat Losses	13
Heat Credits	16
Calculation of Thermal Efficiency	16
Chapter 4 Emission Results	17
Test Matrix Modifications	17

Contents (Continued)

	Emission Concentrations and Emission Factors	18
	Carbon Monoxide	18
	Nitrogen Oxide	22
	Particulate Matter	24
	Total Hydrocarbons	27
Chapter 5	Thermal Efficiency Results	28
	Energy Inputs	30
	Heat Losses	30
Chapter 6	Quality Assurance	33
	CEM, Temperature, and Flow Measurements	33
	CEM Precision	33
	CEM Accuracy	34
	CEM Completeness	35
	Temperature Data	36
	Flow Data	36
	Particulate Matter Measurements	36
	Discrepancies	37
	Audits	37
Chapter 7	Operational Observations	38
	Emulsified #2 Oil	38
	Emulsified Naphtha	38
	References	39
	Appendices	
	A English Engineering - International System Unit Conversions	41
	B Fuel Oil Analyses	42
	C Discrepancies	46
	D Audit Results	47
	Top-Loading Pan Balance Evaluation	47
	Systems Audit of Particulate Matter Collection Process	47

Figures

2-1. Burner end of the North American Package Boiler	5
2-2. Schematic of North American Package Boiler	6
2-3. Schematic of thermal efficiency instrumentation for the North American Package Boiler . . .	9
3-1. Energy flows into and out of the NAPB	14
4-1. Stack O ₂ concentration in volume percent for each test condition	19
4-2. Stack CO concentrations in ppm for each of the conditions, corrected to 3% O ₂	21
4-3. Emission factors for CO in lb/10 ⁶ Btu and lb/1000 gal	21
4-4. Stack NO concentrations in ppm for each of the conditions, corrected to 3% O ₂	22
4-5. Emission factors for NO in lb/10 ⁶ Btu and lb/1000 gal	23
4-6. Stack PM concentrations in mg/dscm for each of the conditions, corrected to 3% O ₂	24
4-7. Emission factors for PM in lb/10 ⁶ Btu and lb/1000 gal	25
4-8. SMPS particle size distributions for the three fuels tested at high load	26
5-1. Thermal efficiencies for each of the nine conditions in percent	29
5-2. Heat losses for each of the nine test conditions as a fraction of the total heat input	32

Tables

2-1. Planned test matrix for verification tests	10
2-2. Ultimate analyses of the fuel oils used in the test program	11
2-3. Trace metal content of the fuel oils tested, in µg/g	12
4-1. Target and actual test conditions achieved during verification testing	17
4-2. Average emission concentrations of O ₂ , CO, NO, PM, and THC for the #2 oil, emulsified #2 oil, and emulsified naphtha	18
4-3. Average emission factors for CO, NO, and PM for #2 oil, emulsified #2 oil, and emulsified naphtha	19
4-4. Percentage reduction in emission concentrations of CO, NO, and PM for emulsified #2 oil and emulsified naphtha compared to the #2 fuel oil	20
4-5. Percentage reduction in emission factors of CO, NO, and PM for emulsified #2 oil and emulsified naphtha compared to the #2 fuel oil	20
5-1. Parameters for determination of thermal efficiency	29
5-2. Thermal efficiencies and heat inputs and losses for all conditions tested	31
6-1. Data quality indicator goals for the project	33
6-2. Maximum percent RSD values for CEM and temperature measurements for all conditions	34
6-3. Cross-run RSD values of the average CEM and temperature measurements for all conditions	35
6-4. Average and maximum deviations of zero and high span CEM readings from calibration gas values for all runs	35
6-5. Data quality indicator goals for PM measurements	36
6-6. Measurements of DQI goals for PM mass measurements	37
B-1. Reported ultimate analysis results for the fuels tested	43
B-2. Corrected analysis results for the fuels tested	43
B-3. Differences in calculated thermal efficiency values using the different fuel analyses	45
D-1. Performance evaluation results for the Mettler AE240	48

Nomenclature and Symbols

B_A	energy supplied by the combustion air, Btu/hr
B_{CM}	energy supplied by the condensate makeup water, Btu/hr
B_F	energy supplied by the fuel sensible heat, Btu/hr
C_b	pounds of carbon per pound of as-fired fuel
$c_{p,A}$	heat capacity of the air in Btu/lb-°F
$c_{p,F}$	heat capacity of the fuel in Btu/lb-°F
$c_{p,FG}$	heat capacity of the flue gas, Btu/lb-°R
$c_{p,i}$	heat capacity of the <i>i</i> th constituent of the flue gas, Btu/lb-°R
$c_{p,w}$	specific heat of water, Btu/lb-°F
D_p	particle diameter, μm
F	fuel heat input, Btu/lb
f_H	percent hydrogen in the fuel (not including hydrogen associated with the moisture)
f_{MF}	percent moisture content of the fuel
h_{ref}	enthalpy of saturated liquid at the reference temperature (68 °F), Btu/lb
h_{WG}	enthalpy of the vapor in the flue gases at the stack temperature and vapor partial pressure (generally assumed to be 1 psia), Btu/lb
K_F	higher heating value of the as-fired fuel, Btu/lb
K_{HC}	heat content of unburned hydrocarbons in the flue gases, Btu/ft ³
L	total heat loss, Btu/hr
L_C	convective heat transfer loss from the boiler surface, Btu/hr
L_{CO}	loss of energy due to the failure of all CO to be completely converted to CO ₂
L_{FG}	loss associated with the sensible heat of the dry flue gas, Btu/hr
L_L	loss of energy through leaks of boiler combustion gas, feedwater, and/or steam, Btu/hr
L_{MF}	loss associated with the moisture in the fuel, Btu/hr
L_{MH}	loss associated with the conversion of hydrogen to water in the combustion process, Btu/hr
L_R	radiative heat transfer loss from the surface of the boiler, Btu/hr
L_{UBC}	loss associated with unburned carbon in the captured particulate, Btu/hr
L_{UHC}	loss of energy associated with emissions of unburned hydrocarbons, Btu/hr
L_{WG}	heat loss due to the moisture in the flue gases, Btu/hr
p_C	concentration of carbon in the ash, % vol
p_{CO}	concentration of CO in the flue gas, % vol
p_{CO_2}	concentration of CO ₂ in the flue gas, % vol
p_{HC}	concentration of hydrocarbons in the flue gas, % vol
p_{N_2}	concentration of N ₂ in the flue gas, % vol
p_{O_2}	concentration of O ₂ in the flue gas, % vol
s_{FG}	specific weight of the flue gas at standard conditions, ft ³ /lb
T_A	ambient air temperature, °F
T_{CA}	combustion air temperature, °F
T_{CM}	condensate makeup water temperature, °F
T_F	fuel temperature, °F
T_{FG}	flue gas temperature, °F
T_{re}	ambient air temperature, °F
V	particle volume, cm ³
W_A	mass flow rate of the combustion air, lb/hr
W_{CM}	condensate makeup water flow rate, lb/hr
W_F	mass flow rate of the fuel flow, lb/hr
W_{FG}	mass flow rate of flue gas, lb/hr
W_p	mass flow rate of the particulate, lb/hr

Nomenclature and Symbols (Continued)

χ_i molar fraction of the i th constituent of the flue gas
 η thermal efficiency, %

Chapter 1

Introduction

EPA Environmental Technology Verification Program

In 1994, the U.S. Environmental Protection Agency (EPA) Office of Research and Development formed a workgroup to plan the implementation of the Environmental Technology Verification (ETV) Program. The goal of ETV is “to verify the environmental performance characteristics of commercial-ready technology through the evaluation of objective and quality assured data, so that potential purchasers and permittees are provided with an independent and credible assessment of what they are buying and permitting.”¹ ETV is currently sponsoring 12 verification pilots, covering a range of technology areas including indoor air products, site characterization and monitoring, drinking water systems, and air pollution control technologies.

Although these pilots are partially funded by EPA during the initiation of the program, the intent of the ETV program is to create an on-going program that is primarily funded by program generated funds mainly from participants. In keeping with this intent, the Air Pollution Prevention and Control Division (APPCD) of EPA’s National Risk Management Research Laboratory (NRMRL) entered into a cooperative research and development agreement (CRADA) with A-55 Limited Partnership (A-55) of Reno, Nevada, to conduct verification testing of the emulsified fuels produced by A-55. This testing was conducted in the Summer and Fall of 1997 at EPA’s Environmental Research Center in Research Triangle Park, North Carolina, by personnel of APPCD’s Air Pollution Technology Branch (APTB) and their on-site contractor, ARCADIS Geraghty & Miller (formerly Acurex Environmental Corporation).

Emulsified Fuel Oils

Emulsions have been proposed for many years as a means of reducing the emissions of criteria pollutants from the combustion of fuel oils. A number of studies have shown the ability of emulsions of water suspended in oil to reduce the emissions from combustion sources²⁻⁴; however, the impacts of oil/water emulsions on particular pollutants vary. For heavy fuel oils, oil/water emulsions tend to reduce particulate, but in general have had a smaller effect on either carbon monoxide (CO) or oxides of nitrogen (NO_x) when operating conditions are kept constant.² With distillate oils, particulate matter (PM) and NO_x have been shown to be reduced when using an oil/water emulsion compared to using the same oil without emulsification, but CO emissions were not significantly changed.³ The use of an emulsified fuel results in improved secondary atomization of the fuels, often allowing operation at a reduced stoichiometric ratio, and also tends to reduce the peak combustion temperature. Both of these effects result in lower NO_x emissions, and the improved atomization can also result in lower CO and PM emissions. Emulsified oils appear to have little impact on emissions of hazardous air pollutants (HAPs) (compounds which are listed as hazardous under Title III of the Clean Air Act Amendments of 1990⁵). A study conducted by EPA concluded that emissions of organic HAPs remained relatively unchanged for an emulsified heavy fuel oil and the same oil that was not emulsified.⁶ Since metal emissions depend primarily upon the amount of metal in the fuel, the major impact on emulsified fuel metal emissions (per unit energy) will depend on the amount of metal (if any) in both the water and the emulsifying agent. In systems with particulate control equipment, the use of an emulsified fuel may also affect metal emissions if the particle size distribution changes in such a way that the net particulate removal efficiency is altered.

The effect of these fuels on operating efficiency will vary according to the particular characteristics of the fuel and the system in which it is used. For combustion systems that rely on the expansion of gases, the water contained in the emulsified fuel can provide additional expansive energy as it is heated along with the combustion products. In other systems where heat transfer is the primary mode of energy transfer, too much water can cause the thermal efficiency to drop because energy is required to heat the water in

the fuel, rather than that energy's being transferred to the process. However, using emulsified fuels can allow a boiler to be operated with less excess air, which in turn reduces the energy required to heat the atmospheric nitrogen and excess oxygen. In short, the thermal efficiency of a unit using emulsified fuels may either increase or decrease compared to the efficiency of the unit using the non-emulsified (base) fuel, depending upon the combustor type and the characteristics of the fuel.

The key disadvantage to the use of emulsions in the past has been the ability of the water to remain in suspension during storage. One method of avoiding this problem has been to mix the oil and water immediately prior to feeding the mixture into the boiler. However, this requires additional fuel and water handling equipment, as well as a system to mix the two liquids. The additional expenses associated with this equipment have not usually been considered worth the resulting reductions in pollutant emissions. As an alternative to separate storage of the oil and water, emulsifying agents that result in a reduced rate of oil/water separation have been developed, allowing "premixed" emulsified oils to maintain their properties for extended periods of time when properly stored. This approach eliminates the need for additional handling and mixing equipment, and utilizes existing fuel handling systems, thereby reducing the cost of use. Current emulsifying agents are much more effective at inhibiting phase separation, allowing emulsified fuels to be effectively used in a variety of applications.

ETV Testing of A-55® Clean Fuels

The CRADA between EPA and A-55 was designed to verify the performance of A-55® Clean Fuels in a small well-instrumented firetube boiler. The A-55® Clean Fuels included "premixed" oil/water emulsions of a #2 fuel oil (diesel) and a petroleum naphtha. Performance of these fuels was compared to the performance of the non-emulsified #2 fuel oil.

The intent of the project was to produce objective data on the pollutant emissions and thermal efficiency of the fuels to provide potential fuel buyers, users, and regulators with information regarding the environmental characteristics of the A-55® Clean Fuels. This report discusses the testing approach and calculations used during the tests, the results of the tests, quality assurance (QA) goals and measures, and operational observations noted during testing.

The objective of these tests is to determine the changes in emissions of CO, nitrogen oxide (NO), and PM, and in boiler thermal efficiency when an emulsified fuel is used in place of a non-emulsified fuel. The tests were designed to ensure that the comparison reflected the impact of using the emulsified fuel, rather than changes in base fuel properties (e.g., nitrogen content) or in the operating characteristics of different combustion systems. To minimize the number of variables influencing emissions, the (non-emulsified) fuel was first combusted in the test boiler under typical operating conditions, followed by testing of the emulsified fuel in the same unit, again under conditions typically maintained when using an emulsified oil. The results are indicative of the ability of the emulsified fuel to affect pollutant emissions and thermal efficiency under the particular conditions of the test.

Limitations of Results

Changing combustion conditions or the system in which the fuels are used can have a considerable effect on emissions and thermal efficiency. It is impossible to develop a limited test protocol that would cover all the possible permutations of operating conditions and combustion system configurations in which an emulsified fuel may be appropriate for use. The approach taken for these tests was to limit the test conditions to a single boiler, and to draw conclusions regarding the performance of the emulsified fuel using the limited test data and an understanding of the physico-chemical processes associated with the fuel's use. This approach provided data as well as an indication of the advantages and disadvantages associated with combustion of emulsified fuels. However, the wide range of possible operating conditions and combustion systems makes emphasis of the limitations critical. The quantitative results apply directly

only to the system tested under the conditions tested. While it is expected that these fuels will behave similarly in other systems, use of these fuels in systems with either different hardware or operating conditions may not result in similar performance. Note that performance may be either better or worse than the results reported here. In any case, it is anticipated that individual systems will require optimization to achieve their best results.

Chapter 2

Equipment and Test Approach

The approach taken to verify the performance of the emulsified fuels compared the pollutant emissions and the thermal efficiencies of the emulsified fuels to the same parameters measured during the combustion of the same fuels without the water or emulsifying agent. Measuring only the emissions and performance of the emulsified fuels would not provide any reference with which to compare. Three different fuels were tested: a #2 (diesel) fuel oil, the same #2 oil emulsified with water (emulsified #2 oil), and a petroleum-naphtha/water emulsion (emulsified naphtha). The #2 oil/water emulsion and the naphtha/water emulsion were compared with the #2 oil, since both the #2 oil/water emulsion and the naphtha/water emulsion are designed to replace the #2 oil in practice.

The fuels were burned in a small firetube package boiler at EPA's Environmental Research Center. While this unit is typical of many small institutional or commercial boilers used to generate low pressure steam, it is of a very different design than a large watertube boiler typically used in large industrial or utility applications. Thus, the performance results cannot be directly compared to these larger systems. However, significant changes in performance between the base and emulsified oils on this small boiler are expected to indicate similar changes in terms of direction and magnitude for larger scale systems. Therefore the results obtained in these tests can be used to evaluate the potential for emission reductions and thermal performance for other external combustion steam generating systems.

North American Firetube Boiler

The tests were performed on APPCD's North American package boiler (NAPB) which is capable of firing natural gas or #2 through #6 fuel oils. The boiler is a three-pass firetube "Scotch" marine-type design built in 1967, model 5-360H-D, shown in Figure 2-1 and schematically in Figure 2-2. The burner is a North American model 6121-2.5H6-A65 rated at 2.5×10^6 Btu/hr* and has a ring-type natural gas burner and an air-atomizing center nozzle oil burner capable of firing #2 through #6 oils. The boiler has 300 ft² of heating surface and generates up to 2400 lb/hr of saturated steam at pressures up to 15 psig. Heat is extracted from the steam through a heat exchanger to an industrial cooling water system that provides the boiler load. Oil temperature can be adjusted using an electric heater to maintain proper oil viscosity, and both fuel and atomizing air pressures are variable to ensure adequate oil atomization.

The flue gases from the unit pass through a manifold to an air pollution control system (APCS) consisting of a natural-gas-fired secondary combustion chamber, an acid gas scrubber, and a fabric filter to ensure proper removal of pollutants generated during tests designed to mimic poor combustion conditions. During the tests reported here, the APCS was operated to provide a constant draft to the NAPB to minimize changes in the induced draft. Although this type of boiler normally operates under forced draft only, the imposition of an induced draft due to the APCS did not significantly affect boiler emissions.

Emissions Measurement Instrumentation

The NAPB is fully instrumented with continuous emission monitors (CEMs) for NO_x, CO, CO₂, O₂, SO₂, and total hydrocarbons (THC). The CEM panel for the NAPB uses seven gas analyzers, each with multiple ranges, and flue gas conditioning equipment. Effluents from the stack are carried to the CEM panel through heated Teflon tubing to a gas dryer and filter.

*See Appendix A for conversion of units to metric system equivalents.

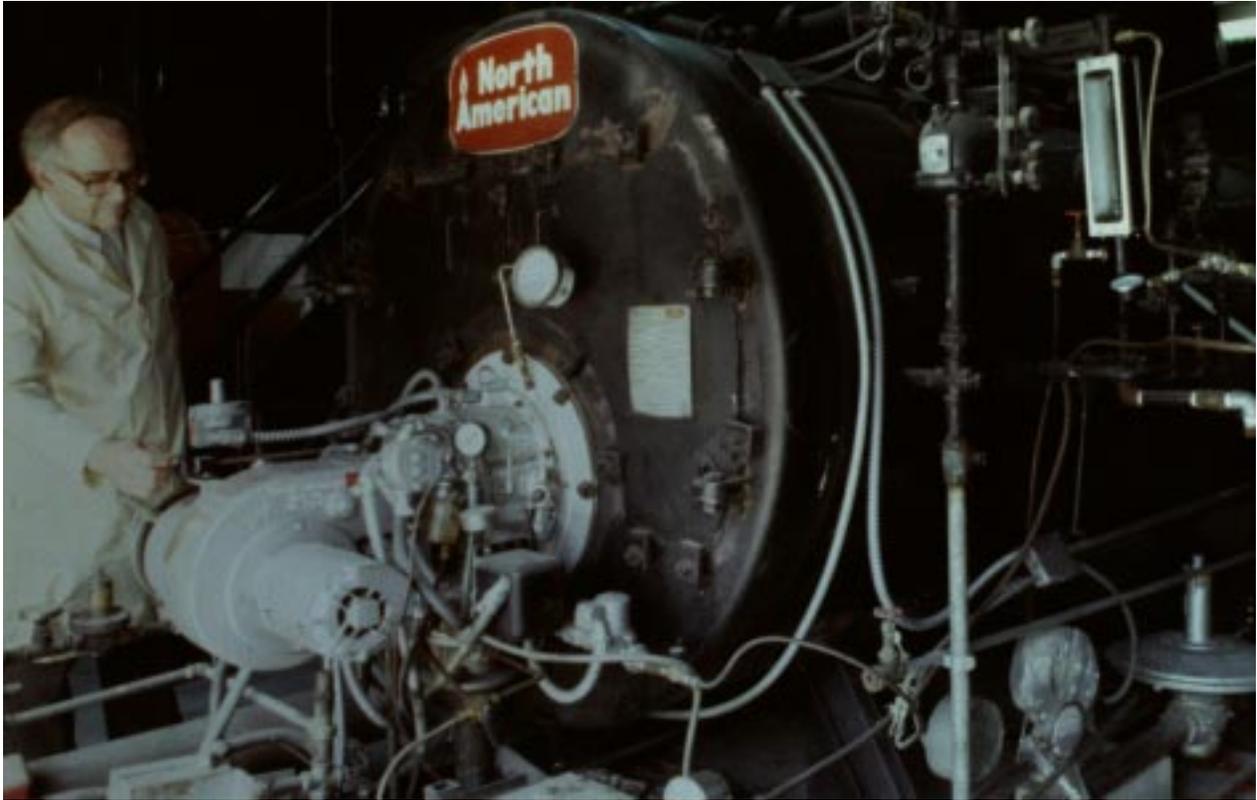


Figure 2-1. Burner end of the North American Package Boiler.

NO/NO_x Analyzer

The NO/NO_x analyzer is a Rosemount Analytical Model 951A that operates via chemiluminescence. In the NO measurement mode, NO is directly measured by light emission from the reaction of the NO with ozone supplied by the analyzer. In the NO_x measurement mode, a portion of the sample is diverted to a converter where the NO₂ is dissociated into NO, and the resulting NO then measured using the analyzer. The monitor has selectable ranges of 0-3; 0-10; 0-30; 0-100; 0-1,000; 0-3,000; 0-10,000; and 0-30,000 ppm of NO or NO_x. Testing used either the 0-100 or 0-1000 ppm range. The analyzer is accurate to 0.5% of full scale.

O₂ Analyzer

The O₂ analyzer is a Rosemount Analytical Model 755R analyzer that operates using the paramagnetic property of oxygen. Other gases present in significant concentrations in combustion flue gases do not exhibit paramagnetism. Measurement ranges for the instrument are 0-5, 0-10, and 0-25% of O₂. The 0-5% scale was used during testing. The analyzer accuracy is specified to be 1% of full scale.

CO and CO₂ Analyzers

The CO and CO₂ analyzers are Rosemount Analytical Model 880A Non-Dispersive Infrared Analyzers. They operate by directing identical infrared beams through an optical sample cell and a sealed optical reference cell. A detector located at the opposite end of each cell continuously measures the difference in the amount of infrared energy absorbed within each cell. The difference is a measure of the concentration of the component of interest in the sample. The ranges of the CO₂ analyzer are 0-5, 0-15, and 0-25%. The ranges of the low CO monitor are 0-500, 0-1000, and 0-2000 ppm, and the ranges of the high CO monitor are 0-1, 0-3, and 0-5%. The CO₂ analyzer was operated using the 0-25% range.

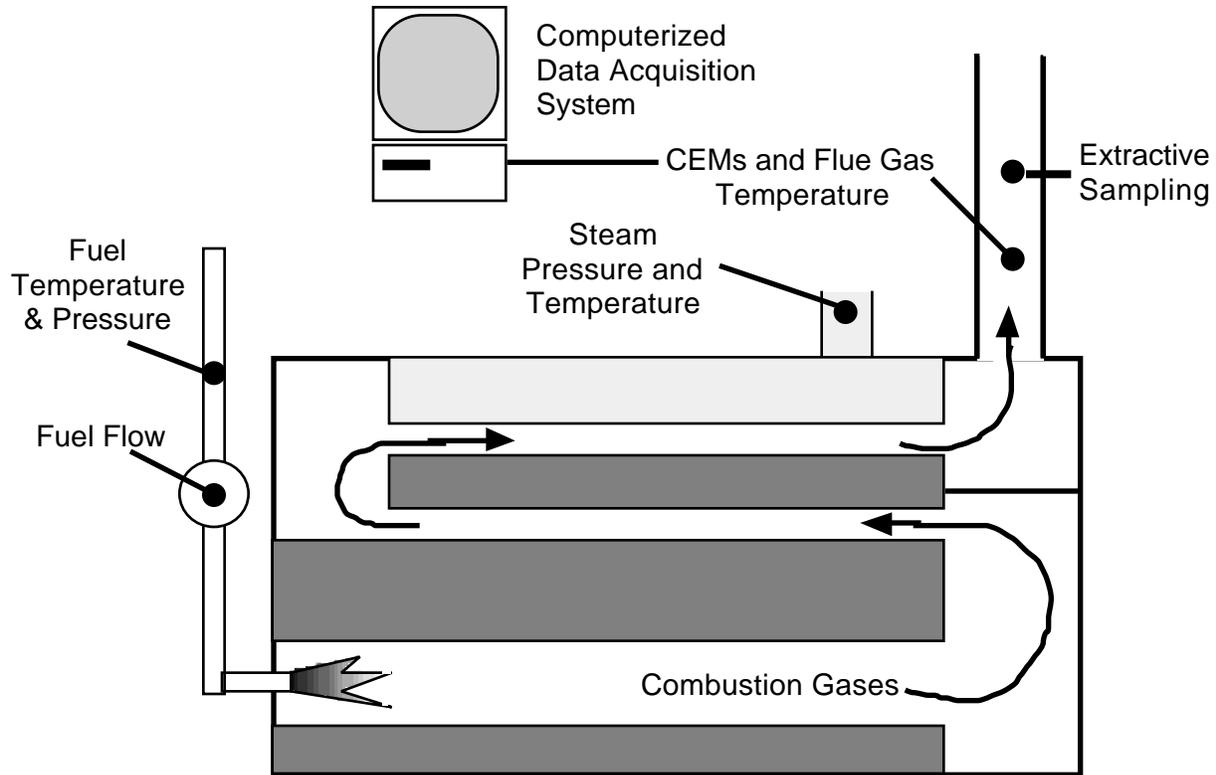


Figure 2-2. Schematic of North American Package Boiler.

The 0-500 ppm scale on the low CO monitor was used during these tests. Analyzer accuracies for the CO and CO₂ monitors are both 1% of full scale.

THC Analyzer

A Rosemount Analytical Model 402 hydrocarbon analyzer was used to measure THC content of the flue gas. The analyzer uses a flame ionization detector (FID) and a heated temperature-controlled sample line with associated electronics. The hydrocarbon sensor in the analyzer uses a burner where a regulated flow of sample gas passes through a flame sustained by regulated flows of fuel and air. Within the flame, the hydrocarbon components of the sample undergo a complex ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through the measuring circuitry of the analyzer. The resulting current is proportional to the concentration of hydrocarbons in the sample. The heated sample line allows the sample to be maintained at the desired temperature to prevent condensation of the heavier hydrocarbon fractions. The analyzer ranges are 0-3; 0-10; 0-30; 0-100; 0-300; 0-1,000; 0- 3,000; 0-10,000; and 0-30,000 ppm. The analyzer was operated using the 0-100 ppm range. Accuracy of the analyzer is 1% of full scale.

Data Acquisition System

A computerized data acquisition system (DAS) was used to record CEM measurements as well as steam and flue gas temperatures. The DAS uses a Macintosh computer and Strawberry Tree data acquisition software. An analog-to-digital converter card allows up to eight standard analyzer outputs to be input to the computer. The software enables preliminary data calculations during data collection, and both raw data and calculated values can be recorded to a disk file for later retrieval. The system can take readings at periodic intervals of 0.1 second or more. All recorded data are time and date stamped to ensure that logged data correlate with data taken manually or otherwise.

Extractive Sampling Methods

Total Particulate

An EPA Method 5 sampling train⁷ is used to collect particulate samples to determine total suspended particle loading in the flue gases of the boiler. Three samples per test condition were planned to evaluate the repeatability of the results. Results are reported both as flue gas concentrations ($\mu\text{g}/\text{m}^3$) and as emission factors ($\text{lb}/10^6 \text{ Btu}$ or $\text{lb}/1000 \text{ gal fuel}$).

Scanning Mobility Particle Sizer

Particle size distributions can be determined for a limited range of particle sizes using a scanning mobility particle sizer (SMPS). The SMPS measures particle size distributions for particles ranging from 0.3 to 10 μm in diameter. These distributions were taken to determine the relative changes between conditions rather than to measure the absolute concentrations of particles of given sizes. Because of the nature of the SMPS, QA measurements to evaluate the precision and accuracy of the results were not made for these tests. Results from the SMPS are reported as relative changes between test conditions.

Cascade Impactor

Particle size distributions can also be measured using a cascade impactor. Cascade impactors classify particles according to their ability to follow gas flow streamlines. Particles of large mass are unable to follow sudden changes in flow direction as the gas passes from one stage to the next, and are deposited on the stage filter. Each stage of the impactor is designed to collect different particle sizes, and the final particle weights on each stage provide data on the size distribution of the sampled particle stream. A California Air Resources Board (CARB) Method 501⁸ was used as the basis for the test method, with the modifications outlined below:

- (1) The CARB method recommends several “trash” runs be discarded to allow for unfamiliarity with equipment, poor initial conditions, or other factors. These trash runs are then to be followed by seven actual runs to ensure that valid data are collected. Due to the non-critical nature of the impactor data for these tests, three Method 501 runs were determined to be adequate to provide the desired information.
- (2) Method 501 requires an *in situ* sampling approach (i.e., the entire impactor is inserted into the flow). However, the impactor is too large to insert into the NAPB stack without severe flow disruption. For these tests, the impactor was mounted external to the stack, and a buttonhook nozzle was used to collect the sample from the flue gas stream. Method 501 also requires use of a straight sampling nozzle, which is possible only if the *in situ* sampling procedure is followed.
- (3) Method 501 requires that upper limits of 50 mg total particle mass and 15 mg particle mass per stage be captured to minimize the possibility of particle carryover from one stage to the next. The test procedures are such that these limits should be achieved; however, the non-critical nature of the impactor measurements allows for exceedance of these limits if an assessment of the test conditions and results indicates that the measurements are valid, even if the limits are not met.

Thermal Efficiency Instrumentation

Measurement Method

Thermal efficiency can be determined in a number of ways. For boilers, the most widely accepted method of thermal efficiency measurements for boilers is the American Society of Mechanical Engineers (ASME) Power Test Code (PTC) 4.1 - Steam Generating Units.⁹ PTC 4.1 covers units ranging from large utility steam generating units and combined cycle systems to high temperature water heaters and is also applicable to firetube package boilers such as the North American unit on which the current tests were conducted.

PTC 4.1 provides two primary methods for determining thermal efficiency: the input-output method

and the heat loss method. The input-output method relies on calculations of the energy input from the fuel and the energy output of the steam and requires accurate measurement of flow rates, temperatures, pressures, and energy contents of the different process flows. The heat loss method measures the energy inputs and losses of energy through radiation, flue gases, and other routes. The difference between the measured energy input and the energy losses is the energy absorbed by the steam. The heat loss method requires measurements of fuel heat content, composition, flow, and temperatures; external boiler temperatures; and flow, composition, and temperature of the boiler flue gases.

Accurate values of the absolute thermal efficiency are meaningful only for the particular boiler being tested. In the current tests, the change in boiler thermal efficiency is of much more importance than the absolute thermal efficiency, because each boiler is unique and the particular efficiencies measured for the NAPB cannot be easily transferred to other units, even those that are of identical design. Thus the focus for the current tests was to calculate the change in thermal efficiency as fuels are changed. This will allow the measurements to focus on the major changes of the fuel's energy content and flow rate and changes in the flue gas composition and temperature. It was expected that other parameters such as boiler skin temperature would remain relatively constant for the different fuels, and would not substantially impact the efficiency measurements.

The current tests used the heat loss method for determining the boiler thermal efficiency. Additional detail on this method is presented in the following chapter.

Instrumentation

Figure 2-3 shows a schematic of the boiler/heat exchanger system with the measurement points and parameters. The primary quantities required to determine the thermal efficiency of the boiler are the energy input from the fuel and other sources and the heat losses through the stack (including sensible heat of the dry flue gas constituents, the energy content of the water vapor, and the energy in the unburned carbon, CO, and hydrocarbons), leaks, and heat transfer to the surroundings. The CEMs are used to determine the composition (C1 in Figure 2-3), and extractive sampling methods are used to determine stack flow rate F2 and fuel heat content H1. Thermocouples are used to measure temperatures at T1, T3, and T4, and flow totalizers provide total flow into the unit at F1 and F3.

Secondary measurements are taken at various points on the system to ensure proper operation. These measurements are shown in the smaller circles in Figure 2-3, and include stack flue gas pressure, fuel pressure, cooling water inlet and outlet temperatures, and cooling water flow. Also included in the secondary measurements are steam temperature T2 and pressure P1. These parameters are secondary because the heat loss method of determining thermal efficiency is used rather than the input-output method.⁹

Fuel flow was measured using a Brooks-Oval Mini-Oil Flowmeter, Model LS-21312, which operates by using a slight pressure drop across the meter to drive a pair of oval gears. The meshed gears seal inlet from outlet to generate the pressure differential. The meter is designed to remain unaffected by changes in liquid viscosity, density, and lubricity, allowing the same meter to be used for a wide range of fuels. Instrument accuracy is specified as $\pm 0.5\%$ of full scale (200 gpm).

Test Matrix

The test matrix was developed to ensure that test results reflected the performance of the emulsified oil under a range of load conditions and to allow comparison with the performance of the non-emulsified fuel it was designed to replace. For each test condition, three Method 5 samples were planned to be taken, and three SMPS sampling runs were planned. CEM and thermal efficiency measurements were planned for each test run. Each test run was expected to last approximately 2 hours, during which CEM measurements were planned to be taken continuously and logged every 20 seconds. Four test runs were planned for each test condition. The test conditions were chosen based primarily on load, with target loads of 1.5×10^6 Btu/hr (low load), 2.0×10^6 Btu/hr (medium load), and

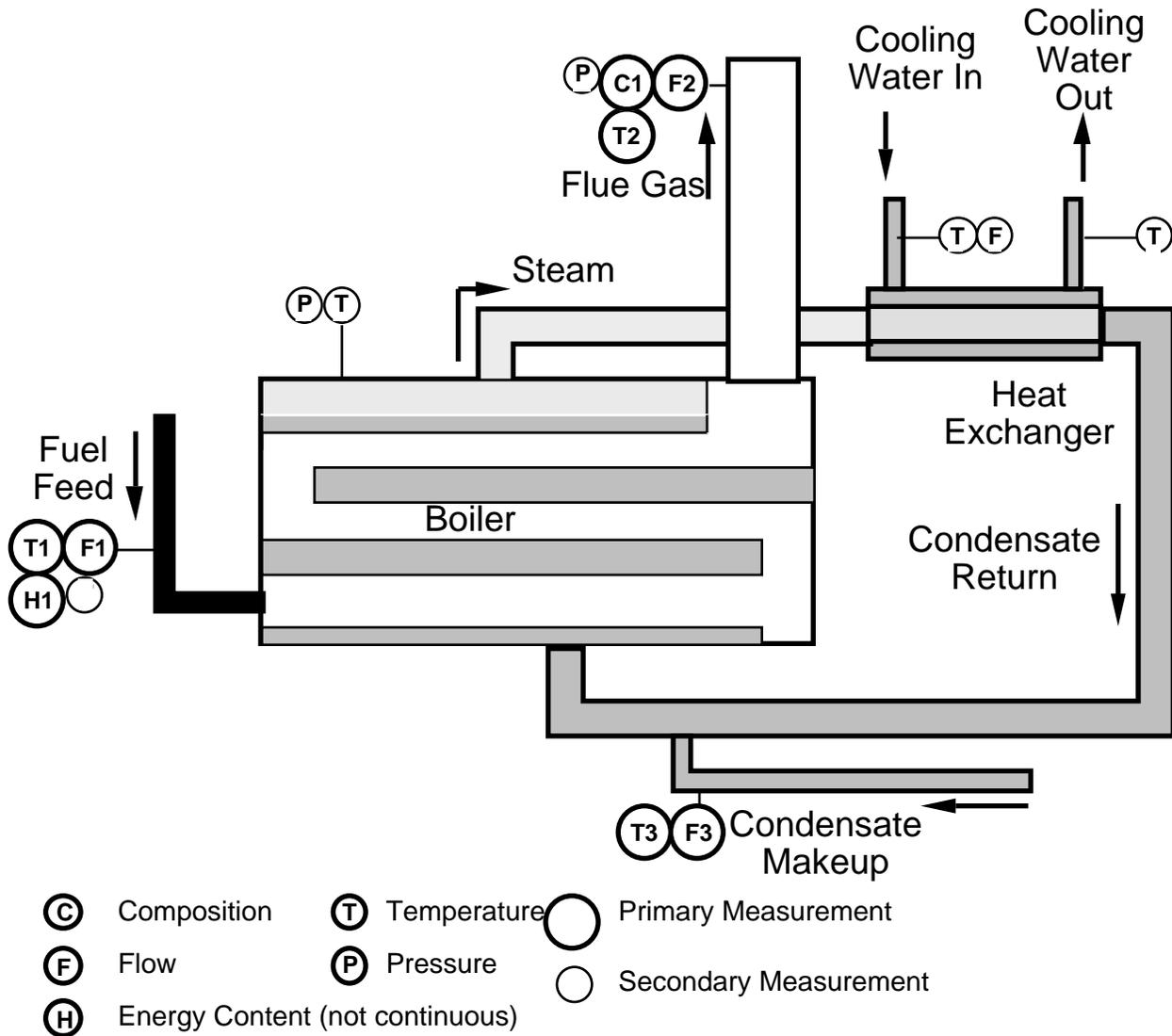


Figure 2-3. Schematic of thermal efficiency instrumentation for the North American Package Boiler. Instruments used for primary measurement of thermal efficiency are in the large circles, while secondary instrumentation is shown in the small circles.

2.5x10⁶ Btu/hr (high load). Table 2-1 shows the test matrix used for each oil tested in the verification tests.

To the extent possible, the high, medium, and low loads were to be held constant for all the fuels tested. This would require significant increases (on the order of 50%) in the emulsified fuel flow relative to the non-emulsified fuel in order to match loads.

In addition to load, it was expected that the stack O₂ level would also be varied for the emulsified fuel test conditions. In general, the secondary atomization created by the water in the emulsified fuels allows the combustion air, and thus the stack O₂, to be reduced relative to the base fuel O₂ level. The target O₂ level was 3% for the base fuels. The target O₂ levels for the emulsified fuels was determined based on the minimum O₂ level that could be achieved without increasing either CO or PM (as

Table 2-1. Planned test matrix for verification tests. An “X” denotes measurements to be taken during the specified test run. This matrix is to be repeated for each of the conditions tested.

Run	1	2	3	4
CEM Measurements (Gaseous emissions)	X	X	X	X
Thermal Efficiency Measurements	X	X	X	X
Method 5 Samples ^a (Total particulate)	X	X		X
SMPS Samples ^a (Particle size distribution)	X	X		X
Cascade Impactor ^a (Particle size distribution)		X	X	X

a. Only three Method 5, SMPS, and cascade impactor samples per condition were planned. The three runs in which these samples were taken were allowed to vary for each condition.

measured by Bacharach smoke number) over the values measured for the corresponding base fuel.

Fuel Composition

The fuels used in the test matrix varied in their composition and characteristics. Table 2-2 provides the ultimate analyses of the fuels. Because of the high level of water in the emulsified fuels, there was some concern regarding the impact of the water on the analyses. The fuel analyses were conducted by independent laboratories following American Society of Testing and Materials (ASTM) methods. These methods rely on combustion of the fuel sample and analysis of the combustion gases for CO₂ and water (H₂O) to determine the carbon and hydrogen contents of the fuel, with oxygen being determined by difference.¹⁰ The moisture content is determined by distillation of the sample prior to conducting the analysis for hydrogen,¹¹ but the possibility arises that the water is not completely driven off by the distillation process. In such an instance, the subsequent hydrogen analysis (which relies on the water from the combustion of the sample) may indicate that the fuel contains more hydrogen than actually present due to the excess water contained in the fuel.

This possibility was considered to be likely due to the unexpectedly high level of oxygen (7.67%) originally reported in the fuel analysis for the emulsified #2 oil. Even accounting for any oxygen in the proprietary emulsifying additives, the oxygen level was expected to be no more than 1%. It was hypothesized that the reported moisture content was lower than actually present in the emulsified fuel and that this difference was responsible for the higher reported oxygen content. Since the fuel hydrogen and moisture contents strongly influences the thermal efficiency due to the combustion-generated water in the flue gas (see Chapter 3), it was important to ensure that the fuel analyses were consistent with the known base oil analyses and the amounts of water added during the emulsification process.

Given the fact that the oxygen level was reported to be significantly higher than anticipated, additional analyses were done to determine whether the reported oxygen values were actually as high as reported, or whether there was the possibility of error in the analyses. One testing laboratory reported the hydrogen and oxygen associated with the water in the total fuel hydrogen and oxygen contents, and also reported water in volume percent. Corrections were made to these reported results to yield hydrogen and oxygen values separate from that included in the water, and to convert the water content to weight percent. Details of the analyses and corrections are given in Appendix B.

The #2 oil, emulsified #2 oil, and emulsified naphtha were also analyzed for trace metal content using standard fuel analysis methods. Concentrations of antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, magnesium, mercury, nickel, selenium, vanadium, and zinc were measured, and the results of these analyses are given in Table 2-3. For all the fuels, the trace metal contents were consistently low. The only metals with concentrations over 1 µg/g in all three

Table 2-2. Ultimate analyses of the fuel oils used in the test program.

Oil	#2 Oil	Emulsified #2 Oil	Emulsified Naphtha
% Carbon ^{a,b}	86.92	57.40	53.36
% Hydrogen	13.01	8.77	9.16
% Oxygen ^c	0.42	2.42	1.10
% Nitrogen	0.49	0.48	0.32
% Sulfur	0.03	0.009	0.002
% Water	<0.05	30.93	36.07
% Ash	0.001	0.003	0.01
Higher Heating Value, Btu/lb	19,450	12,786	12,584
Specific Gravity (60 °F)	0.8607	0.9050	0.8309

a.Percents are by weight.

b.Methods: Carbon, Hydrogen, Nitrogen - ASTM D 5291¹⁰; Sulfur - ASTM D 4294¹²; Water - ASTM D 95¹¹; Heating Value - ASTM D 240¹³; Ash - ASTM D 482.¹⁴

c.Determined by difference.

fuels were iron and vanadium, although antimony in the emulsified naphtha was measured at 1.5 µg/g. Since the emulsifying agent was composed of organic hydrocarbons, it would be expected that the metal concentrations for the emulsified #2 oil would be lower than those for the #2 oil. However, this was not the case for all metals. For some of the metals, the concentrations were low enough to be within the measurement error of the analysis method; however, for iron there was a considerable increase in the emulsified #2 oil compared to the base #2 oil. It is speculated that this increase may be due to contamination from the oil drum. Although some metals could be introduced by the water used in the emulsification, the water was deionized prior to mixing, which should have removed nearly all metals.

Table 2-3. Trace metal content of the fuel oils tested, in µg/g.

	#2 Oil	Emulsified #2 Oil	Emulsified Naphtha
Antimony	0.3	0.4	1.5
Arsenic	< 0.1	< 0.1	< 0.1
Beryllium	< 0.5	< 0.5	< 0.5
Cadmium	0.05	0.10	0.08
Chromium	0.3	0.5	0.4
Copper	0.10	0.19	0.17
Iron	4	56	15
Lead	0.2	0.5	0.3
Magnesium	0.26	NA ^a	0.50
Mercury	0.10	0.09	0.06
Nickel	0.82	0.19	0.17
Selenium	< 0.1	< 0.1	< 0.1
Vanadium	4.68	2.77	2.60
Zinc	0.6	1.0	0.7

a. NA - Not Available

Chapter 3 Thermal Efficiency Determination

The heat loss method* relies on measurements of the input energy (the energy flowing into the system with the fuel and air) and energy losses; i.e., energy that is not absorbed by the steam. Such losses include energy carried out of the system by the flue gases and unburned fuel, energy radiated from the boiler skin to the surroundings, and energy escaping the boiler from leaks. The ASME PTC 4.1 defines efficiency through the heat loss method as:

$$\eta = 100\% - \left(\frac{\text{Heat losses}}{\text{Heat in fuel} + \text{Heat credits}} \right) \times 100\% \quad (3-1)$$

where heat credits involve energy inflow through the boiler feedwater and combustion air. The heat-in-fuel term is the product of the fuel's higher heating value** and the flow rate of the fuel to produce energy per unit time (in this case, 10⁶ Btu/hr). A schematic of energy flows for the NAPB is shown in Figure 3-1.

Heat Losses

Heat losses are illustrated in Figure 3-1 in underlined text. The major heat loss is through the sensible heat in the flue gases; however, other heat losses may also be significant, depending upon the operating characteristics of the particular boiler. In addition to flue gas heat loss, energy may also be lost through leaks of boiler water or combustion gases; the presence of CO, unburned hydrocarbons, and/or unburned carbon in the flue gases; or the presence of water in the fuel. The total heat loss is simply the sum of those losses:

$$L = L_{FG} + L_{WG} + L_L + L_{CO} + L_{UHC} + L_{UBC} + L_R + L_C \quad (3-2)$$

where L_{FG} is the sensible heat loss in the dry flue gases, L_{WG} is the heat loss from the moisture in the flue gases, L_L is the loss due to boiler and combustion gas leaks, L_{CO} is the loss due to the presence of CO (rather than CO₂) in the flue gas, L_{UHC} is the loss associated with the failure of all the hydrocarbons to completely burn, L_{UBC} is the loss associated with unburned carbon in the captured particulate, L_R is the radiative heat transfer loss from the surface of the boiler, and L_C is the convective heat transfer loss from the boiler surface. Each of the losses is calculated in Btu/hr.

L_{FG} is calculated by:

$$L_{FG} = W_{FG} c_{p,FG} (T_{FG} - T_A) \quad (3-3)$$

where W_{FG} is the flow rate of flue gas in lb/hr, $c_{p,FG}$ is the specific heat of the flue gas in Btu/lb-°F, and T_{FG} and T_A are the temperatures of the flue gas and ambient air, respectively, in °F. The mass flow rate of the flue gas can be determined by using the following equation based on measurements

*The more accurate term is “energy loss.” However, “heat loss” is the term used in ASME PTC 4.1 to include both actual heat losses and other energy losses such as those due to unburned carbon.

**This is the higher heating value at constant pressure.

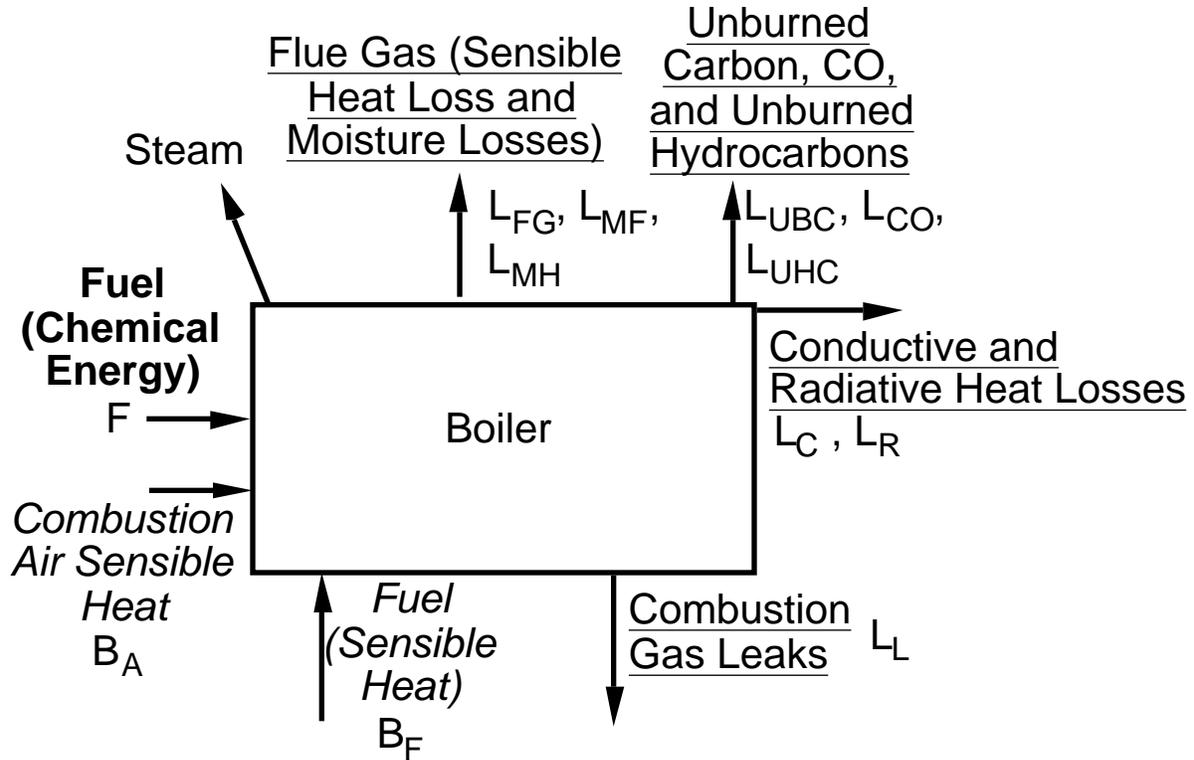


Figure 3-1. Energy flows into and out of the NAPB. Following the terminology of ASME PTC-4.1, energy inputs are shown in bold, energy losses are underlined, and heat credits are in italics.

of the flue gas constituents:

$$W_{FG} = \frac{44.01p_{CO_2} + 32.00p_{O_2} + 28.02p_{N_2} + 28.01p_{CO}}{12.01(p_{CO_2} + p_{CO})} \left(C_b + \frac{12.01f_s}{32.07} \right) W_F \quad (3-4)$$

where p_{CO_2} , p_{CO} , p_{O_2} , and p_{N_2} are the measured concentrations (in volume percent) of the specified flue gas constituents, C_b is the pounds of carbon per pound of as-fired fuel, f_s is the fraction of sulfur in the as-fired fuel, and W_F is the fuel flow in lb/hr. The flue gas specific heat can be calculated by using:

$$c_{p,FG} = \sum_i c_{p,i} \chi_i \quad (3-5)$$

where $c_{p,i}$ and χ_i are the specific heat and molar fraction, respectively, of constituent i of the flue gas.

L_{WG} is the heat loss due to the moisture in the flue gases and is the sum of L_{MF} and L_{MH} , where L_{MF} is the loss associated with the moisture in the fuel and L_{MH} is the loss associated with the conversion of hydrogen to water in the combustion process. L_{MF} can be calculated from:

$$L_{MF} = f_{MF} (h_{WG} - h_{ref}) W_F \quad (3-6)$$

where f_{MF} is the percent moisture content of the fuel, h_{WG} is the enthalpy of the water vapor in the flue gases at the stack temperature and vapor partial pressure (generally assumed to be 1 psia) in Btu/lb, and h_{ref} is the enthalpy of saturated liquid water at the reference temperature (68 °F), also in

Btu/lb. h_{WG} and h_{ref} are determined from standard ASME steam tables.

L_{MH} is calculated using:

$$L_{MH} = 8.936 f_H (h_{WG} - h_{ref}) W_F \quad (3-7)$$

where f_H is the fraction of hydrogen in the fuel (not including hydrogen associated with the moisture) and h_{WG} , h_{ref} , and W_F are as defined above. The 8.936 is the number of pounds of water produced from the complete combustion of a pound of hydrogen.⁹ From Eqs. (3-6) and (3-7), L_{WG} is then given by:

$$L_{WG} = (f_{MF} + 8.936 f_H) (h_{WG} - h_{ref}) W_F \quad (3-8)$$

L_L represents the loss of energy through leaks of boiler combustion gas, feedwater, and/or steam. This value is calculated from an estimated leak rate times the energy content of the leaking material. It is assumed that this value is very small relative to the other losses, particularly for a small unit where such leaks can be easily spotted, and L_L is neglected for these calculations.

L_{CO} is the loss of energy due to the failure of all CO in the flue gas to be completely converted to CO₂, and is given by:

$$L_{CO} = 10,160 \frac{p_{CO}}{p_{CO_2} + p_{CO}} C_b W_F \quad (3-9)$$

where p_{CO} and p_{CO_2} are the percent by volume concentrations of CO and CO₂, respectively, in the flue gas, and C_b is the pounds of carbon burned per pound of as-fired fuel. The 10,160 value is the heat released in Btu when burning 1 lb of CO to CO₂.⁹

L_{UHC} is the loss of energy associated with emissions of unburned hydrocarbons, and is given by:

$$L_{UHC} = \frac{p_{HC} W_{FG} K_{HC}}{100 s_{FG}} \quad (3-10)$$

where p_{HC} is the concentration of hydrocarbons in the flue gas in percent, W_{FG} is the mass flow rate of the flue gas in lb/hr, K_{HC} is the heating value of the hydrocarbons in Btu/ft³, and s_{FG} is the specific weight of the flue gas in ft³/lb. K_{HC} is usually considered to be that for methane, roughly 1010 Btu/ft³. s_{FG} (at 68 °F, 14.7 psia) can be calculated from:⁹

$$s_{FG} = 0.0401 \left[\frac{p_{CO_2}}{35.11} + \frac{p_{O_2}}{48.28} + \frac{p_{CO}}{55.16} + \frac{p_{N_2}}{55.14} + \frac{p_{SO_2}}{24.12} + \frac{p_{HC}}{1545} \right] \quad (3-11)$$

L_{UBC} is the energy loss associated with the emission of unburned carbon in the fly ash, and is calculated by:

$$L_{UBC} = 14,500 W_p p_C \quad (3-12)$$

where W_p is the mass flow rate of the particulate in lb of ash/lb of fuel, and p_C is the mass fraction of carbon in the ash. The 14,500 value is the heating value in Btu of 1 lb of carbon as it occurs in refuse.⁹

L_R and L_C are the losses due to radiative and convective heat transfer, respectively, from the boiler

surface to the surroundings. These values are highly unit specific and can also change substantially as conditions surrounding the unit changes (e.g., increase or decrease in ambient air temperature). In instances such as the current tests, where the surroundings are relatively constant* and no significant changes are expected to occur due to changes in the fuels, L_R and L_C are expected to be negligible compared to the other loss components.

Heat Credits

Heat credits are measures of energy flows into the boiler other than through the fuel (shown in italics in Figure 3-1) and are summarized as:

$$B = B_A + B_F \quad (3-13)$$

where B is the total heat credit, B_A is the energy supplied by the combustion air, and B_F is the energy supplied by the fuel sensible heat, all in Btu/hr. B_A is calculated by:

$$B_A = W_A c_{p,A} (T_{CA} - T_{ref}) \quad (3-14)$$

where W_A is the flow rate of the combustion air in lb/hr, $c_{p,A}$ is the specific heat of the air in Btu/lb-°F, T_{CA} is the temperature of the combustion air in °F, and T_{ref} is the ambient air temperature, also in °F. B_F is given by:

$$B_F = W_F c_{p,F} (T_F - T_{ref}) \quad (3-15)$$

where W_F is the flow rate of the fuel in lb/hr, $c_{p,F}$ is the specific heat of the fuel in Btu/lb-°F, and T_F is the temperature of the fuel in °F.

Calculation of Thermal Efficiency

To calculate the efficiency, the above losses are calculated and the thermal efficiency is then determined using Eq. (3-1) written as:

$$\eta = 100\% - \left(\frac{L}{F + B} \right) 100\% \quad (3-16)$$

where F is the heat input through the fuel, given by:

$$F = W_F K_F \quad (3-17)$$

where K_F is the higher heating value of the as-fired fuel in Btu/lb, measured at constant pressure.

*The unit is located inside a completely enclosed building and is not exposed to weather.

Chapter 4 Emission Results

Tests were conducted in blocks of four runs per condition. Due to the limited availability of the test oils, each of the four replicate test runs per condition was conducted sequentially. CEM data reported below are corrected to account for CEM drift using:

$$X_c = (A - X_0) \frac{X_{ma}}{X_m - X_0} \quad (4-1)$$

where X_c is the corrected gas concentration, A is the average value from CEM measurements, X_0 is the average of the pre- and post-test zero calibration readings, X_m is the average of the pre- and post-test high span calibration readings, and X_{ma} is the actual high span calibration gas concentration. Reported CEM concentration data are also corrected to 3% O_2 (all gas concentrations are given in either volume % or ppmv, at dry conditions).

Test Matrix Modifications

During the course of testing, several changes were made to the test matrix shown in Table 2-1. The reasons for these changes are given below and are also discussed in Appendix B. Table 4-1 shows the actual test conditions achieved during the tests.

Target O_2 concentration for the baseline #2 oil was originally expected to be 3% for all loads. However, very little measurable CO or particulate was noted at this O_2 level, and so it was decided to reduce the O_2 level of the medium load condition to improve the baseline thermal efficiency of the unit. The use of the lower O_2 level for the #2 oil at medium load therefore allowed a direct comparison of the effects of emulsifying the oil, since the O_2 levels at medium load for the emulsified

Table 4-1. Target and actual test conditions achieved during verification testing.

Condition	1	2	3	4	5	6	7	8	9
Fuel	#2 Oil	#2 Oil	#2 Oil	Ems #2 ^a	Ems #2	Ems #2	Ems Nap ^b	Ems Nap	Ems Nap
Target Load (10 ⁶ Btu)	2.0	1.5	1.0	2.0	1.5	1.0	2.0	1.5	1.0
Actual Load (10 ⁶ Btu)	2.20	1.63	1.46	2.23	1.59	1.45	2.09	1.58	1.42
Target O_2 (%) ^c	3.0	1.5	3.0	1.5	1.5	1.5	1.5	1.5	1.5
Actual O_2 (%) ^c	2.95	1.48	2.99	2.10	1.50	2.42	1.97	1.49	2.43
Test Runs	4	4	4	4	4	4	5	4	4

a. Emulsified #2 oil

b. Emulsified naphtha

c. Target O_2 levels were estimates. Actual test O_2 levels were determined by matching particulate emissions (as measured by smoke number) of the base fuel and the emulsified fuel.

#2 and the emulsified naphtha were set at the same nominal O₂ level as the baseline #2 medium load tests.

Emission Concentrations and Emission Factors

Emission results for the nine conditions (the #2 oil, the emulsified #2 oil, and the emulsified naphtha, each at high, medium, and low loads) are presented in Table 4-2 in terms of pollutant concentrations. Figure 4-1 presents the average O₂ concentrations for each of the test conditions. Since one of the advantages normally associated with the use of emulsified fuels in external combustion applications is the ability to operate at reduced O₂ levels, the emulsified fuels are operated at O₂ levels below those of the base fuel, with the exception of the #2 oil medium load condition noted above.

Table 4-3 presents the calculated emission factors in lb/10⁶ Btu and lb/1000 gal of fuel for the different conditions. For the emulsified fuels, the 10⁶ Btu and the 1000 gal represent the heat content and the volume, respectively, of the oil/water/emulsifying agent mix, not of just the oil in the emulsified fuel. Note that although the volumetric fuel flow increased, the net Btu input remained constant for constant load, since negligible energy was provided by the water and emulsifying agent.

The effect of using the emulsified fuel is seen in Tables 4-4 and 4-5, which present the percent change in emissions of the emulsified fuels compared to the corresponding base (non-emulsified) fuels. Table 4-4 presents the percent change in emission concentrations for the emulsified #2 oil, and the emulsified naphtha compared to the #2 oil, and Table 4-5 shows the percent change in emission factors for the emulsified fuels compared to the #2 oil.

Carbon Monoxide

In general, the CO emissions were very low for all conditions tested, with average values for all conditions falling below 10 ppmv (see Tables 4-2 and 4-3). Considerable fluctuation was noticed between the individual test runs, leading to relatively large relative standard errors (See Chapter 6) for each condition. In addition, there were large percent changes in CO emissions when comparing the emulsified fuels with their corresponding base fuel; however, these large percentage changes are not highly significant, due to the very low absolute CO concentration levels. CO levels of less than 10 ppmv are typically considered quite low for practical combustion systems. In addition, the CO CEM is accurate only to 1% of full scale (500 ppmv), meaning that measurements of less than 5 ppmv are essentially the same. Nevertheless, values less than 5 ppmv are reported here for completeness.

Table 4-2. Average emission concentrations of O₂, CO, NO, PM, and THC for the #2 oil, emulsified #2 oil, and emulsified naphtha for the different conditions tested.

Fuel	#2 Oil			Emulsified #2 Oil			Emulsified Naphtha		
	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c
O ₂ (%)	2.95	1.48	2.99	2.10	1.50	2.42	1.97	1.49	2.43
CO (ppmv @ 3% O ₂)	3.63	2.71	1.64	2.30	1.71	2.87	7.76	2.72	2.06
NO (ppmv @ 3% O ₂)	127.	96.1	105.	84.3	79.5	88.7	61.9	62.2	70.3
PM (mg/dscm @ 3% O ₂)	11.67	0.77	0.95	4.58	3.11	3.26	2.87	4.67	4.88
THC (ppmv @ 3% O ₂)	0.52	0.24	ND ^d	0.70	ND	ND	ND	ND	0.33

a. 2.1x10⁶ Btu/hr

b. 1.6x10⁶ Btu/hr

c. 1.4x10⁶ Btu/hr

d. Not Detected

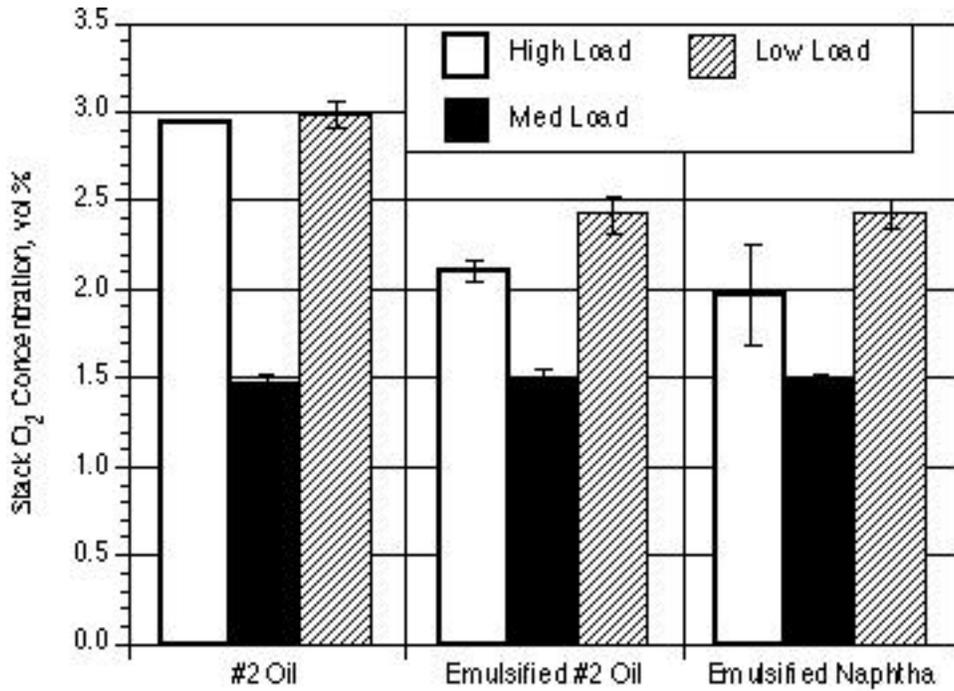


Figure 4-1. Stack O₂ concentration in volume percent for each test condition. Error bars denote relative standard deviation for the four test runs at each condition.

Table 4-3. Average emission factors for CO, NO, and PM for #2 oil, emulsified #2 oil, and emulsified naphtha for the different conditions tested.

Fuel	#2 Oil			Emulsified #2 Oil			Emulsified Naphtha		
	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c
CO (lb/10 ⁶ Btu)	0.0025	0.0022	0.0013	0.0018	0.0014	0.0023	0.0068	0.0021	0.0016
CO (lb/1000 gal)	0.35	0.31	0.19	0.18	0.13	0.22	0.58	0.18	0.14
NO (lb/10 ⁶ Btu)	0.102	0.078	0.084	0.067	0.063	0.070	0.048	0.049	0.055
NO (lb/1000 gal)	14.3	10.9	11.8	6.41	6.05	6.74	4.10	4.15	4.68
PM (lb/10 ⁶ Btu)	0.0077	0.0006	0.0007	0.0031	0.0019	0.0028	0.0019	0.0038	0.0035
PM (lb/1000 gal)	1.08	0.09	0.10	0.30	0.18	0.27	0.16	0.32	0.30

a. 2.1x10⁶ Btu/hr

b. 1.6x10⁶ Btu/hr

c. 1.4x10⁶ Btu/hr

No substantial changes were noted in CO emissions for the fuels tested (#2 oil, emulsified #2 oil, and emulsified naphtha). In all cases but one, the emissions were below 5 ppmv. As seen in Table 4-2 and Figure 4-2, the CO emissions from the emulsified naphtha at high load were somewhat higher than for either the #2 oil or the emulsified #2 oil. Even so, the CO emissions for these conditions were still less than 10 ppm, and could likely be reduced further if necessary by optimizing the combustion O₂ level. This potential was illustrated during setup testing for the emulsified naphtha, when the boiler was operated at the nominal 2x10⁶ Btu/hr load and 3.2% O₂, resulting in CO emissions less than 2 ppm. CO emission factors are shown in Table 4-3 and Figure 4-3. On a per unit energy basis, CO emissions were typically 0.002 lb/10⁶ Btu or less, except for the emulsified naphtha at high load, which was roughly 0.007 lb/10⁶ Btu. The emissions per volume of fuel had a higher variation, due primarily to the differences in fuel energy content per unit volume between the base #2 oil and the emulsified fuels. Per unit volume, the #2 oil CO emission factors ranged between

Table 4-4. Percent reduction in stack gas concentrations of CO, NO, and PM for emulsified #2 oil and emulsified naphtha, compared to the #2 fuel oil. Comparisons are made between conditions at similar boiler load.

Fuel	Emulsified #2 Oil			Emulsified Naphtha		
	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c
CO	36.6	36.9	-74.8	-114	-0.36	-25.2
NO	33.6	17.2	15.2	51.2	35.3	32.7
PM	60.8	-301.	-243.	75.4	-503.	-413.

a. 2.1x10⁶ Btu/hr
b. 1.6x10⁶ Btu/hr
c. 1.4x10⁶ Btu/hr

Table 4-5. Percent reduction in emission factors of CO, NO, and PM for emulsified #2 oil, and emulsified naphtha, compared to the #2 fuel oil. Emulsified naphtha results are in comparison to the #2 fuel oil. Comparisons are made between conditions at similar boiler load.

Fuel	Emulsified #2 Oil			Emulsified Naphtha		
	High ^a	Med ^b	Low ^c	High ^a	Med ^b	Low ^c
lb/10 ⁶ Btu						
CO	26.3	38.0	-71.7	-176.	2.99	-21.3
NO	34.8	18.9	16.8	53.0	37.4	34.9
PM	59.3	-208.	-305.	74.9	-519.	-416.
lb/1000 gal						
CO	49.4	57.4	-17.9	-68.2	40.8	26.0
NO	55.3	44.3	42.9	71.4	61.8	60.3
PM	72.0	-111	-178	84.7	-275.	-215.

a. 2.1x10⁶ Btu/hr
b. 1.6x10⁶ Btu/hr
c. 1.4x10⁶ Btu/hr

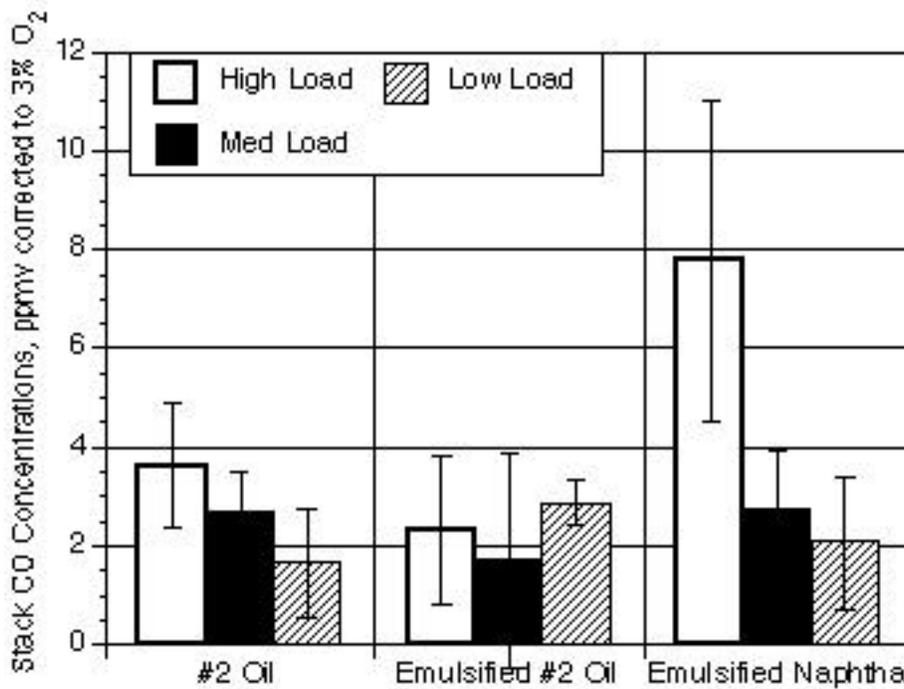


Figure 4-2. Stack CO concentrations in ppm for each of the conditions, corrected to 3% O₂. Error bars denote relative standard deviation for the four test runs at each condition.

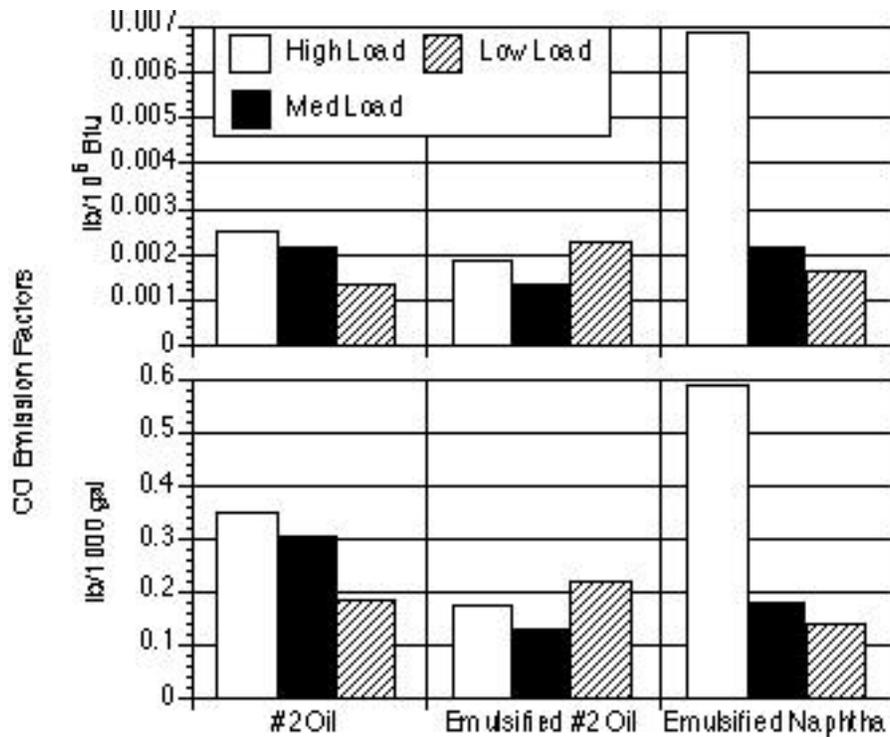


Figure 4-3. Emission factors for CO in lb/10⁶ Btu and lb/1000 gal.

0.19 and 0.35 lb/1000 gal, while for the emulsified fuels emission factors ranged between 0.13 and 0.58 lb/1000 gal, again with the emulsified naphtha at high load exhibiting the highest emissions. These values compare to an emission factor of 5 lb/1000 gal for distillate fuel combustion in a commercial/institutional boiler listed in EPA's AP-42.¹⁶

As discussed above, the percent change in CO emissions should not be regarded as highly significant with respect to the performance of the emulsified fuels, due to the substantial fluctuations in CO emissions across the four test runs at each condition and the low absolute levels for CO emissions for all conditions. As noted above, optimization of the operating conditions beyond what was done for these verification tests is likely to result in lower CO emissions, if such low values are desired.

Nitrogen Oxide

Emission measurements were much more stable for NO than for CO, as measured by the relative standard error across the individual test runs for each condition. The average values for each condition therefore have a substantially higher degree of confidence with respect to the average values than the CO emission values.

Emissions of NO are presented in Table 4-2 and Figure 4-4. NO emissions from the emulsified fuels showed significant reductions compared to the base #2 oil. The baseline emissions of NO averaged 127 ppm at high load, with a low of 96 ppm at medium load (unless otherwise noted, all concentrations are corrected to 3% O₂). At low load, NO emissions from the #2 oil were 105 ppm, slightly higher than the medium load emissions, due to the lower O₂ level at the medium load (1.48% vs. 2.99%). These are compared to the average emulsified #2 oil emissions of 84, 80, and 89 ppm at high, medium, and low loads, respectively. These values represent reductions of approximately 34,

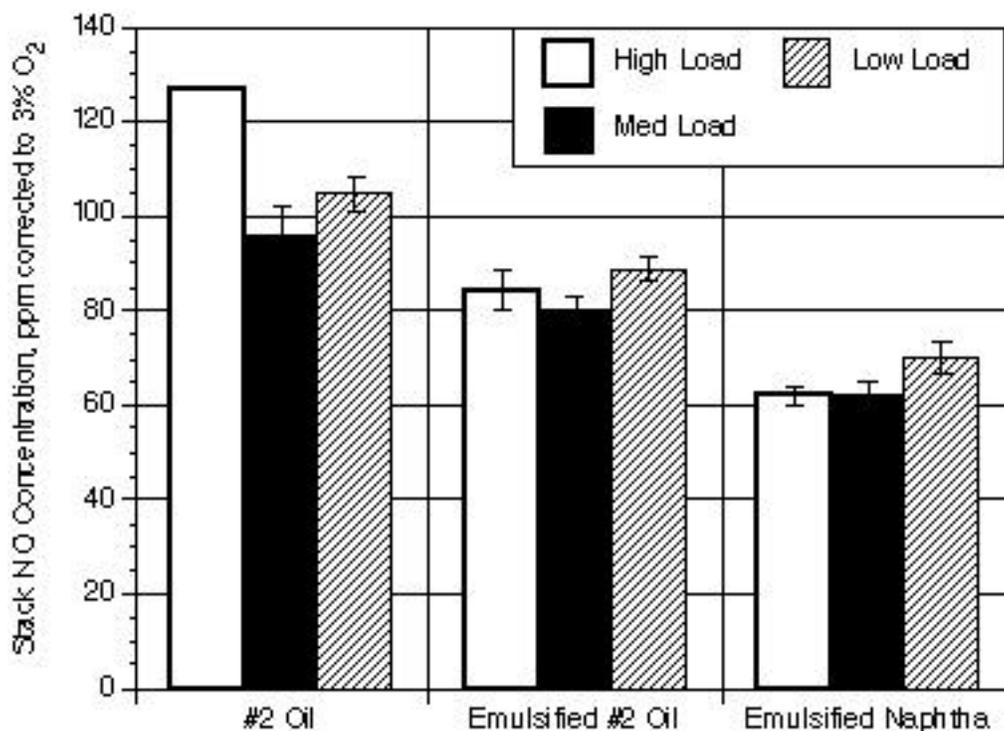


Figure 4-4. Stack NO concentrations in ppm for each of the conditions, corrected to 3% O₂. Error bars denote relative standard deviation for the four test runs at each condition.

17, and 15% compared to the base #2 oil emissions at high, medium, and low loads, respectively. For the emulsified naphtha, emissions were even lower, with 62 ppm and a 51% reduction at high load, 62 ppm and a 35% reduction at medium load, and 70 ppm and a 33% reduction at low load. It is significant to note that at medium load, where the O₂ level remained nearly constant for the three fuels, NO emissions fell 17% for the emulsified #2 oil and 35% for the emulsified naphtha compared to the base #2 oil. These differences can be attributed to the use of the emulsified fuels rather than to any difference in operating conditions.

Emission factors for NO are presented in Table 4-3 and Figure 4-5. On a per unit energy basis, emission factors for NO ranged from 0.078 lb/10⁶ Btu at medium load to 0.102 lb/10⁶ Btu at high load for the #2 oil, from 0.063 lb/10⁶ Btu at medium load to 0.070 lb/10⁶ Btu at low load for the emulsified #2 oil, and from 0.048 lb/10⁶ Btu at high load to 0.055 lb/10⁶ Btu at low load for the emulsified naphtha. Although the NO concentrations are significantly lower for the emulsified naphtha than for either of the other two fuels, the emissions per unit energy input are roughly the same.

On a per unit volume basis, NO emission factors for the #2 oil ranged from 10.9 lb/1000 gal at medium load to 14.3 lb/1000 gal at high load. As was the case for CO, the emission factors calculated per unit volume dropped significantly for the emulsified fuels due to the water in the fuel. For the emulsified #2 oil, the emission factors varied from 6.1 lb/1000 gal at medium load to 6.7 lb/1000 gal at low load, and for the emulsified naphtha, the emission factors ranged from 4.1 lb/1000 gal at high load to 4.7 lb/1000 gal at low load. These values compare to the AP-42 emission factor of 20 lb/1000 gal for distillate fuel oil in both utility and industrial boilers.¹⁶

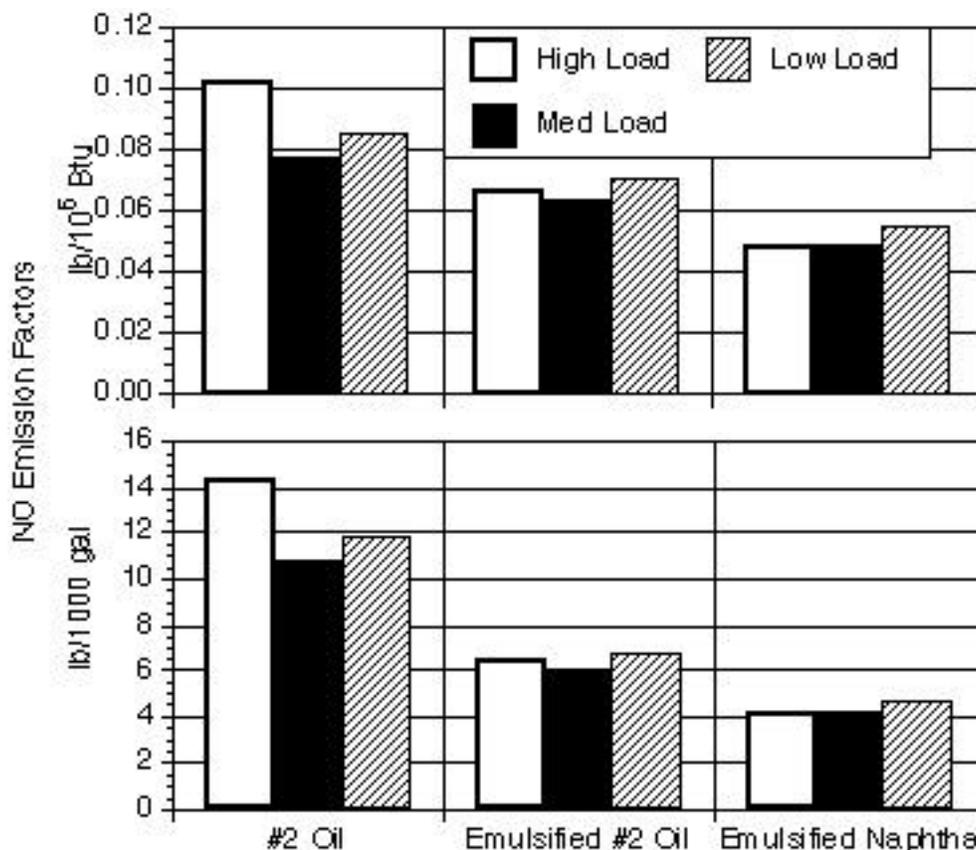


Figure 4-5. Emission factors for NO in lb/10⁶ Btu and lb/1000 gal.

Particulate Matter

PM emissions, presented in Table 4-2 and Figure 4-6, were very low, ranging from a high of 11.7 mg/dscm at high load for the #2 oil to a low of 0.77 mg/dscm at medium load for the #2 oil. There is some uncertainty regarding the value of the PM concentration at high load, because the boiler tubes were cleaned immediately prior to the start of the test program. During the initial test runs (#2 oil at high load), the particulate captured on the Method 5 filter dropped considerably from the first to the last run, even though the test conditions remained relatively constant. The PM emissions measured during runs 1, 2, and 3 of condition 1 were 17.26, 12.14, and 5.60 mg/dscm, respectively. The following six runs resulted in PM concentrations of between 0.65 and 1.31 mg/dscm during the medium and low load tests. For this reason, it is believed that the high PM emissions seen during condition 1 were due to entrainment of particles already present on the boiler tubes that were loosened during the cleaning process. The emulsified #2 oil PM emissions were between 3.11 mg/dscm at medium load and 4.58 mg/dscm at high load, while the PM emissions from the emulsified naphtha ranged from 2.87 mg/dscm at high load to 4.88 mg/dscm at low load. The increases in PM emissions for the two emulsified oils may have been due in part to the lower O₂ levels used during these test conditions. However, for the medium load cases, the O₂ levels were very consistent for all three fuels, with average O₂ levels ranging between 1.48 and 1.50% for the three test conditions. The PM emissions at medium load for both emulsified fuels increased over those measured for the base #2 oil at medium load, leading to the conclusion that factors other than the O₂ level were responsible for the observed differences in PM emissions for this load. PM emissions can be affected by the atomization at the nozzle, which is a function of fuel flow rate, pressure, and viscosity; the flow rate and pressure of the atomizing fluid (in this case, air); and the design of the nozzle. Optimization of these parameters may reduce PM emissions, but such optimization was not conducted during these tests.

Emission factors for PM are presented in Table 4-3 and Figure 4-7. On a per unit energy basis, the PM emission factors for the #2 oil ranged from 6.1×10^{-4} lb/10⁶ Btu at medium load to 8.0×10^{-3}

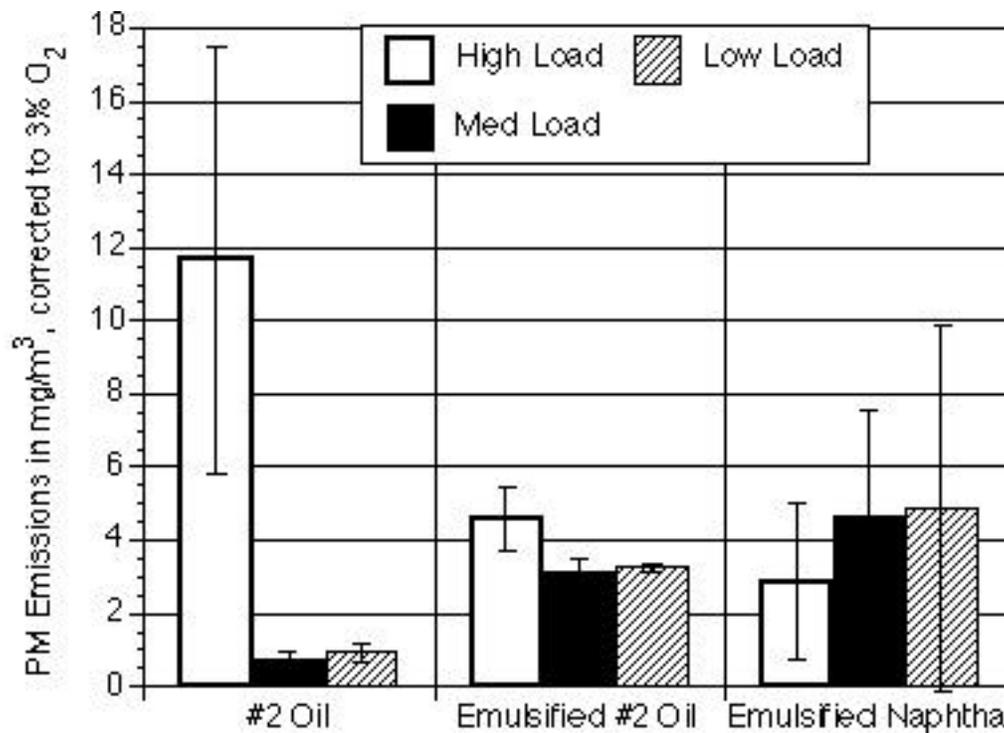


Figure 4-6. Stack PM concentrations in mg/dscm for each of the conditions, corrected to 3% O₂.

lb/10⁶ Btu at high load. For the emulsified #2 oil, the emission factors ranged from 1.9x10⁻³ lb/10⁶ Btu at medium load to 3.1x10⁻³ lb/10⁶ Btu at high load, while the emulsified naphtha PM emission factors ranged from 1.9x10⁻³ at high load to 3.8x10⁻³ at medium load. PM emission factors in terms of mass per volume of fuel feed for the #2 oil ranged from 0.09 lb/1000 gal at medium load to 1.12 lb/1000 gal at high load. For the emulsified #2 oil, the PM emission factors ranged from 0.19 lb/1000 gal at medium load to 0.32 lb/1000 gal at high load. The PM emission factors for the emulsified naphtha ranged from 0.16 lb/1000 gal at high load to 0.32 lb/1000 gal at medium load. The AP-42 emission factor for filterable PM is listed at 2.0 lb/1000 gal for distillate oil for both utility and industrial boilers.¹⁶

Although current regulations limit emission rates of PM, in terms of either mass or opacity, the distribution of particle sizes may become an important factor with recent concern over health effects associated with ambient concentrations of particles smaller than 2.5 μm. For that reason, these tests also measured particle size distributions where possible.

The emissions of total particulate were so low that determining size distributions was very difficult, and consistent size distributions with the cascade impactors were not possible. In most cases, the cascade impactor substrates exhibited weight loss from the initial to the final weighings. This was due to the very low levels of particulate passing through the impactor.

Repeatable data obtained from the SMPS indicated that the particle sizes in the flue gas from the fuels were in the size range from 0.01-0.1 μm (10-100 nm). Figure 4-8 shows representative particle size distributions from the SMPS for all fuels at high load. This figure shows there are clear differences

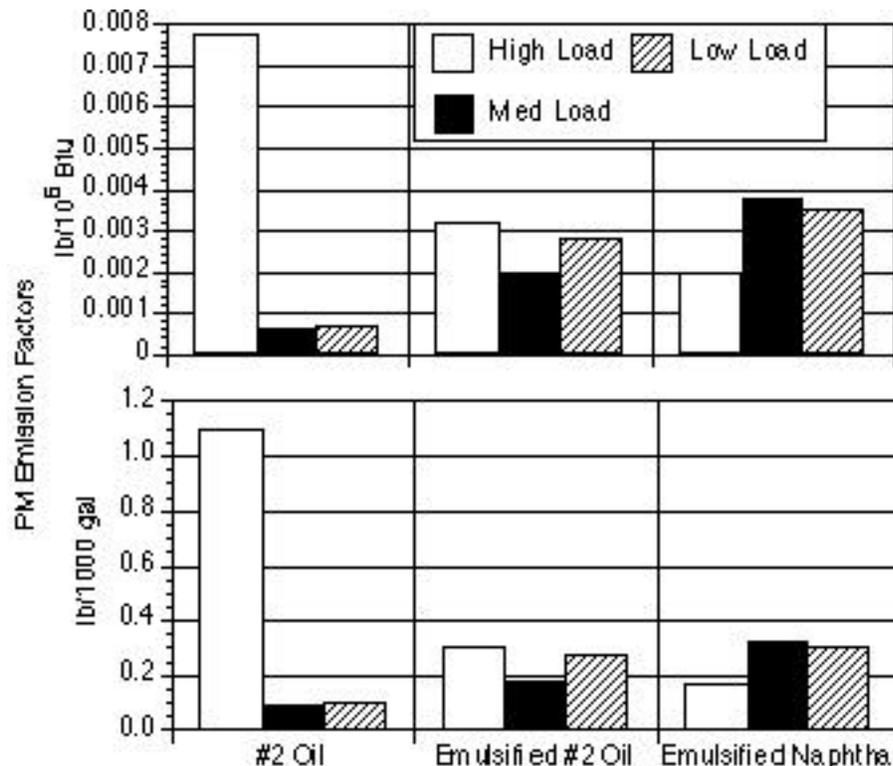


Figure 4-7. Emission factors for PM in lb/10⁶ Btu and lb/1000 gal.

in the distributions between the emulsified and non-emulsified fuels. Figure 4-8 plots $dV/d[\log(D_p)]$, where dV is the differential particle volume and D_p is the particle electrostatic diameter. By assuming a constant particle density, one can use this plot as an indication of the distribution of particle mass as a function of particle size.

The greatest difference in the size distributions is between the #2 oil and the emulsified #2 oil. The size distribution for the #2 oil shows a distinct fine mode (peak) near $0.02 \mu\text{m}$ (20 nm), consistent with a nucleation mode of particle formation. From the peak near $0.02 \mu\text{m}$, the particle mass decreases with increasing particle size until a minimum is reached near $0.06 \mu\text{m}$. At this point, the mass begins to increase with increasing particle size, which suggests the presence of combustion chars. These particles cover a significant size range, up to $100 \mu\text{m}$. The emulsified #2 oil, in contrast, does not show a significant decrease in particle mass with increasing size, but shows a shallow irregular increase in mass as the particle size increases from about $0.02 \mu\text{m}$ to approximately $0.2 \mu\text{m}$, at which point it begins to decrease slowly. This distribution is consistent with the secondary atomization process characteristic of emulsified fuels, in which the mean fuel droplet size decreases due to the microexplosions of the water inside the fuel. Unlike mechanical atomization, which forms relatively large droplets that usually have a characteristic peak in the droplet size distribution, secondary atomization tends to create a continuum of droplet sizes. This results in a particle size distribution with fewer and less distinct maxima or minima. In terms of particle mass, the emulsified

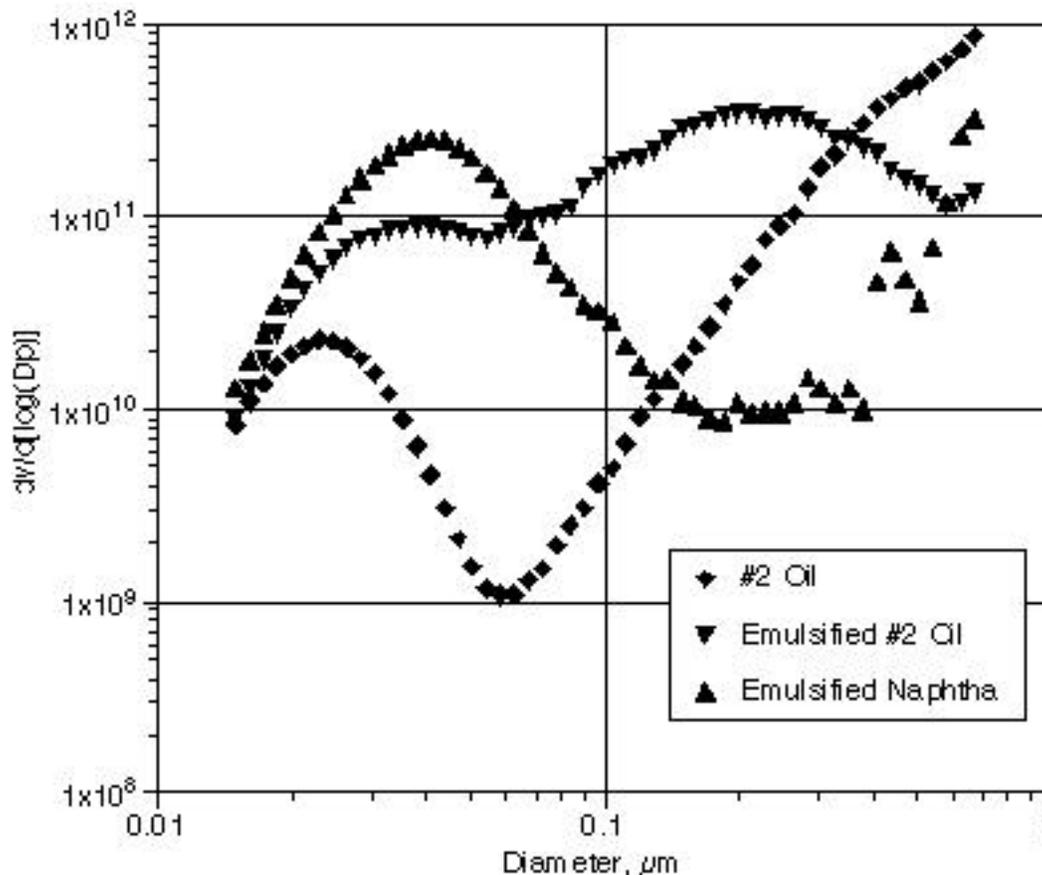


Figure 4-8. SMPS particle size distributions for the three fuels tested, at high load.

fuels tend to shift the average size of particles toward the smaller sizes. This behavior is seen in the difference between the size distributions of the #2 oil and the emulsified #2 oil. The lack of a distinct minimum near 0.02 μm in the emulsified #2 oil distribution indicates that there are significantly more particles in the 0.02-0.2 μm range than for the #2 oil.

The size distribution for the emulsified naphtha does not behave in a manner similar to that for the emulsified #2 oil, but retains the bimodal shape of the #2 oil, although at a higher total mass and at a larger average size. It is not clear how this distribution compares to non-emulsified naphtha, but there are clearly more particles in the 0.02-0.1 μm range for the emulsified naphtha than for the #2 oil.

While the secondary atomization of the fuels by the water in the emulsification most likely is the major influence on particle size, it must also be noted that there were substantial changes in the fuel flow rates between the non-emulsified and emulsified fuels. For instance, the #2 oil flow rate averaged 15.8 gal/hr at high load (2.204×10^6 Btu/hr), while the measured flow rate of the emulsified #2 oil at nearly identical load (2.228×10^6 Btu/hr) averaged 23.2 gal/hr. Such changes in flow rates can affect the particle size distribution, as can changes in atomizing air pressure (which were held at relatively constant levels for the corresponding fuels). Additional testing would be required to determine the impacts of each of these parameters; however, the emulsification is believed to play the dominant role in changing the particle size distributions.

Total Hydrocarbons

Emissions of THC's were very difficult to measure, particularly for the emulsified fuels. The difficulties arose due to the low concentrations of THC's and high levels of water in the flue gases. It has been shown that the presence of water in flue gases can impact the performance of THC monitors using flame ionization detection, by introducing a small negative bias to the reading. Estimates of the negative bias were on the order of 1-5 ppm.¹⁷ This bias would have the effect of reducing the instrument reading below the actual value, but would not mask changes or high levels (>15 ppm) in THC concentrations. The behavior was noted when burning the emulsified #2 oil and the emulsified naphtha, resulting in average THC readings consistently below zero, even though the CEM was calibrated before and after each test day. The negative values therefore indicate that the THC levels were likely to be below 5 ppm.

For the #2 oil, THC emissions were less than 1.5 ppm for all cases. The only measured value greater than zero for the emulsified #2 oil was at high load, at a concentration of 0.7 ppm. THC emissions were measured at quantities greater than zero in the emulsified naphtha only at the low load condition and then only at a level of 0.3 ppm.

Given the low measured values and the impact of the high water content on the performance of the THC analyzers, the measurements given above have a low level of confidence as quantitative values. Qualitatively, however, it can be stated that the THC emissions from the fuels at the tested conditions were found to be very low.

Chapter 5

Thermal Efficiency Results

Changes in thermal efficiency associated with the use of alternative fuels often play a major role in the acceptability of those fuels. In the case of fuels emulsified with water, there may be a significant efficiency penalty associated with the use of those fuels, due to the physical requirement of heating the water in the fuel to steam. As the steam exits the boiler stack, any energy that was expended in the phase change from liquid to steam is not used to heat the process fluid, thereby becoming an energy loss and reducing the thermal efficiency of the process. Conversely, the use of emulsified fuels can allow an operator to reduce the amount of combustion air. The water included in the emulsion creates “microexplosions” as it evaporates in the flame, resulting in a secondary atomization of the fuel and producing smaller fuel droplets that can burn more efficiently. This allows less excess O₂ to be used and, because each mole of O₂ carries along with it 3.76 moles of nitrogen (N₂) when using air, it also reduces the amount of the relatively inert N₂ that passes through the combustion system. Since the N₂ does not react, it acts only as a heat sink that is heated and carries that energy out the boiler stack. As with the steam from the water in the fuel, this heat is lost to the process and thus a reduction in thermal efficiency results. By reducing the amount of combustion air required to burn the same amount of fuel, an increase in thermal efficiency may be realized. Finally, the introduction of water into the combustion process may also reduce the flue gas exit temperature. Since the amount of energy leaving the boiler stack depends upon the volume and temperature of the flue gas, a drop in flue gas temperature will result in an efficiency gain. The degree to which these competing effects cancel each other can depend upon the unit design, the amount of water being used in the emulsified fuel, operating practices, and other factors.

Thermal efficiencies were calculated for each run using the heat loss method described in Chapter 3. Energy losses through the flue gases are subtracted from the total heat input via the fuel and other sources (such as the energy in the air) to determine the amount of energy that is transferred to the steam. This figure is then divided by the total heat input to determine the boiler thermal efficiency (see Eq. 3-17). The energy losses are calculated for each of the primary routes of energy loss from the system. Because the efficiency relative to the baseline condition is more critical in this study than the absolute efficiency, losses due to convection and radiation from the boiler or from boiler leaks were not calculated, since it was felt that these losses would remain relatively constant for all cases, and in any case would not be substantially affected by the choice of fuel.

Thermal efficiency is significantly affected by the composition of the fuel, particularly the moisture and hydrogen contents, as seen in Equations 3-6 and 3-7, respectively. A number of fuel analyses were conducted for this study, particularly for the emulsified fuels. The results of these analyses varied considerably in their hydrogen, oxygen, and moisture contents, differences that potentially could change the calculated thermal efficiency results. A discussion of the different results and the final analyses used are presented in Appendix B. The fuel analyses used in the efficiency calculations are given in Table 2-3.

The average thermal efficiency for each test condition is shown in Figure 5-1. As seen in Figure 5-1, the variation between test runs for each condition was small, as measured by the relative standard deviation for each condition. Table 5-1 shows the parameters that are used (in combination with fuel and flue gas compositions) to calculate the average thermal efficiency. The heat inputs and losses due to each of the major parameters influencing the efficiency are shown for each test condition in Table 5-2.

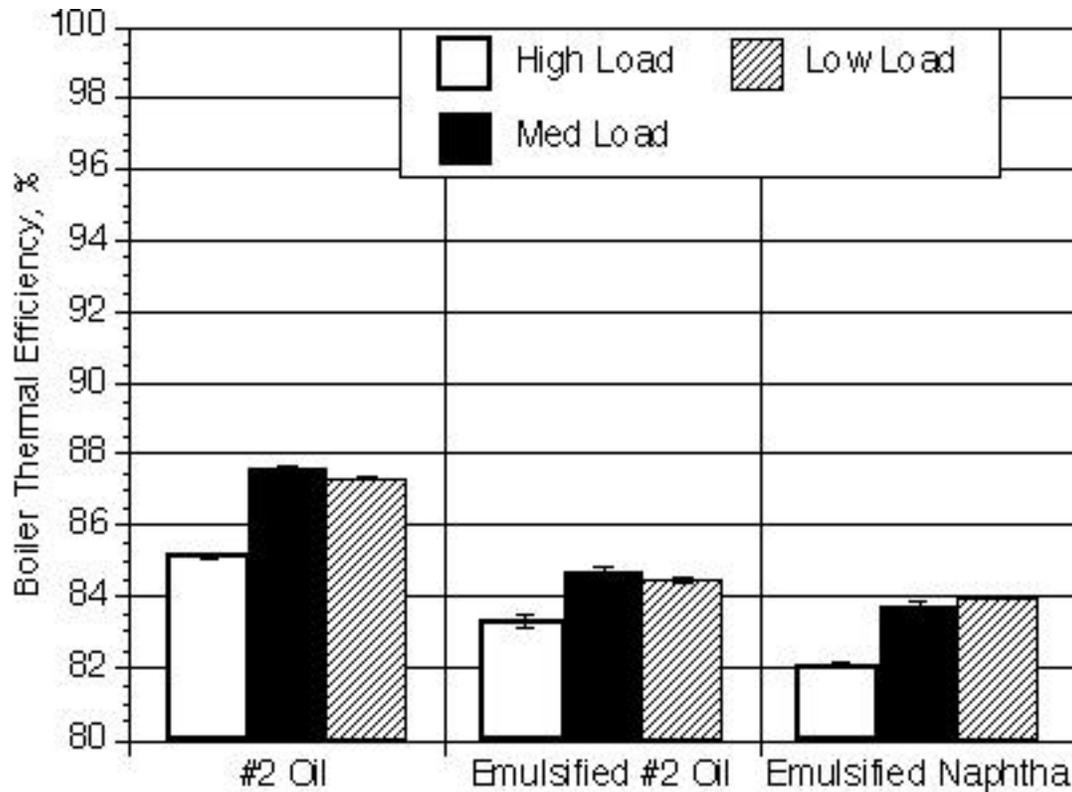


Figure 5-1. Thermal efficiencies for each of the nine test conditions. Error bars indicate the relative standard deviation. High load averaged 2.08×10^6 Btu/hr, medium load averaged 1.55×10^6 Btu/hr, and low load averaged 1.38×10^6 Btu/hr.

Table 5-1. Parameters used for determination of thermal efficiency.

Condition	Fuel Flow, lb/hr	Air Temperature, °F	Stack Temperature, °F	Flue Gas Flow, scfm ^b
#2 Oil, High Load	113.	85 ^a	429.	392.
#2 Oil, Medium Load	83.9	91.0	347.	266.
#2 Oil, Low Load	75.2	95.7	340.	261.
Emuls #2 Oil, High Load	174.	93.9	397.	377.
Emuls #2 Oil, Medium Load	124.	93.0	344.	261.
Emuls #2 Oil, Low Load	113.	83.6	341.	249.
Emuls Naphtha, High Load	168.	81.5	397.	350.
Emuls Naphtha, Medium Load	128.	85.5	344.	261.
Emuls Naphtha, Low Load	115.	89.7	324.	245.

a. Measurements for air temperature were not available for condition 1 (#2 oil at high load). An estimate of 85°F was made for each of the test runs at condition 1.

b. Standard conditions are 77 °F, 1 atm.

It should be emphasized that the thermal efficiency results presented here are highly specific to the test conditions, fuels, and equipment used, although it is expected that similar trends would be found for these fuels used in other systems. The thermal efficiency values presented here are measurements of the thermal efficiencies determined only for the package boiler used in the tests: efficiency measurements using other types of units, or even for similar units in different condition, operating under different parameters, are likely to be different. However, the addition of water and the emulsification agent to a fuel oil is expected to result in similar relative changes when used in other units.

For the #2 oil, emulsified #2 oil, and emulsified naphtha, the impacts on thermal efficiency of using the emulsified fuels can be clearly seen in comparison to the efficiency for the base #2 oil.

The thermal efficiency was lowest for the high load cases, primarily due to the higher flue gas temperature which resulted in significantly higher energy flows out the stack. For the base #2 oil, the thermal efficiency was 85.1% at high load compared to 87.6% at medium load and 87.3% at low load. For the emulsified #2 oil, the efficiencies were 83.3% at high load, 84.7% at medium load, and 84.5% at low load. For the emulsified naphtha, thermal efficiencies ranged from a low of 82.1% at high load to 83.9% at low load.

Energy Inputs

Energy into the boiler was primarily from the fuel, although a small amount of energy entered the system from the combustion air. In general, the energy in the combustion air was between 3,900 and 14,200 Btu/hr for all tests, while the energy in the fuel accounted for between 1.41 and 2.25×10^6 Btu/hr for the three fuels. Relatively little difference was noted in total energy input between the three fuels at similar loads.

Heat Losses

The major heat losses for all cases were the heat loss in the dry flue gases and the heat loss due to moisture from hydrogen in the fuel. In all cases, the heat loss due to moisture in the fuel was no more than the third largest heat loss. However, the major difference between the emulsified fuels and the base #2 oil was the heat loss due to moisture in the fuel. The average heat loss due to moisture in the fuel for the three base #2 oil conditions is roughly 50 Btu/hr, compared to between 41,100 and 64,800 Btu/hr for the emulsified #2 oil and between 47,500 and 71,400 Btu/hr for the emulsified naphtha.

Heat losses in the dry flue gases decreased for the emulsified fuels compared to the base #2 oil. This is due to two causes: (1) lower excess air was used during emulsified fuel operation, leading to lower total mass flow of flue gases; and (2) the flue gas temperatures decreased, resulting in lower energy flow out the stack in the dry flue gases. Other losses, from incomplete combustion of hydrocarbons, CO, and carbon in the ash, accounted for no more than 6,900 Btu/hr in all cases.

Figure 5-2 presents the heat losses as a percent of the total energy input for each of the nine conditions.

Table 5-2. Thermal efficiencies and heat inputs and losses for all conditions tested. Values represent the average of four test runs. Heat inputs and losses are in Btu/hr.

Condition	Efficiency, %	Heat input through fuel	Other heat inputs	Losses in dry flue gases	Losses from moisture in fuel	Losses from hydrogen moisture	Other losses
#2 Oil, High Load	85.1	2,204,000	10,800	165,000	69	161,000	3,500
#2 Oil, Medium Load	87.6	1,632,000	9,400	86,000	49	115,000	2,100
#2 Oil, Low Load	87.3	1,462,000	11,300	82,500	44	103,000	1,400
Emuls #2 Oil, High Load	83.3	2,228,000	16,000	142,000	64,800	164,000	3,800
Emuls #2 Oil, Medium Load	84.7	1,590,000	11,100	82,100	45,300	115,000	2,600
Emuls #2 Oil, Low Load	84.5	1,445,000	7,800	78,500	41,100	104,000	1,500
Emuls Naphtha, High Load	82.1	2,111,000	10,100	135,000	72,800	165,000	7,400
Emuls Naphtha, Medium Load	83.8	1,616,000	9,100	83,700	54,600	124,000	1,900
Emuls Naphtha, Low Load	83.9	1,446,000	9,100	73,600	48,400	110,000	1,800

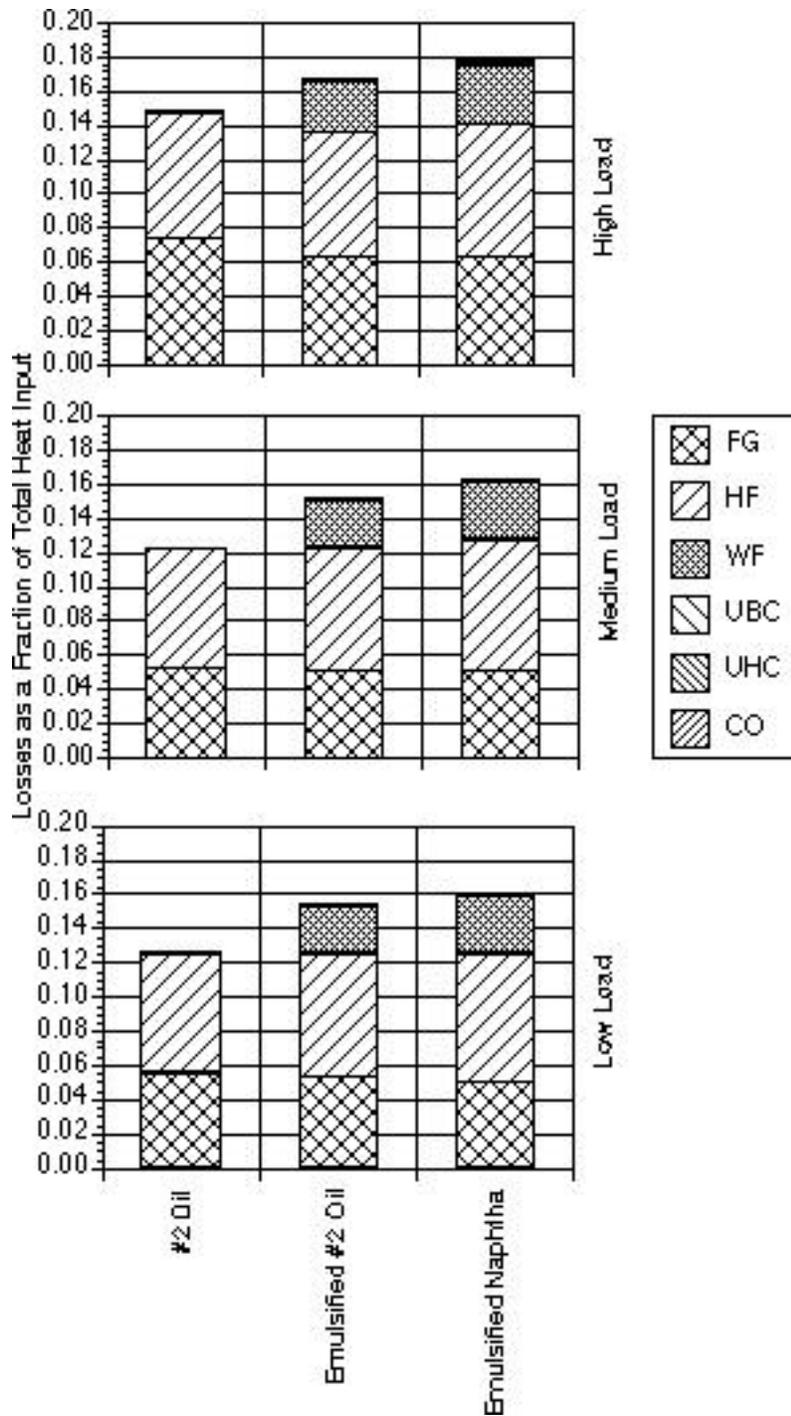


Figure 5-2. Heat losses for each of the nine test conditions as a fraction of the total heat input. FG is the heat loss of the dry flue gases out the stack, HF is the heat loss of the water from the hydrogen in the fuel, WF is the heat loss due to the water in the fuel, UBC is the heat loss due to unburned carbon in the particulate, UHC is the heat loss due to the unburned hydrocarbons in the flue gases, and CO is the heat loss due to CO in the flue gases. Losses due to unburned carbon were negligible and are not shown.

Chapter 6 Quality Assurance

This project was conducted under an approved APPCD Level II Quality Assurance (QA) Project Plan. The plan set forth the operating, sampling, and analysis procedures to be used during the testing, as well as the data quality indicator (DQI) goals for the project. The DQI goals for the project are shown in Table 6-1.

CEM, Temperature, and Flow Measurements

CEM Precision

Table 6-2 presents the maximum relative standard deviation (RSD) values calculated for each of the test runs for each test condition. RSD is determined by calculating the standard deviation of the CEM data for a particular run divided by the average measurement value of that run. Data for CO₂ and NO were all within the DQI goals for precision.

The data for O₂ met the DQI precision goal of <7% RSD for only 6 of 13 test conditions, indicating much higher variation in O₂ levels during testing than for either CO₂ or NO. The failure of the O₂ measurements to achieve the DQI precision goal for these runs does not impact the conclusions of this report concerning NO or PM emissions. However, the O₂ measurements are less precise than desired. This impacts the NO and PM emissions that are reported as concentrations corrected to 3% O₂.

THC and CO data did not meet the precision DQI precision goal for any of the test conditions. The goals for these two compounds were met for none of the test runs for CO, and for only one test run for THC. For both THC and CO, this large variation was most likely due to the fact that both compounds were detected at levels near zero. The measured values for THC and CO do not meet the DQI goals set for this project, making the quantitative values questionable; however, the qualitative results that both THC and CO emissions were near zero in all cases remain valid.

The variation of the four replicate test runs was also measured by calculating the RSD of the four test runs' average values for each condition. This value, the cross-run RSD, was calculated by dividing

Table 6-1. Data quality indicator goals for CEM, temperature, and fuel flow measurements.

Measurement	Method	Precision (RSD ^a), %	Bias, %	Completeness, %
O ₂	CEM	<7	< ±10	>90
CO ₂	CEM	<5	< ±15	>90
CO	CEM	<7	< ±15	>90
NO _x	CEM	<5	< ±10	>90
THC	CEM	<5	< ±10	>90
Temperature	Thermocouple	10	±10	>90
Fuel Flow	Volume Totalizer	10	±10	>90

^aRelative standard deviation

the standard deviation of the four runs' average value by the average of the four runs' average values. The cross-run RSD between test runs was not a critical DQI. These values are shown in Table 6-3 for each of the test conditions. The CO and THC measurements again showed the greatest variation across the tests.

For these three measurements, the highest cross-run RSD was 14.9% for O₂ measured from the emulsified naphtha at high load. The other conditions showed maximum values typically less than 2% for CO₂, and less than 6% for O₂ and NO.

For CO and THC, the cross-run RSD values were quite high, as high as 418%. This was due to the very low values of both CO and THC. These measurements were essentially at the noise level of the instruments, leading to relatively high variability in the measurements and to the large cross-run RSD values.

CEM Accuracy

The accuracy of the CEMs was determined by daily pre- and post-test calibration of the instruments. The deviations from the zero and high span calibration gas concentrations are shown in Table 6-4 for the five flue gas constituents measured. NO met the DQI accuracy goal of less than ±10% deviation in accuracy as measured by the percent deviation from the high span calibration gas concentration, both for the average and maximum deviations for any one run. The O₂ values met the DQI accuracy goal of less than ±10% deviation for all test days. The average deviation for the O₂ analyzer high span reading was -0.01% and 0.23% for the NO analyzer high span reading. The maximum deviation from the zero point was a CEM reading of -0.20% for O₂ and 17 ppm for the NO. For O₂ the high span gas concentration was 8.01%, and for NO the high span gas concentration was 974 ppm for the first few tests and 997 for the remaining tests.

The remaining CEMs showed slightly greater deviations. For CO₂ the average deviation of the high span reading was -0.35%, with two runs having a deviation of 3.31%, but all measurements were within the ±15% DQI goal. The maximum deviation represented a CEM reading of 15.9% compared

Table 6-2. Maximum RSD values, in percent, for CEM and temperature measurements for each condition. The values shown are the maximum values of the individual run RSDs measured during the four replicate test runs for each condition.

Condition	CO	CO ₂	NO	O ₂	THC	Stack Temp
#2 Oil, High Load	85.5	1.41	2.10	6.74	33.8	0.64
#2 Oil, Medium Load	164.	1.01	2.54	9.55	22.6	0.86
#2 Oil, Low Load	NA ^a	0.73	2.71	3.35	240.	0.45
Emuls #2 Oil, High Load	348.	1.19	1.91	8.68	106.	0.43
Emuls #2 Oil, Medium Load	192.	1.47	2.51	14.9	6.95	0.48
Emuls #2 Oil, Low Load	29.4	1.11	0.73	6.73	NA	0.59
Emuls Naphtha, High Load	125.	1.18	2.27	8.13	43.9	0.63
Emuls Naphtha, Medium Load	553.	0.98	2.71	10.5	82.5	0.69
Emuls Naphtha, Low Load	70.6	1.03	3.44	6.97	153.	0.66

a. Not available

to the high span calibration gas concentration of 15.0%. The zero points for CO₂ were very close to zero for all runs, with an average zero reading of 0.002% and a maximum of 0.09%. The THC deviations from the high span calibration gas concentration averaged -0.54% from the high span value of 91 ppm, with a maximum of 5.49% deviation. The zero readings for the THC analyzer averaged 0.53 ppm, with a maximum of 5 ppm. Again, all THC bias values were within the ±10% range specified in the DQI goals.

In all cases, the reported gas concentrations have been corrected for CEM bias using Eq. 4-1 to account for the effect of CEM drift during the test runs.

CEM Completeness

The completeness DQI goal of greater than 90% was met for all CEM measurements (except THC) for all tests. The THC analyzer was not operating during the first two tests of the #2 oil. For all other tests, however, the CEMs were fully operational. During one test, the data acquisition system (DAS) stopped logging data due to a “Disk Full” error. The CEM results reported for this test cover only the period of time during which the DAS was logging data (see Appendix D).

Table 6-3. Cross-run RSD values, in percent, of the average CEM and temperature measurements for all conditions.

Condition	CO	CO ₂	NO _x	O ₂	THC	Stack Temp
#2 Oil, High Load	41.9	0.35	0.37	0.48	53.8	0.37
#2 Oil, Med Load	29.2	1.11	6.25	2.74	223.	0.39
#2 Oil, Low Load	67.1	0.55	3.69	2.44	240.	0.43
Emuls #2 Oil, High Load	66.2	0.78	5.38	2.92	134.	2.26
Emuls #2 Oil, Med Load	126.	0.55	4.27	3.31	228.	0.50
Emuls #2 Oil, Low Load	16.3	2.02	2.41	4.34	42.0	1.42
Emuls Naphtha, High Load	36.1	1.17	4.68	14.9	418.	3.35
Emuls Naphtha, Med Load	43.2	0.26	4.07	2.13	NA ^a	0.94
Emuls Naphtha, Low Load	65.6	0.76	5.30	3.48	242.	0.33

a. Not available

Table 6-4. Average and maximum deviations of zero and high span CEM readings from calibration gas values for all runs. Zero span values are given in ppm for CO, NO, and THC, and in percent for CO₂ and O₂. High span values are given in percent difference from calibration gas values.

		CO	CO ₂	NO	O ₂	THC
Zero	Average	-1.55 ppm	0.00%	2.91 ppm	0.00%	0.53 ppm
	Maximum	-8 ppm	0.09%	17 ppm	-0.20%	5 ppm
High Span	Average	4.01%	-0.35%	0.23%	-0.01%	-0.54%
	Maximum	-27.5%	6.00%	1.61%	4.61%	5.49%

Temperature Data

No bias checks were made of the thermocouples during the test program. However, accuracy was measured prior to beginning the test program. Measurements from the 14 thermocouples used in the test program were compared to measurements from a thermometer standard using an ice bath, boiling water at ambient pressure, and ambient temperature as measurement points. Of the 42 readings (14 thermocouples times 3 readings per thermocouple), 6 readings indicated a difference between the thermocouple and the thermometer standard, each difference being 1 °F. The maximum percent difference was 1.3%. No thermocouple failures occurred during the test program, so the completeness goal of greater than 90% was met.

Flow Data

As discussed in Chapter 2, the fuel flow rate was determined using a fuel totalizer and a stop watch. The totalizer was calibrated to determine the accuracy of the instrument for the #2 oil, and the emulsified #2 oil. The calibration was done using a container of known volume, and comparing the known volume to the totalizer reading. Calibrations with #2 oil and emulsified #2 oil were done after all the tests had been completed. For the #2 oil, the average deviation was slightly higher in magnitude at -3.3%, with a maximum deviation of -5.4%. The emulsified #2 oil's average deviation was -4.7%, with a maximum deviation of -5.4%. These values are well within the DQI accuracy goal of ±10%. Since the totalizer was operational during the entire test series, the completeness goal of greater than 90% was also met. The values reported for fuel flow rates have been corrected to account for the totalizer deviation, and the reported efficiencies and emission factors, both of which depend upon fuel flow rates, were also corrected to account for the difference between totalizer readings and measured volumes during the calibration procedures. The emulsified naphtha flow rate was corrected using the -4.7% factor for the emulsified #2 oil flow rate.

Particulate Matter Measurements

PM values were dependent upon two primary measurements - the mass of the particulate captured and the volume of the gas sampled. These two measurements were combined to determine the concentration of PM in the flue gases. DQI goals for PM measurements are presented in Table 6-5.

For the particulate mass, off-center error and precision of the scale used are determined by calculating the standard deviation of the five measurements of the difference between a certified mass standard and the measured value. Accuracy is determined by the calculation of a linear regression based on the measurement of 10 certified mass standards. The measured values are used to calculate

Table 6-5. Data quality indicator goals for PM measurements.

Mass Measurements					
Capacity Range, g	Display Drift, mg/min	Off-Center Error, mg	Precision, mg	Accuracy	Completeness, %
40	≤ 0.02	Std. Dev. ≤ 0.05	Std. Dev. ≤ 0.05	Linear Regression: y=mX+b m: 0.99998 ≤ m ≤ 1.00002 b: -0.00002 ≤ b ≤ 0.00002 r: ≥ 0.99998	> 70
200	≤ 0.2	Std. Dev. ≤ 0.5	Std. Dev. ≤ 0.5	Linear Regression: y=mX+b m: 0.9998 ≤ m ≤ 1.0002 b: -0.0002 ≤ b ≤ 0.0002 r: ≥ 0.9998	> 70

Table 6-6. Measurements of DQI goals for PM mass measurements.

Capacity Range, g	Display Drift, mg/min	Off-Center Error, mg	Precision, mg	Accuracy	Completeness, %
40 g	0.01 mg/min	Std. Dev. = 0.04 mg	Std. Dev. = 0.02 mg	Linear Regression: y=mX+b m = 1.00000 b = 0.00000 r = 1.00000	100%
200 g	0.01 mg/min	Std. Dev. = 0.3 mg	Std. Dev. = 0.1 mg	Linear Regression: y=mX+b m = 1.00000 b = 0.00000 r = 1.00000	100%

the linear response in the form:

$$y = mX + b \quad (6-1)$$

where y is the measured value, m is the slope, X is the certified mass, and b is the intercept. The regression coefficient, r, is also determined and evaluated as one of the DQI goals.

Measurements were made by APPCD’s QA group to determine the DQI values for the scale, as part of a systems audit performed during the test program. Those measurements are presented in Table 6-6, and show that the scale met all the DQI goals for PM mass measurements.

Discrepancies

A number of relatively minor discrepancies between the test plan and the actual testing occurred and are listed in Appendix C along with the action taken to resolve the discrepancy and the impact on data quality. More significant discrepancies between the test plan and the actual testing were the change in planned O₂ level for the medium load cases discussed in section 4.1. These discrepancies are discussed from the perspective of their impacts on data quality in more detail below.

As discussed in Chapter 4, the target O₂ level for the medium load cases was changed from the originally planned 3% to about 1.5%, because little or no particulate matter was observed during the high load tests at 3% O₂. Although the use of a different O₂ level makes it impossible to directly compare the medium load results with the high and low load results, it does allow evaluation of the impact of changing only the fuel without any changes in the excess air (the primary operating variable that impacts NO, CO, and PM levels). In addition, the difference in load between the medium and low load cases was relatively small, 1.6x10⁶ Btu/hr for medium load and 1.4x10⁶ Btu/hr for low load. Since the tests were conducted following the same procedures as for the high and low loads, there was no change in data quality arising from the use of a different O₂ setpoint. In addition, since the primary objective of the tests was to evaluate the impact of the use of the emulsified fuels in comparison to the base fuels, the change in target O₂ levels did not deviate from evaluating that original objective. Thus, there was no significant impact on data quality or the ability to derive conclusions due to the use of a different O₂ setpoint for the tests in question.

Audits

A number of performance audits were conducted by APPCD’s Quality Assurance staff. The results of those audits are discussed in the QA report prepared for the project, and are provided in Appendix D.

Chapter 7

Operational Observations

This chapter discusses observations regarding the handling and general combustion behavior of the emulsified fuels noted during operation of the boiler. While these observations do not impact the quantitative verification results, they are included here to provide information concerning the performance of the fuels from an operability perspective, at least to the extent that these issues were applicable to the test unit.

Emulsified #2 Oil

The emulsified #2 oil was milky in appearance, with a pink tint from the dye used to distinguish between on-road and off-road use. When the emulsified #2 oil was introduced into the fuel feed system, some difficulty was encountered in maintaining steady fuel flow due to the solvent properties of the fuel. Following the introduction of the emulsified fuel into the system, small particles were picked up by the fuel from the fuel feed piping, turning its appearance to a milky gray. As a remedy to this problem, the fuel supply system was flushed for approximately 30 minutes until the pinkish color was seen in the return line, and normal operations were continued.

The flame was shorter and less luminous at all loads with the emulsified #2 oil than for the base #2 oil, but after the fuel system had been flushed, no problems were noted with the operation of the boiler using the emulsified #2 oil. The O₂ and CO₂ levels did fluctuate more often and more rapidly when using the emulsified #2 oil than they did when using the base #2 oil. As O₂ increased, CO₂ simultaneously decreased by a similar degree and vice versa. It was felt that this behavior was due to changes in the fuel composition. Since the O₂ and CO₂ measurements are based on dry flue gas, the fluctuations were believed to be the result of reduced carbon content (and higher water content) of the fuel at that time. However, no substantial changes were noted in emissions of CO, NO, or THC during these fluctuations.

Emulsified Naphtha

The emulsified naphtha was milky white in appearance, similar to the emulsified #2 oil but without the pink tint. No difficulties were noted with the feed system such as occurred when using the emulsified #2 oil for the first time. The combustion behavior of the emulsified naphtha was very similar to that of the emulsified #2 oil. As with the emulsified #2 oil, the flame was less luminous at all loads than for the #2 oil. The emulsified naphtha also resulted in a region within the flame that exhibited a light blue color, similar to what one would expect from a natural gas flame. This change in appearance did not seem to affect the performance or emissions.

References

1. U.S. Environmental Protection Agency, "Environmental Technology Verification Program: Verification Strategy," EPA-600/K-96-003 (NTIS PB97-160006), Office of Research and Development, Washington, DC, February 1997.
2. Hall, R.E., "The Effect of Water/Residual Oil Emulsions on Air Pollutant Emissions and Efficiency of Commercial Boilers," *Journal of Engineering for Power*, pp. 425-434, October 1976.
3. Hall, R.E., "The Effect of Water/Distillate Oil Emulsions on Pollutants and Efficiency of Residential and Commercial Heating Systems," presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, MA, June 15-20, 1975, paper 75-09.4.
4. Adiga, K.C., "On the Vaporization Behavior of Water-in-Oil Microemulsions," *Comb. Flame*, Vol. 80, p. 214, 1990.
5. Public Law 101-549, Clean Air Act Amendments of 1990, November 15, 1990.
6. Miller, C.A., "Hazardous Air Pollutants from the Combustion of an Emulsified Heavy Fuel Oil in a Firetube Boiler," EPA-600/R-96-019 (NTIS PB96-168281), U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC, February 1996.
7. EPA Test Method 5 - Determination of Particulate Emissions from Stationary Sources, in 40 CFR Part 60 Appendix A, Government Institutes, Inc., Rockville, MD, July 1994.
8. CARB Method 501 - Determination of Size Distribution of Particulate Matter Emissions from Stationary Sources. State of California Air Resources Board Stationary Source Test Methods: Volume 1 - Methods for Determining Compliance with District Nonvehicular (Stationary Source) Emission Standards, Sacramento, CA, adopted March 23, 1998; amended September 12, 1990.
9. American Society of Mechanical Engineers, "Power Test Code PTC 4.1 - Steam Generating Units," ASME, New York, NY, 1991.
10. American Society of Testing and Materials, "Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants," ASTM D 5291-92, Philadelphia, PA, June 1992.
11. American Society of Testing and Materials, "Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation," ASTM D 95, Philadelphia, PA, 1990.
12. American Society of Testing and Materials, "Standard Test Method for Sulfur in Petroleum Products by Energy Dispersive X-Ray Fluorescence Spectroscopy," ASTM D 4294-90, Philadelphia, PA, July 1990.
13. American Society of Testing and Materials, "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter," ASTM D 240-92, Philadelphia, PA, June 1992.
14. American Society of Testing and Materials, "Standard Test Method for Ash from Petroleum Products," ASTM D 482-95, Philadelphia, PA, June 1995.
15. Miller, C.A., Linak, W.P., King, C., and Wendt, J.O.L., "Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler," *Combustion Science and Technology*, in press, 1998.
16. U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emission Factors*, Edition 5, Volume I, AP-42 (GPO 055-000-005-001), Office of Air Quality Planning and Standards, Research Triangle Park, NC, January 1995.

17. Ryan, J.V., Lemieux, P.M., and Groff, P.W., "Evaluation of the Behavior of Flame Ionization Detection Total Hydrocarbon Continuous Emission Monitors at Low Concentrations," presented at the 1997 International Conference on Incineration and Thermal Treatment Technologies, May 12-16, 1997, Oakland, CA.
18. American Society of Testing and Materials, "Standard Method for Testing Top-Loading, Direct-Reading Laboratory Scales and Balances," ASTM E 898-82, Philadelphia, PA, 1982 (latest version ASTM E 898-88, published November 1988).

APPENDIX A

English Engineering to International System Unit Conversions

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \times 5/9$$

$$\text{kg} = \text{lb} \times 0.454$$

$$\text{kg/hr} = \text{lb/hr} \times 0.454$$

$$\text{kJ/kg} = \text{Btu/lb} \times 2.326$$

$$\text{kg/kJ} = \text{lb}/10^6 \text{ Btu} \times 4.299 \times 10^{-7}$$

$$\text{kg/kl} = \text{lb}/1000 \text{ gal} \times 0.1198$$

$$\text{kPa} = \text{psi} \times 6.895$$

$$\text{kW} = \text{Btu/hr} \times 2.93 \times 10^{-4}$$

$$\text{l/min} = \text{gpm} \times 0.2642$$

$$\text{m}^2 = \text{ft}^2 \times 0.0929$$

$$\text{m}^3 = \text{ft}^3 \times 0.028317$$

$$\text{m}^3/\text{min} = \text{cfm} \times 0.028317$$

APPENDIX B Fuel Oil Analyses

The fuel oils were analyzed to determine their chemical composition for use in calculating the thermal efficiencies of the different fuels at the conditions tested. Fuel composition plays a significant role in determination of thermal efficiency through equations (3-6) and (3-7) which account for the moisture in the fuel and the moisture from the hydrogen in the fuel, respectively. The ultimate analyses were conducted initially by one laboratory (Lab A). However, there was concern that the weight percent water reported in the Lab A results for the emulsified fuels did not match the expected values based on the composition of the fuels as mixed by A-55. A second set of analyses was then conducted by a second laboratory (Lab B) on the same fuels. While these results were closer to the expected compositions, concern still remained that the percent of water reported did not agree well with the percent water mixed with the fuel during preparation. At the request of EPA, Lab B re-evaluated their original analyses, and reported revised ultimate analyses for the emulsified #2 and emulsified naphtha samples (see Table B-1). Even with the additional analyses, concerns about the accuracy of the analyses remained.

A further difference between the results reported by Lab A and Lab B was that the hydrogen and oxygen contents reported by Lab B included the hydrogen and oxygen associated with the moisture. This resulted in higher values for both hydrogen and oxygen than were present in the fuel fraction of the emulsification. This is important since the thermal efficiency equations [equations (3-6) and (3-7)] account for the losses due to moisture and those due to moisture generated from the fuel hydrogen separately, and care must be taken not to count these losses more than once.

The method used to determine hydrogen (ASTM D 5291) is based on a measurement of the amount of water generated during combustion of the sample. If the water in the fuel is not completely driven off prior to the combustion step, the amount of hydrogen in the hydrocarbon portion of the emulsified fuel may be overestimated. Second, the oxygen in the fuel is determined by difference, after accounting for the remaining constituents of the hydrocarbon portion of the fuel.

The first area of concern was the oxygen level reported for the emulsified fuels. For example, the Lab A and initial Lab B analyses of the emulsified #2 oil found 7.67 and 6.27% oxygen (corrected to account for the oxygen in the water), respectively, in the samples. Although the emulsifying agent used in the preparation of the emulsified fuels contained a small amount of oxygen, a mass balance on the known inputs of oxygen via the fuel, water, and emulsifying agent predicted oxygen values much less than those reported. The expected oxygen value for the emulsified #2 oil was less than 1%.

A second concern was the accuracy of the hydrogen value. The method used to determine hydrogen (ASTM D 5291) is based on a measurement of the amount of water generated during combustion of the sample. If the water in the fuel is not completely driven off prior to the combustion step, the amount of hydrogen in the sample may be overestimated. Finally, the Lab B analyses reported water in percent volume (vol%), while the Lab A analyses reported water in percent weight (wt%), making it more difficult to compare the results.

The Lab B results were revised to account for the hydrogen and oxygen from the water, and to change the vol% water content to wt%. These results are shown in Table B-2. The approach used in developing the revised table was to first convert the vol% water to an equivalent wt%. The vol% value is given by:

$$\text{vol\%} = \frac{\text{vol}_w}{\text{vol}_f} \times 100\% \quad (\text{B-1})$$

where vol_w is the volume of water and vol_f is the volume of fuel. For 1 gallon of fuel, vol_w is equal to

Table B-1. Reported ultimate analysis results for the fuels tested.

Fuel	#2 Oil		Emulsified #2 Oil			Emulsified Naphtha		
	Laboratory	A	B	A	B	B ^a	A	B
Carbon (wt%)	86.76	86.92	54.86	55.16	57.40	54.25	48.90	53.36
Hydrogen (wt%)	10.68	13.01	8.46	12.59	12.21	9.26	13.47	13.17
Nitrogen (wt%)	0.22	0.49	0.18	0.21	0.48	0.20	0.35	0.32
Sulfur (wt%)	0.07	0.0289	0.03	0.009	NA ^b	0.01	0.002	NA
Ash (wt%)	0.01	0.001	< 0.01	0.003	NA	0.01	0.002	NA
Water (wt%)	< 0.10	NA	28.80	NA	NA	25.60	NA	NA
Water (vol%)	NA	< 0.05	NA	26.7	28.0	NA	31.1	30.0
Oxygen (wt%) (by difference)	≤ 2.16	0.42	≤ 7.67	32.47 ^c	29.92 ^c	10.67	37.98 ^c	33.16 ^c
Btu/lb	19,462	19,450	13,032	12,368	12,786	13,046	11,657	12,584
Btu/gal	139,873	139,592	97,883	93,205 ^d	96,355 ^d	88,491	80,655 ^d	87,069 ^d
Specific Gravity	0.8630	0.8607	0.9019	0.9050	0.9050 ^e	0.8145	0.8309	0.8309 ^e
Density, lb/gal	7.186	7.167	7.510	7.536	7.536	6.782	6.919	6.919

a. Revised analyses

b. Not available

c. Includes the oxygen in the water

d. Calculated from Btu/lb and density values

e. Same as Lab B unrevised analysis

Table B-2. Corrected analysis results for the fuels tested.

Fuel	#2 Oil		Emulsified #2 Oil			Emulsified Naphtha		
	Laboratory	A	B	A	B	B ^a	A	B
Carbon (wt%)	86.76	86.92	54.86	55.16	57.40	54.25	48.90	53.36
Hydrogen (wt%)	10.68	13.01	8.46	9.32 ^b	8.77 ^b	9.26	9.32 ^b	9.16 ^b
Water (wt%)	< 0.10	< 0.058 ^c	28.80	29.47 ^c	30.93 ^c	25.60	37.39 ^c	36.07 ^c
Oxygen (wt%) (by difference)	≤ 2.16	0.42	≤ 7.67	6.27 ^d	2.42 ^d	10.67	4.74 ^d	1.10 ^d

a. Revised analysis

b. Corrected to account for hydrogen in water

c. Calculated from vol%

d. Corrected to account for oxygen in water

vol%, and the mass of water, m_w , in 1 gallon of fuel is given by

$$m_w = \rho_w \text{vol}_w \quad (\text{B-2})$$

where ρ_w is the density of water.

Since the ρ_w is 8.3385 lb/gal at 15.6 °C (60 °F), and the density of the fuel, ρ_f , is $8.3385\gamma_f$ lb/gal, where γ_f is the specific weight of the fuel, then the wt% of water in 1 gallon of fuel is given by:

$$\text{wt}\% = \frac{m_w}{m_f} = \frac{\text{vol}\% \rho_w}{\rho_f} = \frac{\text{vol}\%}{\gamma_f} \quad (\text{B-3})$$

One can then calculate the wt% water for the Lab B analyses.

The second step is to account for the hydrogen and oxygen from the water in order to directly compare the different analyses. Since 1 lb-mole of water (H_2O) weighs 18 lb, and since 16 lb of that is from the oxygen and the remaining 2 lb is from hydrogen, then 8/9 is the fraction of water's mass attributable to oxygen and the remaining 1/9 is attributable to hydrogen. The oxygen content of the fuel, corrected to remove the oxygen from the water, is then given by:

$$O_{\text{corr}} = O_{\text{rep}} - \left(\text{wt}\%_{\text{H}_2\text{O}} \text{H} \frac{8}{9} \right) \quad (\text{B-4})$$

where O_{corr} is the corrected oxygen content of the fuel in wt%, O_{rep} is the reported oxygen content in wt%, and $\text{wt}\%_{\text{H}_2\text{O}}$ is the weight percent of water. Likewise, the corrected hydrogen content is given by:

$$H_{\text{corr}} = H_{\text{rep}} - \left(\text{wt}\%_{\text{H}_2\text{O}} \text{H} \frac{1}{9} \right) \quad (\text{B-5})$$

where H_{corr} is the corrected hydrogen content of the fuel in wt% and H_{rep} is the reported hydrogen content in wt%. The corrected values for oxygen and hydrogen and the wt% water values are given in Table B-2.

Based on the results shown in Table B-2, those most consistent with the known amounts of water added to the fuel and with the calculated oxygen contents of the fuels are the revised Lab B analyses, corrected to account for the oxygen and hydrogen from the water. These values are reported in Table 2-2 and used in the thermal efficiency calculations reported in Chapter 5.

Effects of Changing Fuel Composition

Due to the large impact that the hydrogen and moisture contents of a particular fuel have on thermal efficiency, it is important to understand the relationship between fuel composition and thermal efficiency.

Changes in the fuel composition can affect the calculated value of losses due to energy in the dry flue gas (L_{FG}), hydrogen in the fuel (L_{MH}), and moisture in the fuel (L_{MF}). Eqs. 3-3 and 3-4 show that the primary fuel related variable influencing L_{FG} is the fraction of carbon in the fuel, C_b . Therefore, significant changes in C_b can result in significant changes in thermal efficiency. Likewise, L_{MH} and L_{MF} directly affect the losses due to hydrogen in the fuel, L_{MH} , and moisture in the fuel, L_{MF} . It is important, then, to understand the changes in thermal efficiency associated with the changes in the fuel analysis. In general, as carbon increases, L_{FG} will increase due to the higher dry flue gas flow, L_{MH} will increase as the fuel hydrogen content increases, and L_{MF} will increase as the fuel moisture content increases.

The thermal efficiency was calculated separately using the three fuel analyses discussed above (shown in Table B-2) and the measured values for fuel input, flue gas composition and temperature, and oil

and air temperatures. The results of these calculations are shown in Table B-3. Calculations using Lab A analyses resulted in thermal efficiencies that were higher than those calculated using Lab B analyses, by 0.80-1.32 percentage points. The difference between Lab B and revised Lab B results was much smaller, with calculations using the revised Lab B analyses resulting in thermal efficiencies that were lower by 0.07-0.11 percentage point than those using the unrevised Lab B analyses, for the emulsified #2 oil. For the emulsified naphtha, calculations using the revised Lab B analyses resulted in thermal efficiencies that were slightly higher (0.17-0.30 percentage point) than those calculated using the unrevised Lab B analyses.

These results emphasize the importance of the fuel analyses when evaluating thermal efficiency, particularly when using emulsified fuels that are high in water content. It is suggested that comparisons of oxygen, carbon, or energy contents of the emulsified and non-emulsified fuels be conducted to determine whether the reported analyses are consistent with the addition of known amounts of water. Such comparisons can provide an indication of the reliability of the analyses.

Table B-3. Differences in calculated thermal efficiency values using the different fuel analyses. All other parameters were held constant. Differences are in comparison to the revised Laboratory B analyses.

Fuel	#2 Oil		Emulsified #2 Oil			Emulsified Naphtha		
	A	B	A	B	B ^a	A	B	B ^a
High Load	86.43	85.11	84.34	83.23	83.30	82.89	82.39	82.09
Medium Load	88.88	87.61	85.68	84.60	84.71	84.56	83.93	83.75
Low Load	88.59	87.33	85.47	84.39	84.49	84.74	84.11	83.94
Difference from reported value (Revised Laboratory B data)								
High Load	1.32	– ^b	1.04	-0.07	–	0.80	0.30	–
Medium Load	1.27	–	0.97	-0.11	–	0.81	0.18	–
Low Load	1.26	–	0.98	-0.10	–	0.80	0.17	–

a. Revised analysis

b. Not applicable

APPENDIX C

Discrepancies

The discrepancies below are listed in chronological order. The discrepancy is described, followed by the action taken to resolve the discrepancy, and the impact of the discrepancy on data quality.

1. Date: 8/5/97
Discrepancy: The THC analyzer was not operating during Condition 1, Test 1.
Action: The analyzer was repaired and was in service for the remaining tests.
Impact: Given the extremely low THC values measured during the remaining tests at Condition 1, no substantial impact resulted from the loss of the instrument. The average THC value reported is the average of three rather than four test runs.

2. Date: 8/5/97
Discrepancy: No SO₂ analyzer was available for use in the #2 oil, emulsified #2 oil, or emulsified naphtha tests.
Action: No action taken.
Impact: The levels of sulfur in the #2 oil, emulsified #2 oil, and emulsified naphtha are extremely low. The use of an oil/water emulsion does not impact the emissions of SO₂ (in terms of mass per unit energy input); thus the total emissions per unit time at a given load will not change between the base oil and the emulsified oil. The lack of an SO₂ analyzer had no impact on the test data quality.

3. Date: 8/7/97
Discrepancy: The fuel oil drum being used as the primary feed for the boiler ran dry during Test 2.1, causing boiler shutdown.
Action: The test was discontinued.
Impact: The data from the test were not used. The problem did not impact data quality as the results from this test run were not used.

4. Date: 9/3/97
Discrepancy: The data acquisition system stopped operating due to a "Disk Full" error during Test 6.2, resulting in a temporary loss of data while the data acquisition software was being restarted. The data from this test were lost between the time the program halted and it could be restarted, a period of approximately 6 minutes.
Action: Only the data from the period from the beginning of the test to the program "crash" were used.
Impact: Because the boiler operation and the extractive sampling were not impacted, no significant loss of data was suffered. Although the data from the time of the program restart to the end of the test were gathered (approximately 50 minutes), it was decided that, to avoid any uncertainty regarding the impact of the program restart, only the initial data would be used. Because the boiler operations were very stable with relatively low fluctuations in conditions, no adverse impact is believed to have resulted. from the use of data from only the initial 70 minutes of testing.

5. Date: 9/8/97
Discrepancy: The filter in the Method 5 sampling train tore during particulate sampling.
Action: The test was repeated on 9/17/97.
Impact: Because the test was repeated, there was no impact on data quality.

Appendix D Audit Results

TOP-LOADING PAN BALANCE EVALUATION

The Mettler AE240 top-loading pan balance in room H-202 at the ERC Building of the EPA was audited on August 14, 1997 according to an audit procedure developed by Research Triangle Institute from ASTM Standard E-898-82.¹⁸ Standard class S weights were used to evaluate such characteristics of the balance as the display-drift, off-center error, precision, and accuracy. The working weights used to evaluate the Mettler AE240 were certified on March 8, 1997, by the North Carolina Department of Agriculture, Standards Division.

The performance of the Mettler AE240 is considered satisfactory, and the balance will pass the audit if all of the following are true:

1. None of the following malfunctions occur during the audit.
 - a. Balance cannot be zeroed.
 - b. Air movement and/or vibration interfered with scale clarity or resolution.
2. Display-drift did not exceed 1.5 times the resolution (R) of the balance per minute.
3. The standard deviation of the differences obtained for the off-center error test did not exceed 5 times the resolution (R) of the balance.
4. The standard deviation of the differences obtained for the precision test did not exceed 5 times the resolution (R) of the balance.
5. The results of the least square linear regression equation ($y = mX + b$) for the accuracy test were within audit limits where:
 - y = the display value
 - m = the slope of the line [audit limit: $1.0 \pm 1.5(R)$]
 - X = the total certified mass on the pan load
 - b = the intercept [audit limit: $0.0 \pm 1.5(R)$]and the correlation coefficient (r) of the regression is greater than 0.9998.

Instrument performance for a particular characteristic is considered satisfactory if the measured value for that characteristic is equal to or less than the audit limit value. If the value for the characteristic exceeds the audit limit, then the performance of the Mettler AE240 is considered unsatisfactory for that characteristic and fails the audit. If a balance equipped with two weighing ranges passes the audit on one range and fails the audit on the other range, it will be evaluated for use limited to the passing range.

The overall results of the Environmental Evaluation, the Pre-Audit Test, the Display-Drift Test, the Off-Center Error Test, the Precision Test, and the Accuracy Test were all satisfactory. The air movement and vibration along the counter top were well within the requirements. The scale image was clear, and the zero adjustment and leveling leg screws worked properly. Performance evaluation results are summarized in Table D-1.

SYSTEMS AUDIT OF PARTICULATE MATTER COLLECTION PROCESS

On December 3, 1997, a systems audit of the procedures used to determine the particulate catch using the EPA Method 5 train and the California Air Resources Board Method 501 cascade impactor was

conducted in room H-202 at the ERC Building of the EPA/RTP. Charly King of ARCADIS Geraghty & Miller first explained the use of the Method 5 train and demonstrated the use of the drying chamber and how glass beakers containing acetone probe rinses were processed including how the residue was weighed and the results were recorded. He also explained and demonstrated the conditioning of Method 5 quartz fiber filters, the assembly and disassembly of the CARB Method 501 cascade impactor (Andersen Mark III). A detailed explanation and demonstration of the conditioning and weighing of the filters and impactor surfaces was also given.

It was concluded that proper procedures were being followed in the collection and gravimetric determination of particulate matter using EPA Method 5 and CARB Method 501. Control of humidity in the balance room is less than desirable when the ambient air is very moist. King stated that no weighings are made in the summer when the weather is rainy.

Table D-1. Performance evaluation results for the Mettler AE240

Capacity Range = 40 grams, Readability = 0.00001 grams		
Test Type	Audit Limits	Test Results
Display Drift	≤ 0.00002 g/min	0.00001 g/min
Off-Center Error	Standard deviation ≤ 0.00005 g	0.00004 g
Precision	Standard deviation ≤ 0.00005 g	0.00002 g
Accuracy	Linear regression: m: $0.99998 \leq m \leq 1.00002$ b: $-0.00002 \leq m \leq 0.00002$ r: 0.99998	1.00000 0.00000 1.00000
Capacity Range = 200 grams, Readability = 0.0001 grams		
Test Type	Audit Limits	Test Results
Display-Drift	≤ 0.0002 g/min	0.00001 g/min
Off-Center Error	Standard deviation ≤ 0.0005 g	0.0003 g
Precision	Standard deviation ≤ 0.0005 g	0.0001 g
Accuracy	Linear regression: m: $0.9998 \leq m \leq 1.0002$ b: $-0.0002 \leq m \leq 0.0002$ r: 0.9998	1.0000 0.0000 1.0000