INVESTIGATIONS OF
FLARE GAS EMISSIONS IN ALBERTA

Final Report to:

Environment Canada
Conservation and Protection,
the
Alberta Energy and Utilities Board,
and the
Canadian Association of Petroleum Producers

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FORWARD

The research program on the "Investigations of Flare Gas Emissions in Alberta" was designed in conjunction with the Government/Industry Consultative Committee on Flaring. Membership on the Committee includes Environment Canada, the Alberta Energy and Utilities Board, the Canadian Association of Petroleum Producers, the Alberta Research Council, Alberta Environmental Protection, and the University of Calgary. Funding for the project as well as specific member's contributions are gratefully acknowledged from the following:

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EXECUTIVE SUMMARY

The research program on the characterization of emissions from flaring in Alberta was designed in conjunction with Government and Industry representatives. It was developed as a scientific undertaking to address issues that have been identified around flaring in Alberta for a number of years. The overall terms of reference for the study was to determine experimentally the degree to which flared gases are unburned, and to characterize the products of combustion in the emissions.

The project design developed to meet these objectives consisted of laboratory, pilot scale, and field scale studies. Laboratory studies conducted primarily on pure fuels, were instrumental in the development and testing of equipment required for this program, and for the identification of hydrocarbons that are produced by these flames. Pilot scale studies were used to examine more complex fuel mixtures and under cross winds, make modifications where necessary, and substantiate the findings of the laboratory scale studies. The final field phase consisted of flare emissions characterization for both hydrocarbons and sulfur compounds as produced from two oilfield battery flare systems. The majority of solution gas flaring occurs at oilfield battery sites in Alberta. The following includes some of the major findings of these investigations.

Lab and Pilot Scale Studies

- Pure gas streams such as methane, propane, and commercial natural gas were found to burn with a high degree of efficiency (98% or greater) under most conditions employed in laboratory and pilot scale tests.

- Combustion of all hydrocarbon fuels in both laboratory and pilot scale tests produced a complex variety of hydrocarbon products within the flame primarily by pyrolytic reactions. These reactions and their products are not unique to flaring and can also occur in other combustion processes.

- Acetylene, ethylene, benzene, ethenyl benzene (styrene), ethynyl benzene, and naphthalene were some of the major constituents produced within the flames by the pyrolytic reactions. Polycyclic aromatic hydrocarbons were found to be produced in lesser amounts.

- The majority of the hydrocarbons produced by these reactions within the burning of gaseous fuels were found to be effectively destroyed in the outer combustion zone of the flame, resulting in relatively high combustion efficiency measurements for these flames.

- The addition of liquid hydrocarbon fuels or condensates to pure gas streams had the largest effect on impairing the ability of the resulting flame to destroy produced hydrocarbons as well as the original hydrocarbon fuels directed to the flare.

- The degree to which the combustion efficiency is affected by the addition of liquid fuels to a gaseous stream is dependent on both the amount and type of liquid fuel in the co-flowing stream.

- Crosswinds were also found to reduce the combustion efficiency of the co-flowing gas/condensate flames by causing more unburned fuel and produced hydrocarbons to escape into the emissions.

Field Studies

Field testing of flares was carried out at two oilfield battery sites, one containing sweet gas and the other sour gas. The sweet gas site had considerable liquid hydrocarbon carryover both to and from the liquid knock-out drum en-route to the flare while the sour site by comparison was considerably drier. Both flares were basic jet diffusion flames without any combustion enhancements.

- Flaring of sweet solution gas was found to burn with an efficiency of between 62 to 71%, and varied by either how much fuel was directed to the flare or how much liquid was in the knock-out drum.

- Flaring of the sour solution gas that contained lesser amounts of liquid hydrocarbons directed to flare resulted in a more efficient flame, 84% as calculated by the carbon mass balance and 82% as measured by the sulfur mass balance.

- Hydrocarbons found in the emissions above these flames included unburned hydrocarbons that were present in the fuel stream along with hydrocarbons produced within the flame by the pyrolytic reactions. Benzene, styrene, ethynyl benzene, ethynyl-methyl benzenes, toluene, xylenes, acenaphthalene, biphenyl, and fluorene were in most cases the most abundant compounds found in any of the emissions examined in the field flare testing. The emissions from sour solution gas flaring also contained reduced sulfur compounds and thiophenes.

- To provide a degree of perspective on these findings, an additionally commissioned study which included plume dispersion modeling for the two sites tested was carried out and predicted that ambient air concentrations are expected to be low (downwind of these sites) in relation to ambient air quality criteria, or other observed values.

The hydrocarbons identified in the emissions from each of the two field flares and the concentrations that were measured are specific to each individual flaring operation. Although flaring of all fuels has been shown to produce various levels of hydrocarbons within their respective flames, the amount that escape into the emissions can be very different depending on the composition of the fuel being flared, the flare design itself, and the atmospheric conditions at the time of flaring.

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1.0 INTRODUCTION

Flaring has long been used in the oil, natural gas, and petrochemical industries to manage the disposal of waste hydrocarbon products from production processes and for emergency use in case of operational upsets. Some of these flares have been identified as sources of odour, smoke, and air quality related health concerns by members of the public living in closer proximity to them. Most flare designs include specific requirements to minimize certain aspects such as noise, visibility of plumes (particularly black smoke), and the emissions of hydrocarbon compounds to the environment. Noise and visibility problems that result from flaring can easily be measured. The ability of a flare to effectively burn waste hydrocarbon products, on the other hand, is complex and methods for more detailed examination of emissions from flaring have been somewhat limited. Therefore, relatively little is known about the specifics of emissions from flaring. The broad public focus on environmental protection, coupled with the recent concerns about the protection of the ozone layer, about greenhouse gases causing global warming, and about air quality on a regional scale has increased the need to examine more critically the practice of flaring and, in particular, to characterize the resulting emissions.

In a proactive step, Environment Canada (with funds from the Panel on Energy Research and Development), the Alberta Energy and Utilities Board, the Canadian Association of Petroleum Producers, and the Alberta Research Council formed a funding partnership in 1990 to carry out a study that would examine in more detail the emissions from flaring operations primarily associated with the upstream oil and gas industry in Alberta. Members from these funding organizations along with members from Alberta Environmental Protection and the University of Calgary were instrumental in designing the study with the following goals:

1. To determine the constituents of fuel streams directed to a flare that are left unburned;
2. To characterize the products of combustion; and

3. To determine factors which contribute towards complete/incomplete combustion and the extent of their contribution, including the effects of entrained liquids and strong crosswinds.

The research program that was developed to meet the objectives was carried out in three phases, including laboratory, pilot scale, and field scale studies. In Phase 1, lab studies were carried out primarily to develop and test sampling systems and analytical equipment required to characterize emissions from lab-scale flaring systems capable of handling both pure and mixed fuel streams under controlled conditions. The objective was to understand the reactions that occur within the flames, the products produced, and the concentrations that can be found in the emissions. The Phase 2 pilot scale studies were used to test these sampling and analytical systems on a larger scale in an outdoor environment, to evaluate the effects of more complex fuel mixtures and cross winds, to make modifications where necessary, and to substantiate the findings of the laboratory scale studies. The Phase 3 field studies were focused to the testing of existing flare systems similar to the kind used in the upstream oil and gas industry where the majority of solution gas is flared in Alberta. These studies examined flare emissions for both hydrocarbons and sulfur compounds at two different oilfield battery sites, using equipment and procedures developed and modified, where necessary, from the first two phases of the study.

2.0 BACKGROUND

Alberta is the largest supplier of hydrocarbon energy resources in Canada, producing approximately 83 percent of Canada's natural gas, 80 percent of its oil, and 44 percent of its coal (Legge et al., 1992). The environmental management of this energy production and utilization have long been recognized as an important element in the economic development of Alberta. One environmental aspect that has received increasing attention is in the emissions of volatile organic hydrocarbons and oxides of nitrogen from various operations of this energy production.

The oil and gas industry in Alberta has achieved a conservation rate of 92% of total solution gas production, however the remaining 8% represents significant volumes of these gases. The current methods of handling these waste gases is through incineration, reinjection, venting, or flaring. There are currently more than 5300 active flares in Alberta that burn an estimated 2340 x 10^6 m^3/yr produced by the upstream oil and gas industry annually (EUB, 1995). The estimates have some uncertainty because the flow of some waste gases is only measured on an infrequent basis. The main contributors to the total flared gases include sweet and sour oil production batteries (1920 x 10^6 m^3/yr), followed by sour and sulfur recovery gas plants and gas gathering systems (420 x 10^6 m^3/yr) (EUB, 1995). Most of the gases from the sour and sulfur recovery gas plants however, are incinerated. A similar number of emergency or intermittent flares are operational in Alberta.

Not all the gases flared are hydrocarbons, as evidenced by the estimated emissions of 75-80 tons per day of sulfur produced from flaring solution gas in Alberta (Sandhu et al., 1980). At 100% combustion efficiency this sulfur would be emitted as sulfur dioxide, however, as combustion efficiencies decrease, the character of the emitted gases change, giving rise to other sulfur gas emissions such as hydrogen sulfide, carbonyl sulfide, carbon disulfide, mercaptans (Ashworth et al, 1984; Strosher, 1984).

Emissions from flaring operations are complex and their composition influenced by a variety of factors including flare design, operating conditions, and composition of waste gases. Gas streams with low heating values are unable to maintain a stable flame, thereby reducing overall efficiencies of combustion (McCrillis, 1988). Flared gases with varying amounts of liquid hydrocarbons, carbon dioxide, nitrogen, and/or sulfur gases may not only have reduced combustion efficiencies, the combustion process may also produce undesirable components in the emissions (Pohl and Soelberg, 1985; 1986; and 1986a). Strong cross-winds can produce a significant reduction in the combustion efficiency of a flare by shedding and/or tearing some of the eddies from the flame that contain incomplete or partially combusted gases from the flare (Gallant et al., 1984; Grouset and Plion, 1987).

In light of the many variables that can affect combustion efficiency in flaring, the potential for emissions that may affect air quality, and the widespread use of flares in Alberta, a Government/Industry Consultative Committee on Flaring (GICCOF) was established to examine the whole practice of flaring. They noted that some of the main problems encountered in examining flares were in sampling methodology, knock-out drum effects, and effects of high winds. They concluded that certain investigative and engineering work would be desirable to answer a number of questions related to current flare operations in Alberta.

A review of the most recent literature on flaring, prior to this study included the topics of detection, control, and analysis techniques of flare gases (Karim et al, 1985). In relation to the research topics recommended by the GICCOF review committee as needing to be addressed, some preliminary work has been conducted on optimizing sampling systems (McDaniel, 1983; Pohl et al., 1986) as well as possible effects caused by cross-winds (Gallant et al., 1984; and Grouset and Plion, 1987). There still appears to be little or no research carried out on the effects of flaring caused by co-flowing liquid droplets.

There are a number of different flare designs available for burning waste streams from industrial operations. A common flare system used in flaring operations at oilfield battery sites in Alberta is a simple pipe system without any combustion enhancements, the top 2 to 3 metres usually being constructed from stainless steel. The size of the stack and opening is primarily dictated by the necessity to accommodate maximum anticipated gas release caused by process upset or emergency shutdown at each particular location. These flares are usually equipped with a shroud at the top to reduce blow-out from high cross winds, have an automated ignitor in case of flame blow-out, and are rarely equipped with a nozzle because of the low and fluctuating flow that is directed to them. Although the design and operation of these flare systems is relatively simple, the combustion process itself can be very complex. An understanding of these combustion processes, the predicted reactions that can occur, and the types of compounds that can be produced by these flames was necessary to provide the foundation for the research program that was developed to evaluate these type of flares.

Flare systems commonly used in the majority of upstream oil and gas production operations in Alberta are designed to function as a diffusion flame, which is a combustion process in which the fuel and the air are not premixed. For ideal combustion, the right proportions of fuel and oxygen are required to produce only heat, carbon dioxide and water. If too much oxygen is introduced, the mixture is considered lean and the fire oxidizing. This results in a flame that is shorter and clearer. If insufficient oxygen is available, the mixture is considered to be rich and the fire reducing. This results in a flame that is usually longer and sometimes smoky and is considered as incompletely combusted. Diffusion flames are very difficult to operate with exactly the right proportions of fuel and oxygen for their burning, even sometimes under ideal conditions. Hence flares will tend to lead to some level of incomplete combustion.

There are a number of processes that occur in a diffusion flame that can chemically affect the nature of the emissions. These include the sequential arrangement of precombustion, combustion and post-flame processes (Edwards, 1974). Edwards (1974) noted that precombustion reactions occur before the mixing of fuel with the air. Because the precombustion zone of a diffusion flame can contain only fuel molecules or their fragments, the environment for these reactions is reducing in character and products are expected to be pyrolytic in nature.

The reaction products of these pyrolytic processes are predicted to include unsaturated species such as olefins and acetylenes, and particulate nuclei resulting from polymerization or addition reactions between the unsaturated species. When these particles that are produced pass through the flame, they radiate as black bodies. This produces not only the characteristic luminosity of diffusion flames but also accounts for the transfer of radiant energy to the particle nuclei forming in the precombustion zone. In this zone, which occurs before mixing of the fuel and oxidant produces a combustible mixture, oxidation of the fuel cannot occur regardless of how high the temperature might rise. Ignition in a diffusion flame is therefore controlled by the physical processes that influence mixing such as turbulence and the geometry of the system. Since oxidation cannot occur until fuel and oxygen (air) are mixed, the pyrolytic precombustion reactions will continue until a combustible mixture is obtained. If final mixing is poor, these pyrolytic reactions may produce large quantities of particulates and other pyrolytic species.

There is yet another reason why the pyrolytic reactions and their subsequent emissions are of interest in a diffusion flame. Edwards (1974), demonstrated that a sequence of pyrolytic reactions may lead to the synthesis of relatively large and complicated molecules in the effluent. He illustrated the possible pyrolytic synthesis of polynuclear aromatic hydrocarbons. In the case of precombustion reactions, low temperature pyrolysis reactions proceed via a sequence of distinct intermediates and can range from the paraffinic stage through the olefins, cyclo-olefins, and on to the aromatics. In this sequence, unsaturation of the reactant promotes addition-type reactions between the hydrocarbon species. The emergence of ring structures then becomes a convenient building block for more complex condensed ring structures such as the 2, 3, 4, and 5 ringed polycyclic aromatic hydrocarbons.

The complexity of the combustion process and the hydrocarbon species that can be produced by these flames, together with the findings of previous studies indicated that certain aspects of flaring in Alberta needed to be researched in more detail. In addition to a more in-depth characterization of the products of combustion from flaring, the research needed to include the effects of liquid condensates and other liquid droplets during the flaring of gaseous fuels, the effects of cross-winds on flaring, and a reliable sampling and analytical system to accommodate the measurement of these effects.

3.0 PROJECT DESIGN

Flares are used because of their expected ability to burn the waste gases directed to them effectively. As a result, the measure of efficiency of combustion of these flares has been examined primarily on the ability of the flare to destroy only the gases directed to them. The combustion products normally measured in these efficiency evaluations include carbon dioxide, which is considered the burned species, and the unburned species including carbon monoxide, carbon, and the hydrocarbons that were directed to flare. The use of these data only in evaluating the performance of the flare results in a measure of its destruction efficiency. The limitations of these measurements do not allow for any reactions that might take place in the burning process other than some oxidative ones.

A more comprehensive measurement of the efficiency of a flare, can be carried out on the basis of either global or local combustion. Global efficiency measurements require not only the composition and mass flow of the inlet fuel, but also the composition and mass flow of the products of combustion for the entire emissions. The use of this method in this study to evaluate the efficiency of oilfield flares was not considered for two main reasons. In general, oilfield facilities are not instrumented to measure flow streams of waste gases on a regular or continuous basis, and determination of the mass flow of all combustion products is difficult without capturing the entire plume from a flare.

Local combustion efficiency measurements, on the other hand, require that only the relative amounts of products of combustion in the emissions be determined. This eliminates the need for measurements on mass flows that are difficult to obtain, but it still requires complex measurements of the entire range of combustion products. It also requires that sampling be obtained on as representative a sample as possible within the plume, as emissions from these flames are variable and dependent on atmospheric conditions, even when gas flow is constant to the flare.

The approach used in this study was to examine the various products of combustion in order to provide a more complete description of the products in the flare emissions from both oxidative and pyrolytic reactions, and the degree to which the combustion goes to completion. This approach was needed in order to develop and test the appropriate sampling and analytical capability that was ultimately used to characterize emissions from industrial-scale flaring at two oilfield battery operations in Alberta. Based on the local combustion approach, the resultant efficiency measurements were calculated using either a carbon or sulfur mass balance of all combustion products identified in the emissions. Carbon or sulfur equivalents were calculated from each compound detected and the combustion efficiency determined as follows:

$$CE\% = \frac{(C)(CO_2)}{(C)(CO_2) + (C)(CO) + (C)(HC's) + (C)(soot)}$$

$$CE\% = \frac{(S)(SO_2)}{(S)(SO_2) + (S)(H_2S) + (S)(COS) + (S)(CS_2) + (S)(S\,cmpds)}$$

The study developed to meet the project objectives was carried out in three phases. The general rationale for each of the phases is described below, while the detailed description of the methods and procedures used are provided in Section 4.

3.1 Phase I, Laboratory Studies

The first phase of the study consisted of the development and testing of a laboratory flare system as well as a sampling and analytical capability. Both components were required in order to reliably measure the efficiency of and combustion products produced by flaring fuels under extremely controlled conditions. The laboratory scale flaring system was completely enclosed except for the open top. Ultra high purity fuels were introduced as gases, liquids, or combinations of gas/liquid fuel mixtures. Both fuel and combustion air were precleaned and analyzed prior to flare testing in order to eliminate the possibility that hydrocarbons other than the fuel being tested were being burned in the flare system.

The results obtained in the laboratory investigations were based on very small scale flames where conditions were controlled and very close to ideal. They did, however, provide essential information needed to make the necessary modifications in sampling and analytical procedures used in the next phase of the study.

3.2 Phase II, Pilot Scale Testing

The second phase of the project addressed two purposes. First, it examined the effects that larger scale flaring would have on the character of the emissions produced. Secondly, a sampling system was developed that would define the type needed to examine emissions from an industrial scale flare. The pilot scale flare used in this phase was constructed to provide a flow of either gas or gas/liquid fuel that was at least 10 times the flow used in the phase 1 lab studies. Sampling systems were also developed and constructed to allow both for simultaneous sampling from a cross-sectional area of the flare emissions using a multi-probe system, and for the integrated sampling from specific areas above the flame using various diameters of hood samplers. Exhaustive testing was then carried out using various fuel mixtures to determine the major emission zones associated with the flames that would be both minimally diluted and beyond any further combustion. All testing of this pilot scale flare system was carried out in open atmosphere, and either in calm or in cross-wind conditions.

Based on the findings from the pilot scale tests, a single probe sampling system was developed and tested prior to field sampling. It consisted of a heated probe and heat traced lines that were tested over various temperatures to determine optimum conditions under which the majority of hydrocarbon combustion products could be recovered.

3.3 Phase III, Field Testing

The field testing phase of this project involved the sampling of emissions from flares at two operating oilfield batteries, one handling sweet oil and gas and the other handling sour oil and gas. The sampling system was mounted on a mobile lift that could be manoeuvred easily from the ground level to keep the sampling probe within the emission plume of the flame to the greatest extent possible during the sampling. Samples were collected at various locations along the sampling system, including immediately after the sampling probe, at the basket level of the lift, and at ground level.

4.0 METHODOLOGY

This study was carried out over a period of five years and includes three different phases of investigations. Each phase required development, construction and testing of various equipment to carry out either simulated flaring operations or reliable sampling of emissions from flaring. A description of equipment used in each of these phases is contained in the following sections. Analytical equipment used in the characterization of the products of combustion are then described.

4.1 Phase 1 Lab studies

In order to carry out the objectives of the study, gain a preliminary understanding of the diffusion flame combustion process, and develop the sampling and analytical capabilities that would be required to examine emissions from industrial flares, the first phase of this project was carried out entirely in the laboratory where conditions were easier to control and sampling was less difficult. These laboratory tests involved the flaring of various hydrocarbon based gases, liquids, and combinations of liquids entrained in gases. Accordingly, the laboratory flaring apparatus was constructed to perform a number of functions. These included the ability to produce fuel streams at various velocities, to control the velocity of the surrounding stream of combustion air, to control independently and mix together more than one fuel or diluent, and to provide both co-flowing liquid/gaseous fuel mixtures by either direct addition of liquid droplets or by entraining liquid fuel droplets into the gaseous stream with the use of an evaporator, as occurs in flare knock-out drums.

4.1.1 Flare Test Chamber

The laboratory flare test chamber consisted of a vertical steel cylinder, approximately 150 mm in diameter and 600 mm high with a flat quartz window for viewing the flame (Figure 1). The top end of this combustion chamber was open to the atmosphere. The combustion air stream, which was introduced through the bottom of the chamber, was passed through a flame trap diffuser, a stainless steel wire mesh, a perforated cone, and finally through a honeycomb flow straightener to minimize any turbulence caused by the diffuser.

Fuel and fuel mixtures to the flare tip were supplied through a 6.4 mm stainless steel tube that protruded through the centre of the bottom of the flare test chamber to accommodate the insertion of various flare tips above the honeycomb combustion air flow straightener. The height of the flare tip above the bottom of the chamber could be varied by moving the entire fuel line vertically.

The flare test chamber contained a number of sample probe ports along the height of the cylinder. It allowed for sample acquisition at approximately 9 different vertical distances from the top of the flare tip and an infinite number of horizontal distances from the centre line of the flare. A more integrated sample could also be collected from the open top of the combustion chamber. The flaring apparatus was enclosed in a specifically designed fume hood.

4.1.2 Fuel System

Gaseous fuels were supplied to the flare tip from high pressure cylinders equipped with a series of control and safety devices. Metering nozzles were used to provide a wide range of flow rates. Liquid fuels were supplied to the flare as fine droplets by two different methods. The first method pressurized the fuel and injected it through a fine diameter nozzle (approximately 0.008 mm). The resultant fuel stream was passed through a fine filtering system, a calibrated flow meter and dispersed through the nozzle into a co-flowing stream of combustion air. Introduction of liquid fuel to the flare system in a manner similar to that which occurs in industrial knock-out drums was accomplished by use of a laboratory fuel evaporator system. Liquid fuel was introduced into the fuel line in vapor form entrained in a measured flow of gaseous fuel. This was achieved by bubbling the gaseous fuel through a cylindrical vessel containing the liquid fuel. The amount of fuel vapor entrapped in the gas was varied by changing the liquid fuel temperature. A sintered bronze disk was contained in the bottom of the evaporator to increase residence time of the gas

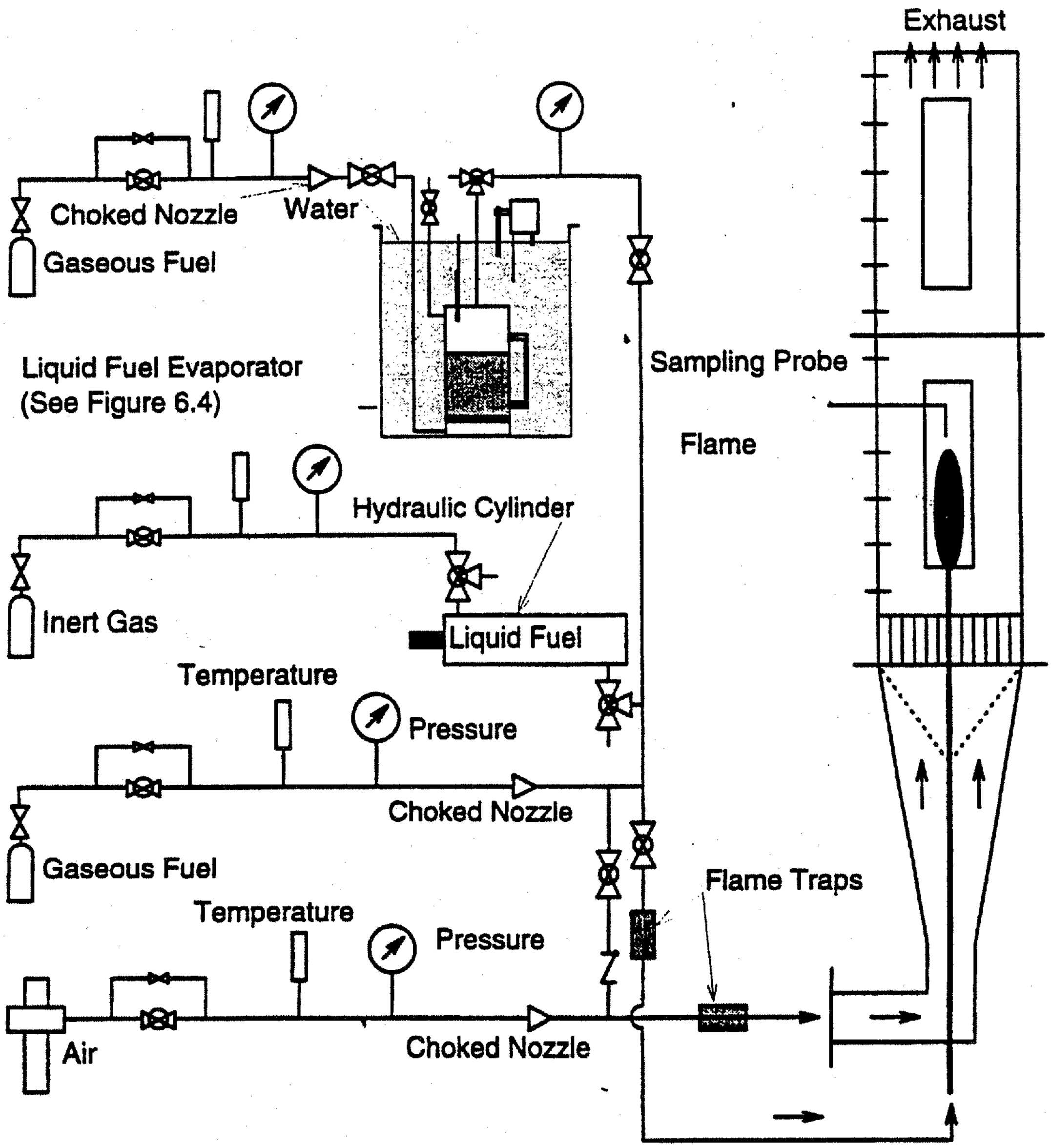

Figure 1. Schematic diagram of the laboratory flare system.

within the liquid fuel, thereby increasing the gas/liquid surface contact and ensuring a saturated vapor-gas mixture.

4.1.3 Flare Tips

For industrial flaring operations, a number of flare tip designs are available for flare stacks. The choice of flare tip depends on many factors including the flame stability characteristics of the tip, the expected composition of the gas to be flared, the availability of purge gas for low or intermittent flare gas flow, and the turndown ratio required. The design should ensure that the discharge velocity of the flared gas is as large as possible to ensure efficient mixing and combustion but without exceeding the flame holding characteristics of the tip.

Flame shape, volume and length are important characteristics of the flare that are dictated by flare tip design and are directly related to the rate of combustion. They influence the combustion efficiency as well as the amount and centre for radiant emissions. Flame length in particular is important because it is an indicator of the reaction time, the extent of exposure of the surroundings to heat transfer from the flame, the size of the combustion zone, and the extent of contact of the combustion gas discharge with the environment.

To accommodate flaring of both gaseous fuel and liquid/gaseous fuel mixtures, several different sharp-edged stainless steel flare tips were used. One aspect incorporated in their design was to minimize the disturbance of the surrounding air flow as it passed over the nozzle. Orifice sizes of the flare tips ranged from 0.1 to 3.0 mm with appropriate sized nozzles used in conjunction with the type and amount of fuel flared. Nozzle tips were chosen such that maximum velocity of the gas did not exceed a Mach number of 0.2 for continuous flaring.

4.1.4 Sampling System

One of the major concerns in flare testing and research is that the sampling and analysis of the emissions at any location in the vicinity of the flare is done in a manner that provides unaltered samples of the gaseous components present at the point of sampling. For example, heated sampling lines normally employed to preserve the vapor state of some of the condensable components can also contribute to the oxidization of others in the presence of oxygen. On the other hand, rapidly cooled samples will naturally condense water vapor to liquid droplets and react with yet other products of combustion.

Another important consideration in the sampling system design is the need to minimize the disturbance of the flare flow field by either the bulk of the sampler or the withdrawal rate of the emission sample. This was achieved by keeping the probe size to a minimum and keeping the sampling flow rate equal to or less than the flow rate of the main gas stream. The ideal sampling rate is one that is equal to the isokinetic sampling rate, which is accomplished by adjusting the sampling rate so that mass flux through the sampling probe is equal to that of the flaring stream.

The sampling system developed for use in these studies employed both heated and non-heated sampling lines. The continuous sample collected by the sampling probe was split into two streams. One stream was connected to a triple-stage Teflon filter pack, then to a heated Teflon sample line maintained at 125°C through which sample was drawn to the on-site analyzers. The second stream was used for obtaining integrated samples collected in Teflon bags and through glass sample traps containing Tenax or Carbon adsorbents for further characterization of the emissions by gas chromatography/mass spectrometry. These samples were acquired from the sample stream immediately adjacent to the end of the sampling probe and were therefore unfiltered and not heated.

4.2 Phase 2 Pilot Flare System

The second phase of the flare testing program was designed to carry out flare testing on a slightly larger scale and in an open atmosphere. The flare system designed and constructed for these studies consisted of the same fuel flow and delivery system used in the laboratory tests (Figure 1), but with a slightly larger fuel transfer line and flare tip nozzles, and no added combustion air. Orfice sizes of the pilot scale flare tips ranged from 2 to 6 mm in diameter, with size corresponding to the type and amount of fuel flared.

One of the major concerns in the pilot scale testing was to obtain representative emission samples from the much more variable flame that occurred, compared to the very steady flames that were examined under the controlled and ideal conditions in laboratory tests. To examine this variability, two different types of sampling systems were used. The first was simultaneous sampling through a series of probes set out in a horizontal plane, perpendicular to the flame. The second was through hood samplers of various diameters that would obtain an integrated sample of the entire emissions from the flame. Once again, samples were either drawn from these samplers for analyses by the on-site analytical equipment, or were collected on adsorbents or in suitable containers for the confirmatory analyses by combined GC/MS.

4.3 Field Flare Testing

Field flare site selection was based on several criteria, including availability, size of flare, presence of liquid knock-out systems, and site characteristics such as accessibility, power availability, and security. For this study, both a sweet and sour oilfield battery site were required. The sweet battery site tested was chosen based on the availability of both sweet gas and liquid hydrocarbon fuels and the ability to control and vary their quantities directed to the flare. A sour oilfield battery site was then selected on the basis of containing sour solution gas ranging from 10 to 30% H_2S. Both sites contained flaring systems typical of the kind used in the upstream oil and gas industry.

The sweet oilfield battery site tested was fed by 24 wellsites producing both crude oil and solution gas as well as co-produced water. The battery site is a central gathering and waterflood facility for one of the major oil pools in Alberta. Saleable crude oil, water dry solution gas, and produced water are all products at this facility. Major components used at this facility consist of a test separator, free water knock-out vessel, group separator, inlet heater, treater, produced water storage and skim tanks, water injection pumps, solution gas compressor, glycol dehydration system, and a flare system. Detailed schematics of these operations are confidential to the owner companies and are therefore not available.

The flare system at this site consisted of a liquid knock-out drum and a free standing flare stack 12 metres in height, and 20 centimeters in diameter at the tip. It was equipped with an auto-ignitor and wind deflector to prevent flame blowout. The top 1.8 metres of the stack was fabricated from stainless steel. It also contained an inlet baffle to prevent liquid accumulation. The majority of feed to this flare was solution gas from the treater with actual flow as measured by industry of approximately 8,000 m^3 per day. Figure 2 displays this flare along with the sampling system used to sample the resulting emissions.

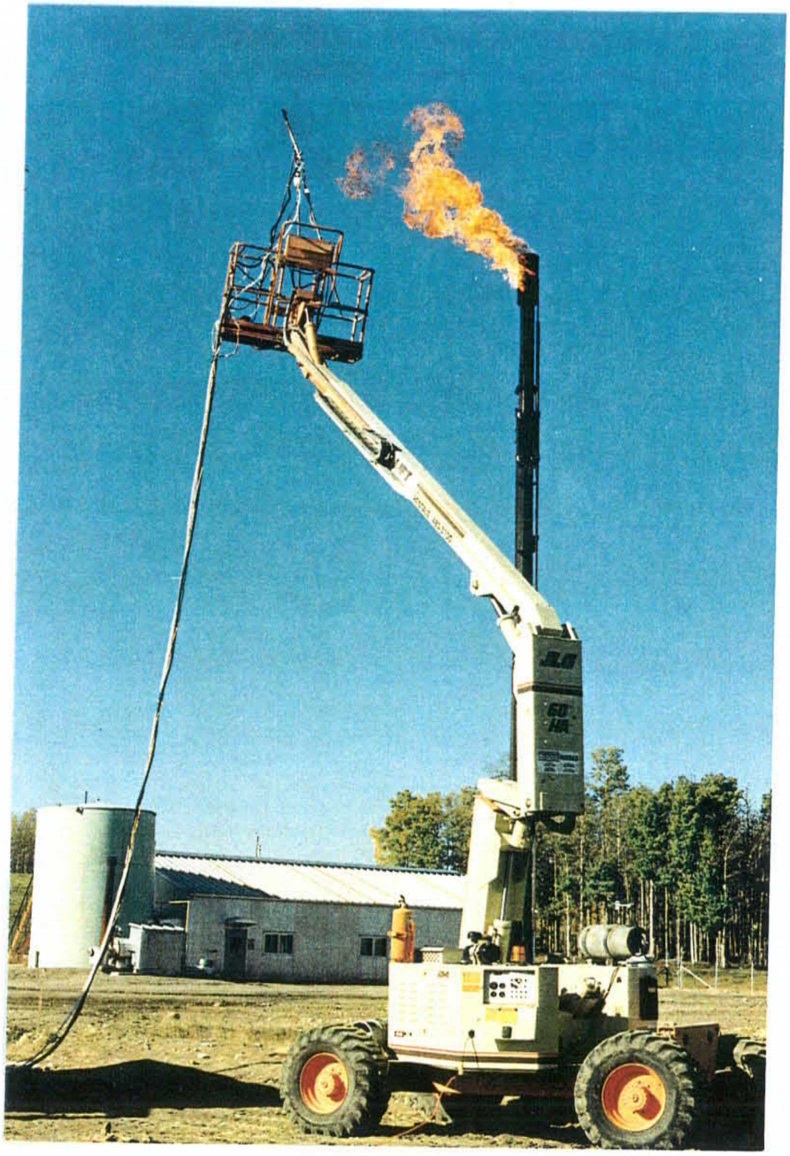

Figure 2. Flare testing at the sweet oilfield battery site. Sampling system consisted of a heated probe, heat traced sampling to the basket, and another heat traced line to ground level.

The sour oilfield battery site chosen was much smaller by comparison. It was fed by two wellsites producing both crude oil and sour solution gas. The much smaller battery operation here consisted basically of a separator, treater, water and oil storage tanks and a flare system. Once again, details of the operation are not available.

This flare system consisted of a liquid knock-out drum and a flare stack approximately 15 metres high and 7.6 cm in diameter at the tip. It was also equipped with an auto-ignitor and a wind deflector to prevent flame blow-out. The stack was fabricated from stainless steel. All solution gas produced from these two wellsites feeding this battery was directed to the flare, and averaged approximately 650 m^3 per day (actual flow as measured by industry). This flare system is shown in Figure 3.

The sampling system designed and chosen for the field studies was based on the sampling results obtained from the different sampling systems used during the pilot scale tests. These tests indicated that over a longer period of time, the concentrations of compounds contained in the emissions from the flame, were relatively uniform under average atmospheric conditions within a circular diameter approximately 20 times the diameter of the flare and within a distance of up to twice the flame length (Strosher, 1994). Based on these findings, a single probe sampling system was developed and tested prior to the field sampling. These tests consisted of measuring standard hydrocarbon mixtures passing through the heated probe and heat traced lines at varying temperatures to determine the most suitable temperature for hydrocarbon recovery.

The sampling system was fitted to a hydraulic basket lift with a 20 metre reach. The 3 metre probe was attached to a 5 metre boom that was in turn fastened to the basket, providing an extra 8 metre reach (Figure 4). Sampling was carried out at several locations along the length of the sampling system, including immediately after the probe where integrated adsorbent tube and polyurethane foam samples were collected (Figure 5), at the basket level where duplicate integrated adsorbent tube samples were collected, and at ground level where samples were collected in Tedlar bags for immediate analyses in the on-site analytical equipment.

Figure 3. Flare testing at the sour oilfield battery site.

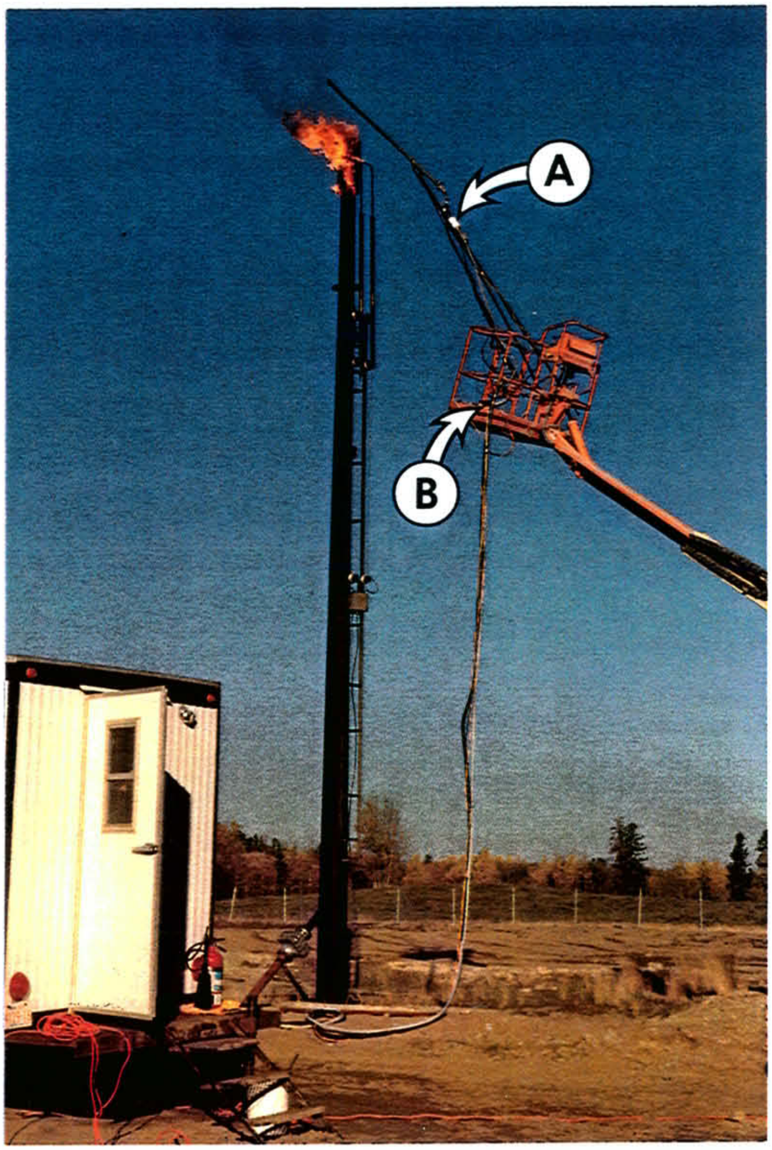

Figure 4. Flare emission sampling system used in the field flare testing program. System consisted of a 3 metre heated probe attached to the end of a 5 metre boom, a 6 metre heated teflon line to the basket level, and a 23 metre heated teflon line to ground level. Samplers were connected immediately after the probe at "A", at the basket level "B", and at the trailer.

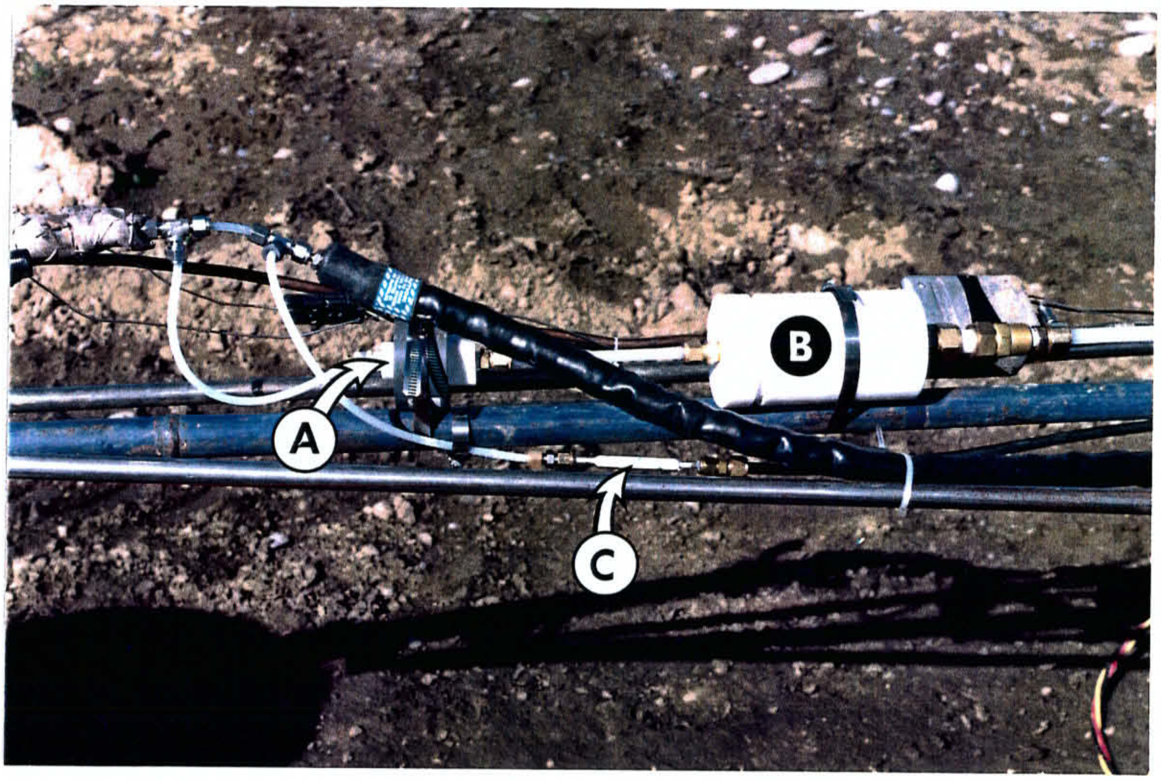

Figure 5. Modified Polycyclic Aromatic Hydrocarbon Sampler connected to the field sampling system immediately after the sampling probe. The glass fibre filter is contained in the teflon holder marked "A" and the polyurethane foam plug is contained in the teflon container marked "B". Additional samples were collected on the glass adsorbent cartridge marked "C".

4.4 Analytical Equipment

There is no single piece of analytical equipment capable of detecting the wide range of potential emission products that need to be examined in order to determine the combustion efficiency of flares and particularly to identify the hydrocarbon components contained in their emissions. As a result, a combination of gas chromatographs, analyzers, and combined gas chromatography/mass spectrometry was used in these investigations. These components are described in the following.

4.4.1 Gas Chromatography

Hydrocarbon analysis can be carried out either as total hydrocarbons within a sample or detected as individual components. In order to determine combustion efficiency in a burning operation, only a total hydrocarbon value is required. One of the main objectives of the current study, however, was to examine the components of combustion such as the individual hydrocarbons that are emitted to obtain a better understanding of the degree to which both flared gases and liquids are combusted. It was therefore necessary to employ gas chromatographs capable of separating the individual hydrocarbons and other gases for subsequent detection and quantification.

A Varian Model 3400 Gas Chromatograph with a flame ionization detector and automated sample valve, coupled to a high resolution solid porous polymer open tubular megabore fused silica column was used to detect the hydrocarbons ranging from methane to naphthalene. Data collection was carried out using either a Perkin Elmer or Hewlett Packard integration system. This chromatographic system was calibrated using standard hydrocarbon mixtures covering the entire range of hydrocarbons analyzed by this system. The lower limits of detection averaged approximately 10 ppb and reproducibility of the system was +/- 10%. Duplicate analyses were carried out whenever possible.

A Hewlett Packard Model 5890A gas chromatograph with a flame photometric detector and automated sample valve, coupled to the same type of fused silica column was used to detect the sulfur-containing compounds ranging from hydrogen sulfide to the light thiophenes. Data collection was carried out using a Hewlett Packard Model 3393 computing integrator. This system was calibrated using standard sulfur compound mixtures covering the entire range of compounds detected by this system. The lower limits of detection of this system ranged from 1 to 10 ppb with a reproducibility also of +/- 10%.

Fixed gases, including carbon dioxide, carbon monoxide, hydrogen, oxygen, nitrogen, and the light hydrocarbons were detected on an MTI Model P200 high speed gas chromatograph. The chromatograph contained two micro-GC's which plug into the main frame of the analyzer and perform high speed gas separations. Each micro module contains a micro-packed or fused silica capillary column, injection system, sample channel, and a miniaturized thermal conductivity detector. Complete analyses for these gases was carried out in approximately 90 seconds. Data handling and instrument control were performed with a M200 data system software package on a personal computer. All analyses were carried out in triplicate with results reported as the mean values.

4.4.2 Gas Chromatography / Mass Spectrometry

Hydrocarbon analyses by GC methods is achieved by matching of elution times with standard hydrocarbons as they pass through the GC column. The better the resolution of compounds through the column, the more accurate the identification can be. In order to obtain more positive identification of the hydrocarbon components collected from the flare emissions, integrated samples of these emissions were taken throughout these studies for additional analyses by combined gas chromatography/ mass spectrometry.

A Finnigan Model 4021 GC/MS, upgraded with a Model 4500 ion source and coupled to a dedicated Superincos Data System was used in the analyses, data acquisition, and data handling of these samples. The GC column used was selected to provide the necessary separation of the individual compounds for identification by the mass spectrometer (Strosher 1992, 1993, 1994, 1995, 1996). Compound identification was accomplished initially by computer matching of the unknown spectrum of sample compounds to the National Bureau of Standards library of spectral responses (43,000), to produce the five best "FITS" with confidence limits greater than 80%. The individual sample spectrum was then manually examined for molecular and fragment ions to ensure validity of identification as produced by the computer library searches. Further enhancement of identification was accomplished for compound isomers that are very similar in mass spectral response by comparing gas chromatographic elution times with that of known standards.

Samples obtained for these investigations were collected either by drawing the flare emission sample stream through specific adsorbents such as Tenax or Carbotrap contained in glass sampling tubes, or by directing the emission sample stream into either Teflon sample bags or glass sampling bombs. In either case, these samples required further manipulation prior to the GC/MS analysis, depending on the abundance of each hydrocarbon contained within them. For the analyses of light hydrocarbons, a cryogenic preconcentrator was designed and used as the initial means of introducing the hydrocarbon samples onto the GC column. A short length of uncoated fused silica tubing was fitted to the injection system and incorporated into the carrier gas system of the gas chromatograph. This was done both to allow the preconcentration of sufficient sample by passing specific volumes through the tube while it was immersed in liquid nitrogen, and also to focus the sample into the very small volume necessary for injection onto the GC. The light hydrocarbons collected on the adsorbents were thermally desorbed from these traps with a helium purge into the cryogenic trap prior to the injection into the GC/MS system.

Standard hydrocarbons consisting of aliphatic hydrocarbons ranging from C5 to C10, aromatic hydrocarbons ranging from benzene to naphthalene substituted compounds, and cyclic hydrocarbons such as cyclohexane were tested in the system. Lower detectable limits for these compounds are governed only by the amount of sample collected in the preconcentrator. Additional tests were carried out on available standards to examine for losses or deterioration in sampling containers or on absorbents for up to two days. No appreciable losses occurred for any of the standards examined and repeatability of results fell within a range of +/-15%.

After thermal desorption, each trap was extracted with a volume of nanograde n-hexane. The extracts were reduced in volume firstly under vacuum then under ultra high purity nitrogen prior to injection into the GC/MS system. These extracts were found to contain hydrocarbons ranging from approximately naphthalenes to six- or seven-ringed aromatic compounds, together with several oxygenated hydrocarbons. Standard hydrocarbons in this range were injected and extracted from blank adsorbent tubes to test for efficiency of recovery and reproducibility. All standards tested showed no appreciable losses and the recovery and repeatability were within +/- 15%.

4.4.3 Polycyclic Aromatic Hydrocarbons

Additional sampling for polycyclic aromatic hydrocarbons was also carried out during these investigations using a modified PAH Sampler. This was employed as a means of providing comparable results to ambient air analyses carried out by Environment Canada and the Ontario Ministry of Environment.

The polycyclic aromatic hydrocarbons identified in previous investigations have varied widely in molecular weights along with corresponding physical properties. Vapor pressure is particularly important relative to sampling techniques. Low vapor pressure compounds are usually associated with particulate matter, while higher vapor pressure compounds are usually found predominantly in the vapor state (Keller and Bidleman, 1984; Yamasaki et al., 1982).

The system used in this study to trap both phases of these compounds consisted of a custom-made mid-volume sampling system, using glass fibre filters to collect the particulate matter and associated hydrocarbons, followed by a Polyurethane Foam (PUF) adsorbent cartridge to collect vapor phase hydrocarbons that passed through the filter. The entire sampling system was made of Teflon and was used in all field investigations (Strosher, 1995, 1996).

The sampling media were pre-extracted with toluene prior to sampling collection. The PAH-free filters and PUF-adsorbent cartridges were placed in their respective containers and connected to the sampling line immediately down-line of the sampling probe. Samples were collected at flow rates ranging from approximately 10 to 20 litres per minute.

The polyurethane foam (PUF) cartridges were extracted in a soxhlet extractor using toluene. Extracts were reduced in volume firstly under vacuum then under ultra high purity nitrogen prior to injection into the GC/MS system. Filter samples were collected for determining both carbon content and for PAH analyses. After weighing the filter to obtain carbon content, a portion of each filter was deposited into a pyrolysis sample inlet system attached to the combined gas chromatograph/ mass spectrometer system, heated to approximately 300°C and analyzed by the GC/MS system as previously mentioned.

5.0 RESULTS AND DISCUSSION

The flaring emissions investigations were carried out in three phases over a five year period. This generated a large amount of information both on hydrocarbons and sulfur compounds produced by various reactions that take place within these flames and on the compounds that can be found in the resulting emissions. The information that was gathered during the three phases of the study is described in the following sections.

5.1 Laboratory Studies

The laboratory flare testing program consisted of an evaluation of pure gaseous, liquid, and co-flowing gas/liquid flames. In order to ensure the accuracy of analytical data being generated during the course of these studies, a quality assurance/quality control (QA/QC) program was carried out as an integral part of the lab studies on flare emissions. One of the QA/QC aspects of the flaring investigations was to verify that fuels being used, particularly in the laboratory flaring operations, were free from any other hydrocarbon compounds that might be measured as products of combustion. The analyses of both ultra high purity methane and propane revealed small quantities of benzene, toluene, and other hydrocarbons at quantities that might possibly alter flare testing results, especially if all of the impurities could escape through the flame unburned. A hydrocarbon scrubber containing activated charcoal was used to remove these hydrocarbons in the fuels being flared.

In the same manner, combustion air purchased in cylinders and of zero grade quality was also passed through activated charcoal scrubbers and tested prior to usage. Liquid fuels did not contain any detectable levels of hydrocarbon components larger than toluene. System blanks were carried out by flowing the prepurified combustion air through the flaring chamber prior to a flare test run.

Data obtained from the tests carried out in the first year of the studies indicated that a very complex mixture of hydrocarbons was being generated within the flames and that probably not all of the hydrocarbons contained in the emissions were being identified by the analytical techniques that had been initially developed. Modifications were made to the techniques between the first and second year of the laboratory studies in order to measure for a more complete range of hydrocarbons from methane to multi-ringed polycyclic hydrocarbons. The following describes the results of these tests.

5.1.1 Methane Flames

Pure methane flaring was carried out under laminar, transitional and turbulent flow conditions to evaluate the effects on emissions. The laminar flow represents as close to ideal conditions as can be accomplished with no cross-winds or turbulent effects. The transitional flame contained significant flickering from top to bottom and was more difficult to sample because of the flame movement. The turbulent flow condition resulted in a highly variable flame that was even more difficult to sample than the transitional flame. This turbulent flame was used to examine the effects of flame eddying and shearing which has been speculated as one of the main causes in reducing overall combustion efficiency.

5.1.1.1 Laminar Methane Flame

The laminar methane flame was sampled at a number of locations both above and within the visible portion of the flame. The data summarized in this section have been limited to one representative sample obtained from both above and within the flame (the complete summary of data obtained from these tests is contained in the annual report (Strosher, 1992). Overall height of this flame averaged 285 mm.

Results of the on-site chemical characterization of samples obtained from the laminar flame are illustrated in Table 1. These results indicate a very efficient flame where basically no carbon monoxide (CO), no carbon particles, and very few hydrocarbons were detected within the limits of the analyzers in samples obtained above the flame. Methane concentrations were detectable at all sampling locations above and within the flame and ranged from approximately 1.5 to 180,000 mg/m^3. Temperature measurement at these sampling locations ranged from 189° Centigrade (°C) at the highest sampling point (235 mm) above the flame to 890°C at the sampling point 112 mm into the flame. The combustion efficiency of this flame was found to be very high, averaging 99.98% and varying by only 0.03 % at all sampling points above the flame. Because of the very limited flow of fuel, repetitive sampling was carried out in sequential tests or at additional locations.

Table 1. Chemical characterization profile at two sampling points along the vertical axis of a laminar methane flame. (All values in mg/m^3 except where noted.)

Sampling points	154 mm above the flame tip	112 mm into the flame
Temp. (°C)	293	890
O_2 (%)	16.7	14.6
N_2 (%)	78.7	76.3
NO	4.2	3.7
NO_2	12.5	16.6
NO_x	16.7	20.3
CO	<10	18300
CO_2	47300	66100
Carbon	<1	240
Methane	1.49	10900
Ethylene	- -	1250
Acetylene	- -	1100
Ethane	- -	80.1
Propylene	- -	34.4
Propane	- -	36.0
Propyne	- -	57.5
Butane	- -	127
Benzene	- -	507
Toluene	- -	48.2
Pentane	- -	--
Heptane	- -	--
Other HC's	2.16	239
Combustion efficiency (%)	99.98	

Flame height - 225 mm
Flare tip - 1.5 mm
Reynolds No. (jet) - 956

Methane flow-1.27standard litres/min (sℓ/min)
Combustion air flow -13.5 sℓ/min

Reproducibility of analytical results fell within the measured variation of the analytical instruments at similar sampling locations in relation to the flame.

Relatively large concentrations of hydrocarbon compounds generated primarily through pyrolysis were detected 150 mm into the methane flame, where up to 1400 mg/m^3 of ethylene and 2360 mg/m^3 of acetylene were detected. Other hydrocarbon compounds such as ethane, propylene, propane, propyne, etc., were also found within the flame but at lower concentrations. The aromatic compounds benzene and toluene were found in concentrations exceeding 820 mg/m^3 and 55 mg/m^3 respectively 150 mm into the flame. The presence of these compounds and the concentrations at which they were found within the flame substantiated the need to determine whether any of these compounds escaped through the flame, either unburned or partially oxidized, and thus could be found in detectable amounts in emissions above the flame.

As previously noted in Table 1, on-site GC analyses revealed very little in the way of any detectable amounts of hydrocarbons other than methane and, in particular, those compounds for which the GC was specifically calibrated to. At most sampling locations above the flame, the hydrocarbons ethylene and acetylene were not detected. If they were present at all, the concentrations were below 0.01 mg or 10 μg per cubic meter of air sampled, which was the lower detection limit of the analytical procedure.

5.1.1.2 Transitional Methane Flame

The transitional methane flame examined in the combustion chamber had a visible average flame height of 323 mm. Results of the on-site chemical characterization did not show appreciable differences in hydrocarbon content of samples taken above the flame in comparison to those detected under laminar conditions (Table 2). The hydrocarbons detected within the flame were, however, somewhat different. The ethylene and acetylene concentrations were similar at comparable distances into the flame, but the content of heavier hydrocarbons such as benzene and toluene increased by up to 5 times over the amounts found in the laminar flame.

More significant differences in results from the transitional flame were noticed in the CO_2 concentrations which reached levels approximately double those detected in

Table 2. Chemical characterization profile at two sampling points along the vertical axis of a transitional flame. (All values in mg/m^3 except where noted.)

Sampling points	223 mm above the flame tip	185 mm into the flame
Temp. (°C)	219	840
O_2 (%)	16.9	6.2
N_2 (%)	77.8	79.0
NO	4.8	0.8
NO_2	12.5	30.5
NO_x	17.3	31.3
CO	<10	39600
CO_2	40900	135600
Carbon	3.3	100
Methane	5.51	20800
Ethylene	0.15	1160
Acetylene	- -	1540
Ethane	0.18	- -
Propylene	- -	33.3
Propane	- -	183
Propyne	- -	800
Butane	- -	232
Benzene	- -	2580
Toluene	- -	100
Pentane	- -	- -
Heptane	- -	- -
Other HC's	2.60	462
Combustion efficiency (%)	99.91	

Flame height - 323 mm
Flare tip - 1.5 mm
Reynolds No. (jet) - 1465

Methane flow - 1.65 sℓ/min
Combustion air flow - 18.5 sℓ/min

laminar flame conditions. These CO_2 concentrations also kept increasing well into the flame reaching peak levels at about two-thirds of the distance into the flame. At this point of sampling, oxygen levels were almost depleted at 1% or less which is in sharp contrast to the 14% levels found in comparative laminar flame samples. Oxides of nitrogen also reached higher levels (33 mg/m^3) and occurred well within the flame. Temperatures at points of sampling were comparable to laminar results, ranging from 219 to 845°C.

Combustion efficiency results as calculated from the carbon mass balance of hydrocarbons, fixed gases, and carbon particles did not reveal any significant difference from the laminar flame results when sampled above the flame. The efficiency of the transitional flame was 99.90% as compared to 99.98% for the laminar flame. Carbon particles were found at detectable levels above the flame and at higher amounts within the flame as compared to amounts collected under laminar flow conditions.

5.1.1.3 Turbulent Methane Flames

The results of the on-site chemical characterization of the turbulent methane flame are illustrated in Table 3. The results indicate a relatively efficient flame but somewhat lower in efficiency than the laminar and transitional methane flames. Carbon monoxide values under these turbulent conditions were now measurable above the flame and ranged from 175 to 375 mg/m^3. Many of the hydrocarbons detected in the flame by the on-site analyzers were also measurable above the flame, including methane, ethylene, acetylene, propylene, and propyne. These findings are definitely in contrast to those for samples obtained above the laminar and transitional methane flames where virtually no detectable amounts of either carbon monoxide or hydrocarbons were found.

The combustion efficiency results for the turbulent methane flame were relatively high at sampling points above the flame, averaging approximately 99%. These values are, however, up to 1% lower than values measured at equivalent distances above laminar (99.96%) or transitional (99.91%) methane flames. The differences are primarily due to the higher levels of carbon monoxide concentrations detected above the turbulent flame. Hydrocarbon concentrations measured above the turbulent flame (15 mg/m^3) were approximately double those of equivalent samples taken above the transitional flame (8 mg/m^3), and three times amounts found above the laminar flame (5 mg/m^3).

Table 3. Chemical characterization profile along the vertical axis of a turbulent methane flame. (All values in mg/m^3 except where otherwise noted.)

Sampling Points	199 mm above the flame tip	152 mm into the flame
Temperature (° C)	270	930
O_2 (%)	15.87	1.94
N_2 (%)	76.33	71.90
H_2	4.00	3440
NO	7.00	7.00
NO_2	4.00	2.00
NO_x	11.0	9.00
CO	175	60000
CO_2	38100	106000
Carbon	<1.00	233
Methane	8.00	33800
Ethylene	0.22	1020
Acetylene	0.44	2190
Propylene	--	34.4
Propane	0.05	408
Propyne	0.25	713
Butane	--	311
Benzene	--	2560
Heptane	--	9.16
Toluene	--	52.9
m,p - xylene	--	174
o - xylene	--	18.1
Styrene	--	10.8
Ethynyl Benzene	--	31.9
Ethynyl methyl benzene	--	599
Naphthalene	--	517
Other Hydrocarbons	7.74	2560
Combustion efficiency (%)	99.14	

Flame height - 333 mm
Flare tip - 1.5 mm

Methane flow - 2.21 sℓ /m
Combustion air flow - 31.1 sℓ /m

Reynolds No. (jet) - 1645

A large amount of hydrocarbons were detected within the turbulent methane flame as found in the laminar and transitional methane flames. Most of the hydrocarbons detected by the on-site analyzers are the direct result of the pyrolytic reactions that occur in this region of the flame, producing concentrations of hydrocarbons such as ethylene varying to maximum amounts of 1300 mg/m^3, acetylene to 2400 mg/m^3, benzene to 2600 mg/m^3 and naphthalene to 500 mg/m^3 depending on sampling location within the flame.

Additional samples taken from above and within the flame were collected on adsorbents. This sampling method enabled the detection and identification of higher molecular weight hydrocarbons as well as those present at lower quantities. These analyses were carried out on the GC/MS system as previously described. A total of 26 hydrocarbons were identified by thermal desorption methods in samples taken within the flame and 23 identified in emissions above it. The majority of the hydrocarbons were aromatic compounds, many with alkyl sidechains attached to them (Table 4). The results of these analyses were also typical for the hydrocarbons identified using the same method in the investigations of both laminar and transitional methane flames.

For samples taken within the flames, the alkyl sidechains attached to the aromatic rings identified in the analyses contained considerable unsaturation. For samples taken outside the flames these compounds were found to have evolved as the saturated analogues. Benzene, toluene, xylenes, and naphthalene were some of the most abundant hydrocarbons produced by these flames, and were also found in the emissions above them. Additionally, ethenyl and ethynyl benzene were produced in significant quantities within the flames but were found only in minor quantities above them.

Extension of these analyses to include compounds up to 7 rings such as coronene was accomplished by solvent extraction of the adsorbents. A total of 22 additional hydrocarbons were detected in samples obtained from both above and within this flame by these methods, and are listed in Table 5. Hydrocarbons, organic acids and other oxygenated hydrocarbons were detected in samples obtained from both within and above this flame. These extended analyses allowed for the identification of compounds up to the 6-ringed polycyclic aromatic hydrocarbon, benzo[ghi]perylene, being produced within the flame by the pyrolytic reactions, and 5-ringed compound, benzo[a]pyrene above it. This latter compound was found to occur at concentrations exceeding 18,000 μg/m^3

Table 4. Hydrocarbons identified in samples taken within and above a turbulent methane flame using thermal desorption methods ($\mu g/m^3$).

Sampled at 152 mm into Flame		Sampled at 199 mm above flame	
Compound	Amount	Compound	Amount
1,3-BUTADIYNE	3910	PENTANE (ACN)(DOT)	0.27
3-PENTEN-1-YNE, (Z)-	6140	HEXANE (DOT)	5.08
HEXANE (DOT)	53000	CYCLOHEXANE(DOT	0.10
1,5-HEXADIEN-3-YNE	6170	BENZENE (ACN)(DOT)	6.97
1,5-HEXADIYNE	40740	PENTANE, 3-ETHYL-	3.50
BENZENE (ACN)(DOT)	1753000	2-BUTENOIC ACID, METHYL ESTER, (Z)-	7.85
PROPANOIC ACID	3290	CYCLOHEXANE, METHYL-	0.07
BENZENE, METHYL-	385300	BENZENE, METHYL-	12.7
BENZENE, ETHYL-	13040	OCTANE (DOT)	1.05
BENZENE, 1,2-DIMETHYL-	4868	CYCLOHEXANE, 1,2-DIMETHYL-, TRANS-	0.10
BENZENE, ETHYNYL-	1083000	CYCLOHEXANE, ETHYL-	0.01
BENZENE, ETHENYL-	142100	BENZENE, ETHYL-	1.43
.ALPHA.-PINENE (ACN)	5522	BENZENE, 1,3-DIMETHYL-	8.33
BENZENE, 1-PROPYNYL-	6617	BENZENE, ETHYNYL-	0.17
BENZENE, 1,2-PROPADIENYL-	3044	BENZENE, 1,2-DIMETHYL-	1.40
BENZENE, 1-ETHENYL-2-METHYL-	1304	NONANE	1.64
BENZENE, 1-ETHYNYL-4-METHYL-	98870	BENZENE, (1-METHYLETHYL)-	0.24
1H-INDENE	2759	BENZENE, 1-ETHYL-2-METHYL-	1.62
1,3-CYCLOPENTANEDIONE, 2,2-DIMETHYL-	2728	BENZENE, 1,3,5-TRIMETHYL-	0.25
BENZENE, 1-METHYL-4-(1-PROPYNYL)-	805	BENZENE, 1-ETHYL-3-METHYL-	0.13
BENZENE, 1-BUTYNYL-	2891	BENZENE, 1,2,3-TRIMETHYL-	0.70
NAPHTHALENE (ACN)(DOT)	400800	DECANE	0.77
NAPHTHALENE, 1-METHYL-	1931	NAPHTHALENE (ACN)(DOT)	2.62
BIPHENYLENE	228960		
9H-FLUORENE	3305		
9H-FLUORENE, 9-METHYLENE-	47320		

Table 5. Hydrocarbons identified in samples taken within and above a turbulent methane flame using solvent extraction methods ($\mu g/m^3$).

Sampled at 152 mm into flame		Sampled at 199 mm above flame	
Compound	Amount	Compound	Amount
ETHANONE, 1-PHENYL-	76740	ETHANONE, 1-PHENYL-	8.02
DECANE, 5,6-DIMETHYL-	272500	DECANE, 5,6-DIMETHYL-	18.0
BENZOIC ACID (ACN)	249300	BENZOIC ACID (ACN)	30.4
1,2-PROPANEDIONE, 1-PHENYL-	20390	BENZOTHIAZOLE	1.39
BENZOIC ACID, 2-METHYLPROPYL ESTER	57520	1-BUTANONE, 1-PHENYL-	1.31
FLUORANTHENE	1378	PHTHALIC ANHYDRIDE	1.68
PYRENE	5636	BIPHENYLENE	2.03
10-UNDECENAL	8784	BENZOIC ACID, 2-METHYLPROPYL ESTER	6.72
PYRENE, 4-METHYL-	4146	9H-FLUORENE, 9-METHYLENE-	8.93
PYRENE, 2-METHYL-	12710	4H-CYCLOPENTA[DEF]PHENANTHRENE	1.62
2(3H)-FURANONE, 5-PHENYL-3-(PHENYLMETHYLENE)-	42360	CYCLOPROPANECARBOXYLIC ACID, 2,2-DIMETHYL-3-(2-METHYL-1-PROPENYL)-,	6.40
2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	1589000	PYRENE	21.4
BENZO[GHI]FLUORANTHENE	23990	11H-BENZO[A]FLUORENE	0.36
CYCLOPENTA[CD]PYRENE	11840	PYRENE, 4-METHYL-	0.45
BENZO[C]PHENANTHRENE	10990	PYRENE, 2-METHYL-	0.38
TRIPHENYLENE	13990	2(3H)-FURANONE, 5-PHENYL-3-(PHENYLMETHYLENE)-	11.0
ANDROSTANE-3,6,17-TRIONE, (5.ALPHA.)-	110300	2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	50.5
BENZENE, (1-METHYLPENTADECYL)-	12160	BENZO[GHI]FLUORANTHENE	0.53
BENZO[J]FLUORANTHENE	18600	TRIPHENYLENE	1.09
BENZO[E]PYRENE	14700	ANDROSTANE-3,6,17-TRIONE, (5.ALPHA.)-	2.02
BENZO[A]PYRENE	18080	BENZO[E]PYRENE	0.32
BENZO[GHI]PERYLENE	8961	BENZO[A]PYRENE	0.28

within the flame and at a level of 0.28 μg/m^3 in emissions above the flame. The presence of significant amounts of organic acids and other oxygenated hydrocarbons in the flame and its emissions confirms that considerable oxidation also occurred within this flame.

5.1.2 Propane Flame

Pure propane was used as a second gaseous fuel in the laboratory investigations to determine what differences, if any, would occur in relation to overall efficiency and hydrocarbon emissions. The most noticeable difference of the propane flame in relation to methane flames was its sooty nature. Results of filter samples taken showed that carbon particulate levels of 90 mg/m^3 were detected at the highest point of sampling above the flame (Table 6). These values increased as samples were taken closer to the flame and deeper into the flame where up to 1200 mg/m^3 of carbon was detected, which is approximately 3 times the maximum levels found in the turbulent methane flame. The production of oxides of nitrogen by this flame also was considerably higher than the turbulent methane flame, exceeding the upper detection limit of the analyzer of 35 mg/m^3 in samples obtained within the flame.

Hydrocarbon levels detected both within and above the propane flame were also much higher than those encountered in methane flames. Ethylene and acetylene production within this flame was about 50% higher than in methane flames and was also found at detectable levels above the flame. This propane flame produced 6 times as much benzene compared to amounts detected in the laminar methane flame and similar amounts as found in the turbulent methane flame. The average combustion efficiency of the propane flame emissions was 98.6%. Carbon particles produced by the propane flame, followed by the hydrocarbons that manage to escape unburned above the flame were the major constituents detected in the emissions.

Further examination of the hydrocarbon content of this flame and hydrocarbons that escape from it revealed similar types and concentrations of hydrocarbons that were produced in the methane flame (Table 7). Approximately twice as many hydrocarbons, however, were identified within the propane flame. These include more substituted indene

Table 6. Chemical characterization of a turbulent propane flame. (All values in mg/m^3 except where otherwise noted.)

Sampling Points	197 mm above the flame tip	187 mm into the flame
Temp. (°C)	233	783
O_2 (%)	6.4	1.3
N_2 (%)	77.8	69.6
NO	3.3	0.3
NO_2	10.2	>35
NO_x	13.5	>35
CO	<10	77200
CO_2	34800	138900
Carbon	90	1213
Methane	1.00	21100
Ethylene	0.18	1560
Acetylene	0.12	1740
Ethane	0.42	121
Propylene	0.25	1980
Propane	21.8	3660
Propyne	0.13	660
Butane	<0.01	980
Benzene	0.43	2180
Toluene	0.13	225
Pentane	7.37	351
Heptane	9.91	--
Other HC's	45.1	1260
Combustion efficiency (%)	98.30	

Flame height - 317 mm
Flare tip - 1.5 mm
Reynolds No. (jet) - 2169

Propane flow - 0.68 sℓ/min
Combustion air flow - 17.1 sℓ/min

Table 7. Hydrocarbons identified by GC/MS within and above a turbulent propane flame (μg/m^3).

Sampled at 187 mm into flame		Sampled at 197 mm above flame tip	
Compound	Amount	Compound	Amount
3-Pentene-1-YNE, (Z)-	18600	3-Pentene-1-YNE, (Z)-	3.88
1,3-Cyclohexadiene	21200	1,3-Cyclohexadiene	0.58
Benzene	1142000	Benzene	554
Bicyclo[2.2.0]Hex-1(4)-ENE	2190	Benzene, Methyl-	124
3-Hepten-1-YNE, (E)-	2950	Benzene, Ethyl-	9.88
1,6-Heptadiyne	2140	Benzene, 1,3-Dimethyl-	1.52
Benzene, Methyl-	110500	Benzene, Ethynyl-	351
Cyclopentene, 1-Ethenyl-3-Methylene-	700	Benzonitrile	165
Benzene, Ethyl-	35500	Benzene, Ethenyl-	117
Benzene, 1,3-Dimethyl-	8920	Benzene, Methoxy-	0.62
Benzene, Isocyano-	101000	Bicyclo[4.2.0]Octa-1,3,5-Triene	2.11
Benzene, Ethynyl-	61200	Benzene, Cyclopropyl-	0.48
Benzene, Ethenyl-	129000	Benzaldehyde	38.3
1,3,7-Octatrien-5-YNE	610	Benzene, 1-Propynyl-	10.5
Bicyclo[4.2.0]Octa-1,3,5-Triene	520	Benzene, 1,2-Propadienyl-	5.68
1,3,5,7-Cyclooctatetraene	990	Benzofuran	11.4
Benzene, Cyclopropyl-	3600	Decane	0.70
Benzene, 2-Propenyl-	2110	Benzene, 1-Ethenyl-2-Methyl-	0.42
Benzene, 1-Ethyl-2-Methyl-	2350	1H-Indene, 2,3-Dihydro-	0.97
Benzene, (1-Methylethyl)-	1090	Benzene, 1-Ethynyl-4-Methyl-	98.2
Benzene, 1-Propynyl-	5230	1H-Indene	4.10
Benzene, 1,2-Propadienyl-	6730	Benzene, 1,3-Diethenyl-	0.22
Benzofuran	10600	1H-Indene, 2,3-Dihydro-1-Methyl-	0.23
Benzene, 1-Ethenyl-2-Methyl-	11100	1H-Indene, 1-Methyl-	4.28
Bezene, 2-Propenyl-	2220	1H-Indene, 1-Methylene-	9.94
1H-Indene, 2,3-Dihydro-	3070	Naphthalene	147
Benzene, 1-Ethynyl-4-Methyl-	82800	Naphthalene, 2-Methyl-	0.26
1H-Indene	6100	Naphthalene, 1-Methyl-	0.56
Benzene, 1-Butynyl-	1990	Biphenylene	1.98
Benzene, 1,3-Diethenyl-	3080	Fluoranthene	1.48
Benzene, Diethenyl-	1230	Pyrene	0.97
1H-Indene, 1-Methyl-	15300		
1H-Indene, 1-Methylene-	24600		
Naphthalene	118000		
Naphthalene, 1,2-Dihydro-3-Methyl-	820		
1H-Indene, 1-Ethylidene-	6020		
Naphthalene, 2-Methyl-	15200		
Naphthalene, 1-Methyl-	8290		
1,4-Methanonaphthalene, 1,4-Dihydro	880		
1,1'-Biphenyl	3490		
Naphthalene, 2-Ethyl-	810		
Biphenylene	4270		
Naphthalene, 1-Ethyl-	610		
Naphthalene, 2-Ethenyl-	810		
Acenaphthylene	12900		
Acenaphthene	70		
9H-Fluorene	1310		
9H-Fluorene, 9-Methylene	140		
1H-Phenalene	340		
1,3,7,11-Cyclotetradecatetraene-5,9,13-Triyn	4020		
Phenanthrene	470		
Anthracene	1950		
Fluoranthene	830		
Pyrene	1410		

and naphthalene compounds along with the higher molecular weight polycyclic aromatic hydrocarbons such as fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. Hydrocarbons identified above this flame include many of the unsaturated species found to exist within, as well as a number of oxygenated hydrocarbons. Unlike the methane flame where the more saturated species seemed to prevail outside the flame, many of the unsaturated compounds were found at levels approaching that of the most abundant hydrocarbon, benzene. Ethenyl benzene (styrene) and ethynyl benzene were detected at levels of 117 and 351 $\mu g/m^3$, respectively. Lesser amounts of oxygenated hydrocarbons were found outside the flame, including compounds such as methoxy benzene, benzaldehyde and benzofuran. Some of the polycyclic aromatic hydrocarbons found in the flame have also been found to survive the flame and occur above it, such as fluoranthene and pyrene. The higher molecular weight polycyclics were not determined in the propane tests, as these were first year studies that were carried out before the extension of the analytical techniques.

5.1.3 Natural Gas Flames

Laboratory flaring of the natural gas streams were initiated primarily to obtain data on the identity of hydrocarbons that are produced and their combustion efficiency prior to any scale-up experiments carried out in proposed pilot or field studies. Natural gas, depending on its source, contains primarily methane, usually at concentrations of 90% or more, ethane at less than 10% and other hydrocarbons at lower concentrations. Experiments using natural gas were carried out in the laboratory combustion chamber system and in the open atmosphere without the combustion chamber and with and without controlled cross-winds. The following describes the results of these investigations.

5.1.3.1. Laboratory scale flaring

Natural gas was flared in the laboratory flare chamber under turbulent conditions producing a highly variable flame from top to bottom which was sampled at a number of points from within and above the visible flame. Results of the on-site chemical characterization of this flame from 2 of several locations sampled during these tests are illustrated in Table 8. These results are very similar to those obtained by flaring pure

Table 8. Chemical characterization of a turbulent natural gas flame. (All values in mg/m^3 except where otherwise noted.)

Sampling Points	234 mm above the flame tip	122 mm into the flame
Temperature (°C)	310	930
O_2 (%)	16.79	0.96
N_2 (%)	76.06	72.41
H_2	5.79	4150
NO	7.5	>12
NO_2	1.9	0
NO_x	9.4	>12
CO	11	72100
CO_2	29200	115000
Carbon	2.50	430
Methane	2.06	35500
Ethylene	0.16	1100
Acetylene	0.50	2110
Propylene	0.04	43.7
Propane	--	385
Propyne	0.13	639
Butane	--	278
Benzene	--	2740
Heptane	--	6.24
Toluene	0.28	65.1
m,p - xylene	--	1990
o - xylene	0.04	26.9
Styrene	--	12.6
Ethynyl Benzene	--	65.4
Ethynyl methyl benzene	--	2530
Naphthalene	0.43	682
Other Hydrocarbons	7.6	2030
Combustion efficiency %	99.8	

Flame height - 302 mm Natural gas flow - 2.14 sℓ /min

Flare tip - 1.5 mm Combustion air flow - 27.0 sℓ /min

Reynolds No. (jet) - 1596

methane under the same conditions. Levels of oxygen, nitrogen, hydrogen and oxides of nitrogen levels were all similar to those obtained in the methane tests. Carbon monoxide and CO_2 concentrations above the natural gas flame were somewhat lower, particularly at the highest sampling point. The sampling distance from the top of the natural gas flame, however, was 35 mm higher than that of the corresponding methane flame thereby allowing for more dilution which accounts for at least some of the lower concentrations.

Hydrocarbons produced within the natural gas flame were similar to those generated in the methane flame, both in types and concentration, at least up to the compound toluene. The xylenes, ethynyl benzene, ethynyl methyl benzene, and naphthalene were all produced in higher concentrations within the natural gas flame. The total amount of hydrocarbons produced is also significantly higher, as over 10 times more unidentified hydrocarbons were detected in the natural gas flame. Emissions of all hydrocarbons above these flames and as detected by these methods, however, are very comparable.

Combustion efficiency measurements of this flame were also comparable to those of the methane flame except at the highest sampling point above them. Once again, the comparison is difficult as the distances of sampling above the flames are not quite the same, thereby allowing for more dilution. The major reason for the higher efficiency, however, is that lower amounts of carbon monoxide were detected above the natural gas flame.

A total of 41 compounds were detected by the GC/MS system using thermal desorption techniques for a sample collected within the natural gas flame (Table 9). Acenaphthylene was the most abundant compound produced in the flame at over 1000 mg/m^3 , followed by naphthalene at 660 mg/m^3, toluene at 500 mg/m^3 , and ethynyl benzene at 250 mg/m^3. Unsaturation was also prevalent in the alkyl sidechains attached to aromatic benzene and naphthalene based compounds. There were 41 compounds also detected in the emissions above this flame, the major components of which were xylenes, toluene and straight chained aliphatic hydrocarbons. Very little unsaturation was found in alkyl sidechains attached to the aromatic hydrocarbons.

Table 9. Hydrocarbons identified by GC/MS within and above a turbulent natural gas flame using thermal desorption methods ($\mu g/m^3$).

Sampled at 122 mm into flame		Sampled at 234 mm above flame	
Compound	Amount	Compound	Amount
BENZENE (ACN)(DOT)	2,713,000	PENTANE (ACN)(DOT)	1.08
HEPTANE (DOT)	78,800	4-PENTEN-1-OL	3.39
CYCLOHEXANE, METHYL-	30,400	CYCLOHEXANE(DOT	6.12
CYCLOPENTANE, ETHYL-	2,500	BENZENE (ACN)(DOT)	7.15
BENZENE, METHYL-	494,000	PENTANE, 3-ETHYL-	4.23
CYCLOHEXANE, 1,2-DIMETHYL-, TRANS-	15,200	CYCLOPENTANE, 1,2-DIMETHYL-	3.16
CYCLOHEXANE, 1,1-DIMETHYL-	1,280	HEPTANE (DOT)	34.4
CYCLOPENTANE, 1-ETHYL-2-METHYL-, CIS-	2,600	2-BUTENOIC ACID, METHYL ESTER, (E)-	0.66
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	1,940	CYCLOHEXANE, METHYL-	7.05
OCTANE (DOT)	18,200	BENZENE, METHYL-	54.7
CYCLOHEXANE, ETHYL-	9,300	HEXANE, 2,5-DIMETHYL-	7.00
BENZENE, ETHYL-	11,600	CYCLOPENTANE, 1-ETHYL-1-METHYL-	1.81
HEPTANE, 2,3-DIMETHYL-	2,990	CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	1.17
BENZENE, 1,3-DIMETHYL-	15,300	OCTANE (DOT)	27.7
BENZENE, ETHYNYL-	244,000	CYCLOHEXANE, ETHYL-	7.99
BENZENE, ETHENYL-	52,000	HEXANE, 4-ETHYL-2-METHYL-	3.80
NONANE	6,370	3-HEPTENE, 4-ETHYL-	0.38
CYCLOHEXANE, 1-ETHYL-2-METHYL-, TRANS-	1,050	CYCLOHEXANE, 1,3,5-TRIMETHYL-	1.00
ALPHA.-PINENE (ACN)	2,180	HEPTANE, 2,3-DIMETHYL-	1.36
BENZENE, 1-ETHYNYL-4-METHYL-	26,600	BENZENE, ETHYL-	10.9
1,3-CYCLOPENTANEDIONE, 2,2-DIMETHYL-	1,830	BENZENE, 1,4-DIMETHYL-	55.6
BENZENE, 1-METHYL-4-(1-PROPYNYL)-	2,200	HEXANE, 4-ETHYL-2-METHYL-	9.91
1H-INDENE, 1-METHYLENE-	11,700	CYCLOHEXANE, 1,2,3-TRIMETHYL-, (1.ALPHA.,2.ALPHA.,3.BETA.)-	5.07
NAPHTHALENE (ACN)(DOT)	658,000	BENZENE, 1,3-DIMETHYL-	12.6
NAPHTHALENE, 2-METHYL-	32,600	NONANE	28.0
NAPHTHALENE, 1-METHYL-	370	CYCLOHEXANE, 1-ETHYL-2-METHYL-, TRANS-	1.44
1,1'-BIPHENYL	35,800	BENZENE, (1-METHYLETHYL)-	0.70
BIPHENYLENE	103,800	CYCLOHEXANE, PROPYL-	3.74
NAPHTHALENE, 2-ETHENYL-	10,200	NONANE, 3-METHYL-	8.34
ACENAPHTHYLENE	1,131,000	CYCLOPENTANE, 1-METHYL-3-(2-METHYLPROPYL)-	3.27
ACENAPHTHENE	2,140	3-HEXENE, 2,2,5,5-TETRAMETHYL-, (Z)-	0.21
CYCLOBUTA[1,2:3,4]DICYCLOOCTENE,	21,000	BENZENE, 1-ETHYL-2-METHYL-	4.95
9H-FLUORENE	75,900	NONANE, 5-METHYL-	8.79
BENZALDEHYDE, 2,4-DIHYDROXY-3,6-DIMETHYL-	15,200	BENZENE, 1,3,5-TRIMETHYL-	0.49
1,3,7,11-CYCLOTETRADECATETRAENE-5,9,13-TRIYNE	1.49	CYCLOHEXANE, (2-METHYLPROPYL)-	2.68
PHENANTHRENE	0.21	BENZENE, 1,2,3-TRIMETHYL-	1.91
9H-FLUORENE, 9-METHYLENE-	4.34	CYCLOPENTANE, 1,2-DIMETHYL-3-(1-METHYLETHYL)-	0.32
1H-INDENE, 1-(PHENYLMETHYLENE)-	0.05	DECANE	5.82
4H-CYCLOPENTA[DEF]PHENANTHRENE	0.24	CYCLOHEXANE, BUTYL-	0.37
FLUORANTHENE	0.03	BENZALDEHYDE, 4-METHYL-	0.90
PYRENE	0.05	UNDECANE	0.44

The GC/MS analyses of extracted adsorbent collected samples identified 34 compounds from a sample collected within the flame and 30 above (Table 10). Oxidation reactions were also found to occur within this flame producing organic acids, aldehydes, and ketones, some of which also were found in the emissions above it. Benzo(a)pyrene, one of the higher molecular weight polycyclics, which was found to be produced in the methane flame was also produced within the natural gas burning process at over 12,000 $\mu g/m^3$ and was found at approximately 0.4 $\mu g/m^3$ in the sample taken at the highest point above the flame.

5.1.3.2 Open atmosphere flaring

Natural gas was also flared without the combustion chamber in an open atmosphere. Analyses by on-site analyzers for this experiment determined that temperatures at equivalent sampling points above this flame were considerably lower than what occurred in the flare chamber experiment. Oxygen levels were higher and CO_2 levels were approximately one-third of the chamber levels at comparable distances from the flame demonstrating a much wider dissipation of the emissions than what occurred in the examined vertical profile of the chamber experiment.

Flaring in the open atmosphere had little effect on the types of light hydrocarbons produced in the flame or the types found in the emissions above it, in comparison to the flare chamber experiment. Any differences in the concentrations can be attributed to either the difference in dissipation and hence dilution of the compounds above the flame, or the inability to extract a sample from completely inside the much more variable flame. On the average, the hydrocarbon results were very comparable to the chamber experiments.

Examination of the combustion efficiency data, however, reveal considerable differences to that obtained in the chamber experiments. The efficiency of this flame dropped by close to 4% to levels near 96%. This reduction was caused primarily by the presence of larger amounts of unburned methane and carbon monoxide in its emissions in relation to the lower CO_2 levels detected at these sampling locations.

Thermal desorption of adsorbents and subsequent GC/MS analyses identified 25 compounds that were produced by and emitted from this natural gas flame. Benzene was the most abundant compound produced in this flame at over 2000 mg/m^3 and was one of

Table 10. Hydrocarbons identified by GC/MS within and above a turbulent natural gas flame using solvent extraction methods ($\mu g/m^3$).

Sampled at 122 mm into flame		Sampled at 234 mm above flame	
Compound	Amount	Compound	Amount
BENZALDEHYDE (ACN)(DOT)	11600	NAPHTHALENE ((ACN)(DOT)	15.1
ETHANONE, 1-PHENYL-	17990	NAPHTHALENE, 2-METHYL-	0.18
BENZOIC ACID (ACN)	70820	ACENAPHTHYLENE	1.44
1-BUTANONE, 1-PHENYL-	2273	1H-PHENALENE	0.20
BENZOIC ACID, 2-METHYLPROPYL ESTER	5305	9H-FLUORENE	0.98
1H-PHENALENE	4560	9H-FLUORENE, 9-METHYLENE-	1.80
BENZOPHENONE	6898	ETHANONE, 1-PHENYL-	3.15
ANTHRACENE	3704	BENZOIC ACID (ACN)	19.7
ETHANEDIONE, DIPHENYL-	19110	2-PROPENAL, 3-PHENYL-	0.47
1H-PHENALEN-1-ONE	25110	1-BUTANONE, 1-PHENYL-	0.61
4H-CYCLOPENTA[DEF]PHENANTHRENE	7683	NAPHTHALENE, 1-METHYL-	0.61
HEXADECANOIC ACID	22100	1,1'-BIPHENYL	0.44
[1,1'-BIPHENYL]-4,4'-DICARBONITRILE	5264	BENZOIC ACID, 2-METHYLPROPYL ESTER	1.26
2-BUTENE-1,4-DIONE, 1,4-DIPHENYL-	30730	1,3,7,11-CYCLOTETRADECATETRAENE-5,9,13-TRIYNE	0.83
11H-BENZO[A]FLUORENE	4344	BENZO[C]CINNOLINE	1.23
[1,1':3',1"-TERPHENYL]-4'-OL	5175	ANTHRACENE	2.60
11H-BENZO[B]FLUORENE	5853	4H-CYCLOPENTA[DEF]PHENANTHRENE	1.61
PYRENE, 4-METHYL-	8585	FLUORANTHENE	2.91
PYRENE, 2-METHYL-	7119	PYRENE	0.89
2(3H)-FURANONE, 5-PHENYL-3-PHENYLMETHYLENE	24310	11H-BENZO[A]FLUORENE	0.39
2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	925900	2(3H)-FURANONE, 5-PHENYL-3-(PHENYLMETHYLENE)-	3.05
BENZO[GHI]FLUORANTHENE	71580	2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	40.5
CYCLOPENTA[CD]PYRENE	30960	BENZO[GHI]FLUORANTHENE	0.03
BENZO[C]PHENANTHRENE	2319	TRIPHENYLENE	0.89
TRIPHENYLENE	18560	ANDROSTANE-3,6,17-TRIONE, (5.ALPHA.)-	1.71
ANDROSTANE-3,6,17-TRIONE, (5.ALPHA.)-	7508	4H-PYRAN-4-ONE, 2,6-DIPHENYL-	1.50
4H-PYRAN-4-ONE, 2,6-DIPHENYL-	12520	BENZO[J]FLUORANTHENE	1.06
PHENOL, 2-[[2-(BENZOYLOXY)PHENYL]METHYL]-	6843	BENZO[K]FLUORANTHENE	0.32
BENZO[J]FLUORANTHENE	10550	BENZO[E]PYRENE	0.18
BENZO[K]FLUORANTHENE	1925	BENZO[A]PYRENE	0.39
BENZO[E]PYRENE	1333		
BENZO[A]PYRENE	12530		
INDENO[1,2,3-CD]PYRENE	5456		
BENZO[GHI]PERYLENE	24780		

the most abundant emitted from it at over 50 μg/m^3. As in the analyses of pure methane flames and natural gas flames in flare chamber studies, unsaturation in the alkyl sidechains attached to the aromatic rings was predominant in hydrocarbons produced within the natural gas flame while their saturated analogues predominated in the emissions.

Expanding this hydrocarbon analyses with the extraction procedure extended the ability to identify hydrocarbons produced in this flame to the 6-ringed benzo[ghi]perylene molecule within the flame and the 5-ringed benzo[a]pyrene compounds in emissions above it. Benzo[a]pyrene was also produced in this natural gas flame and was identified in the emissions at approximately 3 times the concentration found above the pure methane flame and more than twice that found in emissions above the flame in the natural gas flare chamber experiment.

5.1.3.3 Flaring in cross-winds

Natural gas flaring was also examined in a cross-wind experiment. Sampling of this flame within the major part of the plume was difficult. Standard gas analyses and temperature measurements were carried out at various positions within this plume to optimize its positioning. Results of the analyses carried out with the on-site analyzers at these optimized locations revealed that the temperature dropped more rapidly at comparable distances examined in the previous experiment. Carbon dioxide levels measured above the flame were once again lower indicating considerable dilution of the emissions. The CO_2 levels within the flame were considerably higher indicating that the effects of the cross-winds were creating more complete combustion even inside the flame boundary. Light hydrocarbons, however, including ethylene, acetylene, benzene, and naphthalene were still being produced in significant quantities and were also found in the emissions beyond the flame tip.

Combustion efficiency measurements indicated a relatively effective burning of this flame, reaching close to 99.4% at the farthest sampling location from the flame tip. Measurements made near the flame tip and within the flame are approximately comparable to those obtained in the lab scale chamber experiments.

Hydrocarbons identified by the GC/MS system on thermally desorbed samples collected on adsorbent tubes revealed a total of 54 compounds identified as being produced within the flame including the major components of benzene, ethynyl benzene, naphthalene, acenaphthylene, toluene, and ethenyl benzene. There were 28 identified compounds in the emissions collected 115 mm beyond the flame tip. The levels at which these compounds were found in the emissions was relatively high considering the very high air flow passing it and the much higher dilution that would be expected. The concentrations were a minimum of 3 to 4 times higher than those found in all flaring experiments of either natural gas or methane without consideration of any dilution.

Extension of the hydrocarbon analyses as provided by the extraction procedure revealed a total of 39 identified compounds produced in the flare and 47 that were emitted from it. A large number of these hydrocarbons were oxygenated and included organic acids and some ketones, particularly in the emissions from this flame. Polycyclic aromatic hydrocarbons were found both in samples collected within the flame and above it.

5.1.4 Liquid Fuel Flaring

Pure liquid fuels were examined in the laboratory flare system solely for the purpose of determining the types of compounds that can be produced by the burning of various liquid fuels in a flare system. This information was required for a better understanding of the subsequent examination of co-flowing gas/liquid fuel mixtures that commonly occurs in industrial flaring operations. The liquid fuels were injected under pressure through a much smaller diameter tip (0.1 mm) to produce a fuel stream that would attempt to burn the majority of the fuel. Four different pure liquid fuels were examined in these tests, the results of which follow.

5.1.4.1 Pentane Flames

The analyses of emissions from the pentane flame as provided by the on-site analyzers revealed that very high levels of hydrocarbons can escape from this flame and are found at all sampled locations above it. Pentane itself was found at concentrations exceeding 5 grams per cubic metre of air and was the single largest component in the emissions. Produced hydrocarbons such as ethylene at 2500 mg/m^3 and propylene at 4800 mg/m^3 as found within the flame were found at concentrations of 20 and 10 mg/m^3, respectively, above the flame. These concentrations are much larger than those found in emissions above the much cleaner burning gaseous flames.

Hydrocarbons as detected and identified in the GC/MS analyses included ethynyl benzene which was the most abundant compound created within the flame at over 174 mg/m^3 (Table 11). It was also one of the most abundant compounds detected in emissions above the flame at approximately 2 mg/m^3. Much like the gaseous flames, unsaturated side chains connected to the benzene ring are abundantly produced within the flame, but unlike the types of compounds found in emissions above the gaseous flames, many of the unsaturated species continued to exist above the pentane flame.

5.1.4.2 Heptane Flames

In examining the emissions from flaring heptane in the lab flare chamber, the most abundant hydrocarbon detected above the flame was once again the unburned fuel itself at up to 200 mg/m^3. Methane was the most abundant hydrocarbon produced within the flame, followed by benzene. Both ethylene and propylene were found to be produced within this flame at similar amounts produced within the pentane flame. Above the flame, however, these compounds were detected at only 5 % of the amounts detected above the pentane flame.

Although more of the original fuel was burned in this flame in comparison to what occurred in the pentane flame, considerably more hydrocarbon compounds were produced through pyrolysis within the heptane flame. Naphthalene was the most abundant compound produced in this flame. It was detected at levels near 11 g/m^3 (Table 12). Other major hydrocarbons produced by pyrolysis in this flame included toluene, styrene, ethynyl-methyl benzene, ethynyl benzene, and benzene. As in the methane flames, very few of the unsaturated species of hydrocarbons produced within the flame managed to escape at detectable levels beyond the flame. The majority of the substituted benzene and naphthalene compounds identified above the flame had saturated aliphatic hydrocarbon side chains attached to them. Heptane was also the most abundant compound detected above the flame followed by two oxygenated heptanedione isomers, acenaphthylene, toluene, and naphthalene. This was opposite to what was found above the pentane flame.

Table 11. Hydrocarbons identified by GC/MS within and above a laminar pentane flame using thermal desorption methods ($\mu g/m^3$).

Sampled at 92 mm into flame	
Compound	Amount
Pentane	7390
2-Pentene, (E)-	3720
Benzene	97100
Heptane	9680
Benzene, Methyl-	55900
Benzene, Ethyl-	1420
Benzene, 1,3-Dimethyl-	971
Benzene, Ethynyl-	174300
Benzene, Ethenyl-	71070
Benzaldehyde	1560
Benzene, 1-Propynyl-	1470
Benzene, 1,2-Propadienyl-	2220
Benzene, 1-Ethenyl-2-Methyl-	1260
Benzene, 2-Propenyl-	1610
Benzene, Cyclopropyl-	97
1H-Indene, 2,3-Dihydro-	178
Benzene, 1-Ethynyl-4-Methyl-	21500
1H-Indene	20470
Napthalene	19800
Napthalene, 2-methyl-	3210
Naphthalene, 1-Methyl-	32
1,1'-Biphenyl	1420
Biphenylene	2100
Naphthalene, 2-Ethenyl-	242
Acenaphthylene	9840
9H-Fluorene	68
9H-Fluoren-9-One	2440
Anthracene	13400
Naphthalene, 1-Phenyl-	417
4H-Cyclopenta[DEF]Phenanthrene	402

Sampled at 98 mm above flame tip	
Compound	Amount
Pentane	723
2-Pentene, (E)-	301
Furan, 2-Methyl-	126
Benzene	595
Hexane	567
Heptane	303
Benzene, Methyl-	2259
Furan, Tetrahydro-2,4-Dimethyl-, Cis-	1390
Benzene, Ethyl-	737
Benzene, 1,3-Dimethyl-	202
Benzene, Ethynyl-	2020
Benzene, Ethenyl-	1000
Benzene, (1-Methylethyl)-	130
Benzaldehyde	260
3-Penten-1-YNE, (Z)-	61
Benzene, 1,2-Propadienyl-	37
Benzene, 1,2,3-Trimethyl-	51
Benzene, 1-Ethynyl-4-Methyl-	85
1H-Indene	397
Benzene, 1-Butynyl-	34
Naphthalene	2710
Naphthalene, 2-Methyl-	96
Naphthalene, 1-Methyl-	83
1,1'-Biphenyl	65
Anthracene	27

Table 12. Hydrocarbons identified by GC/MS within and above a laminar heptane flame using thermal desorption methods ($\mu g/m^3$).

Sampled at 159 mm into flame		Sampled at 220 mm above flame tip	
Compound	Amount	Compound	Amount
3-Pentene-1-YNE, (Z)-	465390	Hexane	402
Benzene	3211500	Benzene	550
Heptane	21695000	Heptane	413500
Cyclopentane, 1,3-Dimethyl-, Trans-	287800	Benzene, Methyl-	15650
Benzene, Methyl-	5688900	Cyclobutene, 1,2,3,4-Tetramethyl-,CIS-	9400
Benzene, Ethyl-	1078900	Octane	4110
Benzene, 1,3-Dimethyl-	250700	Benzene, Ethyl-	46100
Benzene, Ethynyl-	3519500	3-Heptene, 4-Methyl-	23900
Benzene, Ethenyl-	5510500	Benzene, (1-Methylethyl)-	7920
Benzene, 2-Propenyl-	97400	2,4-Heptanedione	58400
Benzene, Propyl-	41400	2H-Pyran-2-One, 6-Ethyltetra-hydro-	17100
Benzene, 1-Ethyl-2-Methyl-	72500	Benzene, 1,3,5-Trimethyl-	5200
Benzene, 1-Propynyl-	246900	Decane	1550
Benzene, 1-Ethenyl-2-Methyl-	675800	Benzene, 1,2,3-Trimethyl-	10820
1H-Indene, 2,3-Dihydro-	190300	3,5-Heptanedione	121200
Benzene, 1-Ethynyl-4-Methyl-	4720700	2-Heptanone, 6-Methyl-	12380
1H-Indene	413700	Naphthalene	36990
Ethanone, 1-Phenyl-	607500	Naphthalene, 2-Methyl-	149
Benzene, (1-Methyl-2-Cyclopropen-1-YL)-	88300	Naphthalene, 1-Methyl-	110
Benzene, 2-Ethenyl-1,4-Dimethyl-	79600	1,1'-Biphenyl	5180
Naphthalene, 1,2-Dihydro-	414200	Biphenylene	11570
Benzene, 1,3-Diethenyl-	199700	Naphthalene, 2-Ethenyl-	1310
1H-Indene, 1-Methyl-	1147900	Acenaphthylene	74680
1H-Indene, 1-Methylene-	1676600	1H-Phenalene	1060
Naphthalene	10900000	9H-Fluoren-9-One	3530
1H-Indene, 1-Ethylidene-	107900	Naphthalene, 1-Phenyl-	827
1,4-Methanonaphthalene, 1,4-Dihydro-	205200	Phenanthrene, 2-methyl-	445
Naphthalene, 2-Methyl-	1282500	4H-Cyclopenta[DEF]-Phenanthrene	11890
Naphthalene, 1-Methyl-	896400		
1,1'-Biphenyl	330100		
Naphthalene, 2-Ethyl-	21700		
Naphthalene, 2-Ethenyl-	403000		
Acenaphthylene	3130900		
Acenaphthene	131300		
1,1'-Biphenyl, 3-Methyl-	5680		
1H-Phenalene	104500		
9H-Fluorene	300500		
Anthracene	195200		
4H-Cyclopenta[DEF]-Phenanthrene	109500		
Naphthalene, 2-Phenyl-	10100		
Fluoranthene	220200		
Pyrene	359900		

5.1.4.3 Cyclohexane Flames

In sharp contrast to the aliphatic liquid hydrocarbon flames examined (pentane and heptane), cyclohexane burned with a very sooty flame. Filter samples collected in emissions above this flame detected 200 to 300 mg/m^3 of particulate carbon. Another major difference noted in the emissions from this flame compared to the pentane and heptane flames was the high levels of carbon monoxide found here. The CO levels ranged from 146 mg/m^3 at the highest sampling location above the flame to almost 700 mg/m^3 just above it. Both the unburned cyclohexane and the generated hydrocarbon benzene were the most abundant hydrocarbons found both within and above this flame.

Further examination of the hydrocarbon data as acquired from the samples collected on adsorbents and identified by GC/MS indicated that naphthalene was the most abundantly produced compound found in this fraction followed by the unsaturated hydrocarbon benzene derivatives, such as styrene, ethynyl benzene and ethynyl-methyl benzene (Table 13). Benzene and toluene were also produced at similar concentrations. Above the flame, unburned cyclohexane was the most abundant compound detected. A number of the unsaturated hydrocarbons that were produced within this flame were also detected above, much in the same manner as found when pentane was flared and opposite to the results derived from the heptane flare testing.

5.1.4.4 Toluene Flames

The toluene flame was by far the poorest quality of the liquid hydrocarbon flames tested. It also produced the highest levels of carbon particles. Between 4 to 6 g/m^3 of particulate carbon was collected in emissions above the flame while 13 to 23 g/m^3 were collected from sampling within the flame. Carbon monoxide levels were also much higher than those found from flaring any other liquid fuel, ranging between 1.5 to 2.6 g/m^3. A large amount of unburned toluene was found in the emissions above the flame while benzene was produced by pyrolysis in the highest quantities within it. Acetylene was the next highest in abundance, both within and above the flame.

Table 13. Hydrocarbons identified by GC/MS within and above a turbulent cyclohexane flame using thermal desorption methods ($\mu g/m^3$).

Sampled at 110 mm into flame		Sampled at 80 mm above flame tip	
Compound	Amount	Compound	Amount
3-Pentene-1-YNE, (Z)-	3060	Cyclopentane, 1-Methyl-	106
1,4-Pentadiene, 3-Methyl-	5680	Benzene	775
Benzene	522000	Cyclohexane	6770
Cyclohexane	2815000	Cyclohexene	6340
Cyclohexene	397000	Benzene, Methyl-	385
Benzene, Methyl-	522000	1-Heptene	165
Benzene, Ethyl-	64400	7-Oxabicylo[2.2.1]Heptane	1550
Benzene, 1,3-Dimethyl-	57900	Benzene, Ethyl-	32
Benzene, Ethynyl-	586000	Benzene, Ethynyl-	1010
Benzene, Ethenyl-	716000	Benzene, Ethenyl-	560
1,3,5,7-Cyclooctateraene	1450	2-Butenal, 2-Ethenyl-	1040
Benzene, 2-Propenyl-	17600	Cyclohexane, Methyl-	33
Benzaldehyde	14600	2-Cyclohexen-1-Ol	295
Benzene, 1-Propynyl-	40400	Cyclohexene, 3-Methyl-	189
Benzene, 1,2-Propadienyl-	17500	2,4-Hexadienal, (E,E)-	71
Benzene, Ethenylmethyl-	143000	Benzaldehyde	78
Benzene, 1-Ethenyl-2-Methyl-	24000	Benzofuran	173
1H-Indene, 2,3-Dihydro-	11900	Phenol	605
Benzene, 1-Ethynyl-4-Methyl-	892000	Benzene, (1-Methylethyl)-	42
1H-Indene	22100	1H-Indene, 1-Methyl-	20
Benzene, 1-Butynyl-	19600	Naphthalene, 1,2-Dihydro-	75
Naphthalene, 1,2-Dihydro-	3220	Naphthalene	1270
1H-Indene, 1-Methyl-	43700	Naphthalene, 2-Methyl-	21
1H-Indene, 1-Methylene-	103000	Naphthalene, 1-Methyl-	19
Naphthalene	1240000	1,1'-Biphenyl	15
Naphthalene, 2-Methyl-	15600	Naphthalene, 2-Ethenyl-	10
Naphthalene, 1-Methyl-	67600	Acenaphthylene	288
1,1'-Biphenyl	74200	Phenol, 2,6-Bis(1,1-Dimethylethyl)-4-Methyl-	30
Biphenylene	94200	3-Heptanone, 2-Methyl-	10
Naphthalene, 2-Ethenyl-	22500	9H-Fluorene	11
Acenaphthylene	322000	1H-Phenalene	51
Acenaphthene	6190	Anthracene	8
9H-Fluorene	5480		
1H-Phenalene	37700		
Phenanthrene	15000		
9H-Fluoren-9-One	19200		
Anthracene	407000		
Naphthalene, 1-Phenyl-	10200		
Phenanthrene, 2-Methyl-	2880		
4H-Cyclopenta[DEF]Phenanthrene	94100		
Naphthalene, 2-Phenyl-	2380		
Fluoranthene	8830		
Pyrene	4110		

A large number of hydrocarbons were identified in samples from both within and above this flame by the GC/MS system (Table 14). Many of the substituted benzene compounds, particularly the unsaturated variety so often found within other flames, were also produced within this flame. These hydrocarbons also managed to survive at significant quantities beyond the flame. Additionally, many oxygenated hydrocarbons were produced in this flame, including phenol and some alkylated phenol compounds. These phenolic compounds were also detected in substantial quantities above this flame. Polycyclic aromatics were found to be produced in much higher amounts in this flame than any of the other flames examined. Of the compounds produced by this flame, benzene and naphthalene were found in the greatest concentrations above the flame.

5.1.5 Co-flowing Gaseous/Liquid Hydrocarbon Flames

One of the primary objectives of the flare emissions study was to examine the effects of co-flowing gaseous/liquid streams on the overall efficiency of combustion of these flames and to characterize the emissions that may be created. The results obtained in the previous experiments with pure gaseous and pure liquid fuels was an important step in determining the individual contributions of each fuel. The introduction of liquid fuel to the laboratory flare system similar to that which might occur downstream of an industrial knock-out drum was accomplished by use of the fuel evaporator system using pure heptane to produce combined fuel streams containing 3 different levels of this liquid fuel in methane.

The results of these tests showed that adding 15% heptane content to the methane fuel had an effect of reducing the combustion efficiency of the flame by over 2% to 97.8%, from what occurs when burning pure methane (99.9%). When the heptane content was increased to 23%, the efficiency of the resultant flame to combust the methane/heptane fuel along with the hydrocarbons produced by the pyrolytic reactions within the flame was reduced a further 5% to approximately 92.7% (Table 15). When the heptane content was increased to 32%, the efficiency dropped to 81.4%.

Table 14. Hydrocarbons identified by GC/MS from within and above a turbulent toluene flame using thermal desorption methods (μg/m^3).

Sampled at 110 mm into flame		Sampled at 80 mm above flame tip	
Compound	Amount	Compound	Amount
3-Pentene-1-YNE, (Z)-	5020	3-Pentene-1-YNE, (Z)-	70
Benzene	3890000	1,5-Hexadiyne	23000
Benzene, Methyl-	12500000	Benzene	160000
Benzene, Ethyl-	827000	1,3,5-Cycloheptatriene	27900
Benzene, 1,3-Dimethyl-	353000	Benzene, Methyl-	1324000
Benzene, Ethynyl-	997000	Benzene, Ethyl-	39800
Benzene, Ethenyl-	1250000	Benzene, 1,3-Dimethyl-	13200
1,3,5,7-Cyclooctatetraene	9010	Benzene, Ethynyl-	39400
Benzene, 2-Propenyl-	14000	Benzene, Ethenyl-	50800
Benzaldehyde	389000	Benzene, Methoxy-	2130
Benzene, 1-Propynyl-	93300	1,3,5,7-Cyclooctatetraene	2210
Benzene, 1,2-Propadienyl-	201000	Benzene, 2-Propenyl-	710
Phenol	96800	Benzaldehyde	19500
Benzene, 1-Ethenyl-3-Methyl-	104000	Benzofuran	652
Benzene, 2-Propenyl-	12900	Phenol	92800
Benzene, 1-Ethynyl-4-Methyl-	2960000	Benzene, 1-Propynyl-	103000
1H-Indene	18900	Benzaldehyde, 2-Hydroxy-	32000
Phenol, 2-Methyl-	21500	Phenol, 2-Methyl-	88000
Benzene, 1-Butynyl-	20100	Phenol, 3-Methyl-	66100
Phenol, 4-Methyl-	3960	1H-Indene, 1-Methyl-	16600
1H-Indene, 1-Methylene-	5450	1H-Indene, 1-Methylene-	13200
1H-Indene, 1-Methyl-	109000	Phenol, 2,6-Dimethyl-	1100
Naphthalene	1483000	Naphthalene	124000
Naphthalene, 2-Methyl-	97100	2-Propenal, 3-Phenyl-	3180
Naphthalene, 1-Methyl-	1220	1H-Inden-1-One, 2,3-Dihydro-	5220
1,1'-Biphenyl	235000	Naphthalene, 2-Methyl-	18300
1,1'-Biphenyl, 2-Methyl-	29300	Naphthalene, 1-Methyl-	13300
Biphenylene	28500	1,4-Methanonaphthalene, 1,4-Dihydro-	750
Benzene, 1,1'-Methylenebis-	25100	1H-Indene, 1-Ethylidene-	1180
Acenephthylene	246000	1,1'-Biphenyl	12400
1,1'-Biphenyl, 3-Methyl-	27600	Biphenylene	10300
1,1'-Biphenyl, 4-Methyl	16300	Naphthalene, 2-Ethenyl-	1390
Benzene, 1,1'-(1,2-Ethanediyl)Bis-	138000	1,2'-Biphenyl, 2-Methyl-	3000
Benzene, 1-Methyl-4-(Phenylmethyl)-	10300	Acenaphthylene	3380
1H-Phenalene	2430	Benzene, 1,1'-Methylenebis-	2070
9H-Fluorene	146000	Benzene, 1,1'-(1,2-Ethanediyl)Bis-	30700
1,1'-Biphenyl, 3,3'-Dimethyl-	20600	1H-Phenalene	1520
Phenanthrene	2660	9H-Fluorene	19300
Benzene, 1,1'-Ethenylidenebis-	31100	1,1'-Biphenyl, 3,3'-Dimethyl-	3390
Anthracene	7450	Benzene, 1,1'-Ethenylidenebis-	398
9H-Fluoren-9-One	19700	Anthracene	747
1H-Indene, 1-Phenyl-	8530	9H-Fluorene, 9-Methylene-	180
9H-Fluorene, 9-Methylene-	360000	9H-Fluoren-9-One	145
Naphthalene, 1-Phenyl-	21100		
1H-Indene, 2-Phenyl	12700		
4H-Cyclopenta[DEF]Phenanthrene	54600		
Naphthalene, 2-Phenyl-	13700		
Pyrene	5260		

Table 15. Chemical characterization of emissions above a methane flame containing 15, 23, and 32% heptane vapour. (All values in mg/m^3 except where otherwise noted.)

Percentage of heptane in methane fuel stream	15	23	32
Temperature (^{0}C)	390	268	275
O_2 (%)	14.87	17.00	16.45
N_2 (%)	77.19	78.21	76.27
H_2	0.30	0.57	0.83
NO	8.74	3.75	2.50
NO_2	1.92	0.96	5.75
NO_x	10.7	4.71	8.24
CO	71.1	30.3	55.9
CO_2	59900	41000	44500
Carbon	65.0	60.0	60.0
Methane	1.20	1.73	48.0
Ethylene	2.34	1.64	8.30
Acetylene	0.19	0.54	0.52
Propylene	0.87	0.33	2.27
Propane	--	--	--
Propyne	--	0.13	--
Butane	--	--	0.60
Benzene	--	1.01	1.59
Heptane	291	820	2540
Toluene	--	0.46	0.19
m,p - xylene	--	--	--
o - xylene	1.59	0.13	--
Styrene	--	--	0.52
Ethynyl Benzene	--	--	--
Ethynyl methyl benzene	--	16.4	44.9
Naphthalene	--	75.1	128
Other Hydrocarbons	28.2	29.7	411
Combustion efficiency (%)	97.8	92.7	81.4

The addition of increasing amounts of heptane to the pure methane stream appeared to impair the ability of the flames to correspondingly burn all the hydrocarbon fuel fed to the flare as well as the higher amounts of hydrocarbons that are subsequently produced within these flames. Unburned heptane escaping from these flames increased from 300 mg/m^3 at the lowest level of heptane in methane tested to 820 mg/m^3 in the 23% heptane test, and to 2540 mg/m^3 while burning 32% heptane. Corresponding unburned methane levels measured above these flames increased from 1.3 to 2.7 and 48 mg/m^3. respectively.

Comparison of the hydrocarbons produced by pyrolysis within these flames and the amounts which escape in their emissions is best illustrated with the compounds ethynyl methyl benzene and naphthalene. In the 15% heptane flare test, there were no detectable amounts of these compounds in the emissions as determined by the on-site analyzers. By increasing the heptane level in the fuel flow to 23%, the substituted benzene and naphthalene concentrations found in the emissions from this flame were measured at 16.4 and 75.1 mg/m^3, respectively. When the amount of heptane was increased to 32%, these levels respectively increased to 44.9 and 128 mg/m^3 in the resulting emissions. The amounts of the heavier hydrocarbon compounds detected in these emissions will be conservative as these compounds readily attach to co-produced carbon particles that are filtered out prior to being sampled by the on-site analyzers.

5.2 Pilot Scale Studies

Phase 2 of the overall study was carried out on a small pilot scale flare in the open atmosphere. The purpose of Phase 2 was not only to address the previous findings, but also to address the problems of sampling and analytical procedures that would be encountered in characterizing larger flares. Fuel flow to this pilot flare was approximately 10 times the amount used in laboratory flare testing. Preliminary testing to help develop sampling systems such as the multi-probes and hood samplers was carried out using co-flowing methane with approximately 20% heptane under as close to ideal conditions as possible. Further testing of the developed systems was then carried out using natural gas and co-flowing natural gas with condensate obtained from a nearby gas plant.

Considerable effort was made to find the best location in relation to the length of the flame, and its centre line that would provide the emissions minimally diluted by the surrounding atmosphere, yet beyond the combustion zone. Identification of this sampling zone was achieved by exhaustive testing of emissions at varying distances from the flame tip, and with the aid of infra-red thermography. A continuous filming camera fitted with infra-red detection was used to examine temperature profiles surrounding the flame and to determine the extent of the combustion zone beyond the normal flame tip area. The results of the tests carried out on natural gas and co-flowing natural gas with a condensate stream are presented in the following section.

5.2.1 Natural Gas Flaring

Extensive flare testing using natural gas as fuel was carried out in the previous laboratory studies, under ideal conditions in a flare chamber, in controlled open atmosphere setting, and under simulated cross-wind conditions. The tests carried out in this second phase by comparison, were performed under open atmosphere conditions with calm winds. The following describes the results of these investigations.

5.2.1.1 Emission characterization

Natural gas flaring in the pilot scale flare system was carried out under turbulent conditions. This produced a highly variable flame throughout, with many eddies and pockets of burning gas that evolved from the upper region of the flame. Sampling was carried out using both the multi-probe system as well as a sampling hood covering a similar area of emissions as the probes.

The results of on-site chemical characterization of emissions collected 500 mm above this flame are contained in Table 16. Examination of the CO_2 data obtained by probe sampling indicates a relatively narrow zone of high emissions that are marginally undiluted by the surrounding air. It should be noted that these samples were collected simultaneously

Table 16. Chemical characterization of emissions collected 500 mm above a turbulent natural gas flame. (All values in mg/m^3 except where otherwise noted.)

	Sample Type					
	Probes					Hood (dia mm)
Distance from vertical centre of flame (mm)	150	75	0	75	150	300
Temperature (Celsius)	81	102	162	141	96	155
O_2 (%)	20.1	19.7	18.0	19.0	20.1	18.8
N_2 (%)	77.3	76.7	75.9	75.5	76.4	77.1
H_2	13	15	33	21	14	30
CO	--	--	13	--	--	8
CO_2	1760	2470	21300	11800	2480	17700
Carbon	0	1	5	3	0	6
Methane	5.1	6.7	16.1	10.2	6.7	18.2
Ethylene	0.1	0.1	0.5	0.2	0.1	0.3
Acetylene	0.4	0.3	1.9	1.1	0.5	1.1
Benzene	2	4	9	7	3	8
Toluene	1	1	10	8	0.9	9
Xylenes	0.5	0.6	10	3	0.3	7
Styrene	0.5	0.7	8	3	0.6	6
Ethynyl Benzene	0.1	0.2	2	1	0.2	2
Naphthalene	1	1	17	11	2	11
Other Hydrocarbons	6	5	64	43	8	39
Combustion Efficiency (%)	97.3	97.6	97.9	97.8	97.5	98.2

and over a short period of time (approximately 30 seconds) and the results do not reflect overall variability of the turbulence of this flame. The samples, collected in Tedlar bags and analyzed soon after, are considered to more closely reflect instantaneous emissions.

Concentrations of light gases in these emissions, such as methane, ethylene and acetylene were comparable to the amounts found in laboratory studies. The concentrations of larger molecular weight hydrocarbons including benzene, toluene and xylenes, however, were considerably higher. Concentrations of these hydrocarbons were found to be from 10 to 100 times higher than those from comparable tests carried out in the laboratory scale flare tests. The occurrence of these hydrocarbons were the primary reason for the lower combustion efficiency measurements at these locations of approximately 97 to 98%.

Emissions from this flame were also collected by use of a 300 mm diameter stainless steel hood which covered the same radial distance from the vertical centre of the flame as the probe system did. Results from this sample, collected over the same time frame as the probe system, closely approximated those obtained from the centre probe. It appears that the funnel shape of the hood sampler and the sampling rate drawn through it allowed for more preferential flow of the centre stream without much mixing of the outer areas of the emissions. Combustion efficiency measurements, based on the overall carbon balance in the emissions varied by approximately 1% throughout both probe and hood sampling.

5.2.1.2. Volatile hydrocarbons

Integrated sampling was additionally carried out through both the probe and hood sampling systems. These samples were collected at a very much slower rate for a period of 1 hour. Results from these analyses therefore reflect an average picture of the overall emissions that are given off from the flaring process at the different locations above the flame.

There were 65 compounds most commonly identified in samples simultaneously collected on adsorbents and analyzed by GC/MS using the thermal desorption technique (Table 17). Benzene, toluene, xylenes and naphthalene were the most abundant hydrocarbons identified in these emissions ranging from approximately 10 to 20 mg/m^3 in samples from the centre probe and hood samplers. Samples obtained from the outer

Table 17. Hydrocarbons identified above a natural gas flame from probe and hood samplers, thermal methods (mg/m^3).

Compound	Probes (distance from vertical centre mm)					Hood (dia. mm)
	150	75	0	75	150	300
PENTANE (ACN)(DOT)	0.14	0.16	0.23	0.14	0.13	0.44
3-PENTEN-1-YNE, (Z)-	0.22	0.63	1.03	0.54	0.24	1.22
HEXANE (DOT)	0.20	0.56	1.27	0.52	0.12	1.88
CYCLOHEXANE(DOT	0.15	0.67	1.11	0.84	0.17	1.65
BENZENE (ACN)(DOT)	2.11	3.60	11.93	3.46	2.38	9.21
PENTANE, 3,3-DIMETHYL-	0.02	0.08	0.27	0.13	0.04	0.31
HEXANE, 3-METHYL-	0.03	0.15	0.30	0.16	0.03	0.55
CYCLOPENTANE, 1,2-DIMETHYL-	0.01	0.12	0.26	0.13	0.05	0.38
HEPTANE (DOT)	0.18	0.77	1.45	0.95	0.27	1.57
CYCLOHEXANE, METHYL-	0.05	0.14	0.63	0.29	0.07	1.05
BENZENE, METHYL-	1.44	3.25	12.82	3.10	1.47	13.73
1-HEXENE, 2,5-DIMETHYL-	1.17	1.67	3.00	2.07	1.36	3.38
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	0.52	0.85	1.72	0.98	0.71	1.55
OCTANE (DOT)	1.97	2.66	4.38	3.69	1.59	7.39
HEXANE, 3-ETHYL-	0.17	0.69	0.91	0.82	0.33	1.01
HEPTANE, 3,4-DIMETHYL-	0.59	1.66	2.55	1.49	1.53	2.41
CYCLOHEXANE, ETHYL-	1.96	2.94	3.56	2.57	1.30	3.67
CYCLOHEXANE, 1,2,4-TRIMETHYL-	0.57	0.56	0.85	0.63	0.56	1.25
BENZENE, ETHYL-	2.84	3.83	6.45	4.47	2.19	5.10
CYCLOPENTENE, 1-ETHENYL-3-METHYLENE-	3.19	5.16	9.49	6.72	5.56	13.63
2H-PYRAN-2-ONE, TETRAHYDRO-6,6-DIMETHYL-	1.44	3.40	6.31	3.44	2.35	7.26
CYCLOHEXANE, 1,3,5-TRIMETHYL-	1.30	1.97	3.36	1.70	1.63	3.00
BENZENE, 1,4-DIMETHYL-	1.08	4.08	6.87	4.34	1.63	8.07
BENZENE, 1,2-DIMETHYL-	0.99	2.65	5.27	2.26	0.91	5.78
NONANE	1.57	2.49	8.58	2.67	1.16	7.57
BENZENE, ETHYNYL-	0.40	0.64	2.44	1.43	0.29	3.85
BENZENE, ETHENYL-	1.21	2.21	3.95	1.96	0.90	6.42
BENZENE, 1-ETHENYL-2-METHYL-	0.57	1.54	2.87	1.10	0.81	3.01
NONANE, 3-METHYL-	0.43	0.97	2.06	1.25	0.48	2.23
BENZENE, PROPYL-	1.09	2.50	3.09	2.70	1.44	3.56
BENZALDEHYDE (ACN)(DOT)	1.26	3.01	7.42	3.31	1.48	7.73
BENZENE, (1-METHYLETHYL)-	0.57	1.63	2.99	1.57	0.86	2.55

Table 17 (continued)

Compound	Probes (distance from vertical centre mm)					Hood (dia. mm)
	150	75	0	75	150	300
BENZENE, 1-ETHYL-2-METHYL-	0.72	1.46	2.11	1.44	0.97	2.51
CYCLOPENTANE, 1-METHYL-3-(2-METHYLPROPYL)-	1.21	0.96	2.43	1.94	1.58	2.79
BENZENE, 1,2,4-TRIMETHYL-	1.20	4.39	6.88	4.11	1.46	6.11
DECANE	1.42	2.39	7.71	2.95	1.03	7.32
2,5-CYCLOHEXADIENE-1,4-DIONE, 2-METHYL-	0.29	1.20	1.77	1.27	0.39	1.70
BENZENE, 1,3,5-TRIMETHYL-	0.99	0.94	2.05	1.13	0.51	2.29
BENZENE, DIETHYL-	0.73	3.97	4.36	2.81	1.51	4.22
BENZENE, 1-METHYL-2-PROPYL-	0.71	3.44	6.04	3.58	1.17	6.99
DECANE, 3-METHYL-	0.66	1.21	1.75	1.02	0.89	1.67
CYCLOHEXANE, (2-METHYLPROPYL)-	0.43	1.19	2.19	1.88	0.65	1.72
BENZENE, 1-ETHYL-2,3-DIMETHYL-	0.57	0.88	2.42	1.19	0.67	2.94
BENZENE, 1,2,3,4-TETRAMETHYL-	0.31	0.65	1.34	0.58	0.46	1.46
BENZENE, METHYL(1-METHYLETHYL)-	0.25	1.50	4.09	2.09	0.41	3.50
BENZENE, 1,2,3,5-TETRAMETHYL-	0.30	0.71	3.09	0.81	0.15	3.03
UNDECANE	1.08	1.93	3.40	1.73	1.03	3.15
BENZENE, 4-ETHYL-1,2-DIMETHYL-	0.70	1.51	3.16	1.79	1.30	3.61
BENZENE, 1,2,4,5-TETRAMETHYL-	0.76	1.49	2.08	1.57	0.37	1.88
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	0.12	0.57	1.32	0.74	0.48	2.21
BENZENE, (1,1-DIMETHYLPROPYL)-	0.15	0.51	1.10	0.75	0.20	1.44
BENZENE, (1-METHYL-1-PROPENYL)-, (E)-	0.58	0.84	1.91	1.52	0.72	2.49
BENZENE, 2-ETHENYL-1,4-DIMETHYL-	0.64	0.51	1.70	0.95	0.57	1.32
BENZENE, (1-ETHYLPROPYL)-	0.22	0.16	1.52	1.18	0.50	1.22
BENZENE, (1-METHYLBUTYL)-	0.26	0.26	0.60	0.35	0.31	1.08
BENZENE, 1-METHYL-4-(2-METHYLPROPYL)-	0.11	0.64	1.21	1.09	0.69	1.88
BENZENE, 1,3-DIETHYL-5-METHYL-	0.11	0.20	0.77	0.46	0.31	0.77
NAPHTHALENE (ACN)(DOT)	1.34	3.53	20.63	3.57	2.47	18.45
DODECANE	0.23	0.51	0.89	0.47	0.30	1.13
NAPHTHALENE, 2-METHYL-	0.16	0.62	2.07	1.19	0.16	2.32
NAPHTHALENE, 1-METHYL-	0.11	0.54	1.05	0.89	0.09	1.73
1,1'-BIPHENYL	0.09	0.63	2.19	0.84	0.14	2.62
BIPHENYLENE	0.13	0.42	1.57	0.36	0.14	1.85
ACENAPHTHYLENE	0.05	0.12	0.31	0.10	0.12	0.22
9H-FLUORENE, 9-METHYLENE-	0.31	0.40	0.95	0.45	0.34	0.91

location probes contained lower concentrations of these hydrocarbons ranging from approximately 1 to 3 mg/m^3.

The majority of hydrocarbons identified in these emissions were aromatic with saturated alkyl sidechains followed by straight and branch chain aliphatics, some unsaturated and cyclic hydrocarbons and a few oxygenated hydrocarbons. Occurrence of unsaturation of alkyl sidechains attached to aromatic rings was minimal, which was also the case in results obtained in the laboratory studies.

5.2.1.3 Non-volatile hydrocarbons

The integrated samples collected on adsorbents additionally contained less volatile hydrocarbons that ultimately required extraction with solvents to remove them prior to further analyses by the GC/MS system. This extension of analyses allowed for the examination and identification of multi-ringed polycyclic aromatic hydrocarbons that were found to be produced within the flames.

A total of 90 hydrocarbons were identified in the emissions from the natural gas flame by this method (Table 18), 20 of which were previously identified in the thermal desorption analyses and were not completely removed from the adsorbent due to their lower volatility. The 70 additional hydrocarbons ranged from highly substituted benzene compounds to multi-ringed hydrocarbons such as the benzopyrenes. The polycyclics were found in concentrations approximately 10 times the amounts detected in the smaller, open-atmosphere laboratory tests.

5.2.2 Co-Flowing Gas/Condensate Flaring

The major part of the pilot-scale flare testing study was carried out using a combined natural gas/condensate fuel stream. Condensate was obtained from a gas plant for examination in the pilot flare system. The tests conducted using this fuel system consisted of sample collection at varying distances above the flame, sampling with different hood sizes as well as multi-probe sampling, and flaring in cross-wind conditions.

The composition of the condensate included the major components hexane at 21%, heptane at 59%, isopentane at 8%, and pentane at 7%. The remaining lesser components such as butane and isobutane made up the remaining 5%.

Table 18. Hydrocarbons identified above a natural gas flame from the centre probe sampler, using extraction methods ($\mu g/m^3$).

Compound	Amount
BENZENE, DIETHYL-	307.0
BENZENE, 1-METHYL-2-PROPYL-	850.0
BENZENE, 1-ETHYL-2,3-DIMETHYL-	724.3
BENZENE, METHYL(1-METHYLETHYL)-	509.3
BENZENE, 1,2,3,4-TETRAMETHYL-	637.7
BENZENE, 1,2,3,5-TETRAMETHYL-	570.7
UNDECANE	377.0
BENZENE, 4-ETHYL-1,2-DIMETHYL-	158.9
BENZENE, 1,2,4,5-TETRAMETHYL-	394.6
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	513.7
BENZENE, (1-METHYL-1-PROPENYL)-, (E)-	215.4
BENZENE, (1,1-DIMETHYLPROPYL)-	171.1
1H-INDENE, 2,3-DIHYDRO-4-METHYL-	498.1
BENZENE, (1-ETHYLPROPYL)-	504.0
BENZENE, 1,3-DIETHYL-5-METHYL-	149.0
BENZENE, DIETHYLMETHYL-	84.5
NAPHTHALENE (ACN)(DOT)	713.7
BENZENE, 1-ETHYL-3-(1-METHYLETHYL)-	153.1
DODECANE	228.7
BENZENE, ETHYL-1,2,4-TRIMETHYL-	51.7
BENZENE, CYCLOPENTYL-	23.2
BENZENE, 1-ETHYL-2,4,5-TRIMETHYL-	10.5
BENZENE, 1-PENTENYL-	25.6
BENZENE, 2,4-DIMETHYL-1-(1-METHYLPROPYL)-	29.8
BENZENE, 1,4-DIMETHYL-2-(2-METHYLPROPYL)-	9.4
1H-INDENE, 2,3-DIHYDRO-4,7-DIMETHYL-	101.0
1H-INDENE, 2,3-DIHYDRO-1,2-DIMETHYL-	60.9
BENZENE, PENTAMETHYL-	70.4
NAPHTHALENE, 2-METHYL-	14.3
NAPHTHALENE, 1-METHYL-	6.5
BENZENE, 4-(2-BUTENYL)-1,2-DIMETHYL-, (E)-	5.3
1,1'-BIPHENYL	59.6
NAPHTHALENE, 1-ETHYL-	63.6
NAPHTHALENE, 1,5-DIMETHYL-	142.2
NAPHTHALENE, 2-ETHYL-	35.1
1,1'-BIPHENYL, 2-METHYL-	13.5
NAPHTHALENE, 2,3-DIMETHYL-	65.6
BIPHENYLENE	12.5
NAPHTHALENE, 1,2-DIMETHYL-	28.2
1,1'-BIPHENYL, 3-METHYL-	36.5
NAPHTHO[2,1-B]FURAN	14.7
NAPHTHALENE, 1,4,5-TRIMETHYL-	8.9
NAPHTHALENE, 1,3,6-TRIMETHYL-	45.7
NAPHTHALENE, 1,6,7-TRIMETHYL-	33.9
BENZENE, 1-METHYL-4-(PHENYLMETHYL)-	23.8
NAPHTHALENE, 1,4,6-TRIMETHYL-	48.5

Table 18 continued

Compound	Amount
NAPHTHALENE, 2,3,6-TRIMETHYL-	31.2
QUINOLINE, 4-PROPYL-	14.5
BENZENE, 1,1'-METHYLENEBIS[4-METHYL-	50.3
BENZENE, 1,1'-METHYLENEBIS[3-METHYL-	50.7
BENZENE, 1,1'-(1-METHYL-1,2-ETHANEDIYL)BIS-	34.9
BENZENE, 1-METHYL-2-[(3-METHYLPHENYL)METHYL]-	51.8
BENZENE, 1-METHYL-3-[(4-METHYLPHENYL)METHYL]-	10.7
NAPHTHALENE, 1-METHYL-7-(1-METHYLETHYL)-	15.1
9H-FLUORENE, 1-METHYL-	29.8
9H-FLUORENE, 2-METHYL-	18.9
9H-FLUORENE, 4-METHYL-	11.3
BENZENE, 1,1'-(1,2-ETHENEDIYL)BIS[2-METHYL-	12.8
NAPHTHALENE, 1,2,3-TRIMETHYL-4-PROPENYL-, (E)-	7.6
9H-FLUORENE, 9-METHYLENE-	103.7
ANTHRACENE	13.7
9H-FLUORENE, 2,3-DIMETHYL-	27.2
BENZENE, 1-METHYL-3-(2-PHENYLETHENYL)-, (E)-	26.3
BENZENE, 1-METHYL-2-(2-PHENYLETHENYL)-	23.4
1,1'-BIPHENYL, (1-METHYLETHENYL)-	7.6
NAPHTHALENE, 1-PHENYL-	89.8
ANTHRACENE, 2-METHYL-	8.7
NAPHTHALENE, 2-PHENYL-	10.9
PHENANTHRENE, 2,5-DIMETHYL-	9.7
PHENANTHRENE, 3,6-DIMETHYL-	21.4
PHENANTHRENE, 2,3-DIMETHYL-	10.7
NAPHTHALENE, 1-PHENYL-	15.6
ANTHRACENE, 2-ETHYL-	8.4
FLUORANTHENE	45.9
NAPHTHALENE, 2-(PHENYLMETHYL)-	5.8
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	9.9
PYRENE	64.5
PHENANTHRENE, 2,3,5-TRIMETHYL-	5.7
11H-BENZO[A]FLUORENE	6.3
11H-BENZO[B]FLUORENE	14.6
PYRENE, 4-METHYL-	32.3
NAPHTHALENE, 1-(PHENYLMETHYL)-	33.2
PYRENE, 2-METHYL-	10.8
2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	187.8
BENZENE, 1,1'-[1,4-BIS(1-METHYLETHYL)-1,2,3-BUTATRIENE-1,4-DIYL]BIS-	18.5
CHRYSENE	4.1
TRIPHENYLENE	2.9
BENZO[B]THIOPHENE, 3-(2-NAPHTHALENYL)-	4.9
BENZO[E]PYRENE	4.4
BENZO[A]PYRENE	7.9

The pilot-scale flare testing using the gas/condensate fuel was also carried out under turbulent conditions. Natural gas flow in all tests was 10 standard litres per minute (sℓpm) which was directed through condensate fuel at a temperature which produced a 23% condensate vapour stream co-flowing with the natural gas. The resulting flame was highly variable and produced occasional visible billows of smoke as well as the many fireballs of burning liquid fuel. Results of these tests are described in the following sections.

5.2.2.1 Emissions characterization

Comparative sampling and analyses using on-site analyzers was carried out at distances of 250 and 500 mm above the gas/condensate flame. Results obtained from these two locations were very similar and data from the 500 mm location are included in Table 19 along with data from the 250mm location in Table 19a. The emissions from this flame appeared to diffuse much wider at the 500 mm location and are therefore more uniform across the horizontal plane sampled. Carbon dioxide levels ranged from a low of 4200 mg/m^3 at one of the samples taken 150 mm from the vertical centre of the flame to 7630 mg/m^3 at the centre location. The combustion efficiencies measured at this distance from the flame (88 to 90%) were almost identical to those found closer to the flame (87 to 89%). Hydrocarbons were the largest reason for these reduced efficiencies, primarily the unburned hydrocarbons, followed closely by the hydrocarbons produced in the flame. Benzene, toluene, xylenes and naphthalene were some of the major pyrolytic products found in the emissions in concentrations up to 80 mg/m^3. Results from hood sampling also closely approximated the results obtained from the centre probe above this flame, indicating similar channelling of emissions through the hood sampler.

5.2.2.2 Comparison of hood samplers

As previously mentioned in the analytical section, different hood sizes were constructed and tested in these studies. The hood sizes used for comparison were 230 mm, 300 mm, and 400 mm in diameter. Comparative results from samples collected through these hood samplers at a distance of 500 mm above the same natural gas/condensate flame are displayed in Table 20.

Table 19. Chemical characterization of emissions collected 500 mm above a natural gas flame containing 23% condensate vapor. (All values in mg/m^3 except where otherwise noted.)

	Sample Type					
	Probes					Hood (dia mm)
Distance from vertical centre of flame (mm)	150	75	0	75	150	300
Temperature (Celsius)	82	101	110	97	77	110
0_2 (%)	20.5	20.2	20.2	20.1	20.5	19.9
N_2 (%)	77.4	77.2	77.1	76.7	77.2	77.2
H_2	32	41	46	39	26	44
CO	0	4	6	3	0	5
CO_2	5400	7230	7630	6420	4160	9550
Carbon	1	3	4	2	1	9
Methane	8.9	10.4	12.6	9.7	8.2	13.8
Ethylene	0.1	0.1	0.1	0.1	0.1	0.2
Acetylene	0.4	0.7	0.6	0.5	0.3	0.7
Benzene	29	45	49	38	23	57
Toluene	19	26	31	24	15	28
Xylenes	27	41	44	38	31	47
Styrene	3	5	7	6	3	12
Ethynyl Benzene	1	1	2	1	0.5	5
Naphthalene	27	50	63	44	21	69
Other Hydrocarbons	84	101	127	89	76	136
Combustion Efficiency (%)	90.1	89.7	88.3	89.6	88.8	89.5

Table 19a. Chemical characterization of emissions collected 250 mm above a natural gas flame containing 23% condensate vapor. (All values in mg/m^3 except where otherwise noted.)

	Sample Type					
	Probes					Hood (dia mm)
Distance from vertical centre of flame (mm)	150	75	0	75	150	300
Temperature (Celsius)	176	155	167	121	88	163
0_2 (%)	20.2	19.7	19.9	20.2	20.1	19.5
N_2 (%)	78.0	76.0	76.0	76.0	75.3	75.9
H_2	39	53	62	44	31	57
CO	0	3	8	0	0	8
CO_2	3100	8170	8240	2770	1630	10100
Carbon	4	9	14	10	4	12
Methane	9.4	7.3	8.9	3.6	3.1	9.1
Ethylene	1.9	5.6	6.3	1.7	1.2	6.5
Acetylene	0.9	0.7	0.7	0.5	0.3	0.9
Benzene	19	56	63	17	12	65
Toluene	14	38	44	10	10	47
Xylenes	12	32	40	9	6	39
Styrene	5	8	9	4	2	10
Ethynyl Benzene	1	3	3	1	1	4
Naphthalene	21	64	71	16	10	83
Other Hydrocarbons	46	126	138	35	26	159
Combustion Efficiency (%)	88.7	88.6	87.2	89.6	87.8	88.6

Table 20. Chemical characterization of emissions collected 500 mm above a natural gas flame containing 23% condensate vapour and using different size hood samplers. (All values in mg/m^3 except where otherwise noted.)

	Sample Hoods		
Hood sizes (diameter in mm)	230	300	400
Temperature (Celsius)	110	110	110
O_2 (%)	19.5	19.9	20.3
N_2 (%)	75.7	77.2	77.6
H_2	41	44	36
CO	5	5	3
CO_2	9450	9550	6150
Carbon	7	9	5
Methane	12.6	13.8	12.2
Ethylene	0.1	0.2	0.1
Acetylene	0.5	0.7	0.4
Benzene	54	57	33
Toluene	33	28	20
Xylenes	50	47	39
Styrene	10	12	5
Ethynyl Benzene	3	5	1
Naphthalene	55	69	43
Other Hydrocarbons	132	136	95
Combustion Efficiency (%)	89.2	88.5	89.1

Results indicate that samples obtained through the 230 mm and 300 mm diameter hoods are almost identical. The samples obtained through the 400 mm diameter hood, on the other hand, show that dilution occurs by extending the sampling zone out farther than the 150 mm radial distance from the vertical centre of the flame. All results are comparable to those obtained by sampling through the centre probe of the multi-probe system.

5.2.2.3 Volatile hydrocarbons

Emission samples were also collected on adsorbents for identification by GC/MS of both volatile and non-volatile fractions. As in the case of the natural gas flare testing, these samples were collected at a very much slower rate for a period of one hour. Volatile hydrocarbons were thermally desorbed from the adsorbent samples and GC/MS results of these findings are given in Table 21.

A total of 63 of the most commonly identified compounds found in samples simultaneously collected from the various locations across the flame are listed in this table. Straight chain hydrocarbons, many of which were components of the condensate, were also some of the major components of this volatile hydrocarbon fraction that were unburned and escaped into the emissions. Benzene, toluene, xylenes and naphthalene were also major components ranging in individual concentrations from approximately 10 to 80 mg/m^3. Occurrence of unsaturation in alkyl side chains attached to benzene rings was more prevalent in these emissions compared to the emissions from the natural gas flame. Compounds such as benzaldehyde, substituted benzaldehydes and pyranones were also present in significant quantities indicating partial oxidation of some of the hydrocarbons in this flame.

5.2.2.4 Non-volatile hydrocarbons

Extraction of the samples collected on adsorbents, extended the list of identified hydrocarbons in the emissions above this flame by an additional 55 compounds (Table 22). These less-volatile compounds which were not removed by the thermal desorption analyses included the more highly substituted benzene compounds, naphthalene compounds and many 3, 4, and 5-ringed benzene compounds.

Table 21. Hydrocarbons identified above a natural gas flame containing 23% condensate vapour, using thermal desorption methods (mg/m^3).

Compounds	Probes (distance from vertical centre in mm)					Hood (dia. mm)
	150	75	0	75	150	300
PENTANE (ACN)(DOT)	1.89	2.49	3.57	3.16	2.02	3.35
CARBON DISULFIDE (ACN)(DOT)	0.83	1.88	4.22	2.61	1.78	3.40
3-PENTEN-1-YNE, (Z)-	1.68	3.51	4.62	3.81	1.73	4.03
HEXANE (DOT)	8.82	9.56	12.79	8.07	7.37	11.95
CYCLOHEXANE(DOT	3.61	4.23	7.87	5.42	4.97	7.58
BENZENE (ACN)(DOT)	19.55	31.24	46.75	37.45	18.32	54.95
PENTANE, 3,3-DIMETHYL-	8.94	14.18	28.21	15.41	6.55	25.00
HEXANE, 3-METHYL-	2.49	8.85	17.15	5.38	3.80	15.75
CYCLOPENTANE, 1,2-DIMETHYL-	3.48	6.70	14.17	5.39	4.80	14.06
HEPTANE (DOT)	51.40	88.18	123.75	97.64	62.27	120.85
CYCLOHEXANE, METHYL-	15.12	17.93	31.44	19.39	16.92	29.20
BENZENE, METHYL-	21.28	35.34	47.50	39.74	22.61	55.28
1-HEXENE, 2,5-DIMETHYL-	16.41	19.87	26.15	25.74	23.05	23.82
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	0.97	1.14	3.73	1.79	0.53	2.98
OCTANE (DOT)	60.49	75.45	152.33	129.83	66.93	162.24
HEXANE, 3-ETHYL-	0.83	1.22	3.05	1.48	0.98	3.33
CYCLOHEXANE, ETHYL-	9.52	11.46	15.41	12.75	10.13	16.24
HEPTANE, 3,4-DIMETHYL-	8.35	13.53	16.66	12.94	10.41	14.90
CYCLOHEXANE, 1,2,4-TRIMETHYL-	1.32	1.59	2.74	1.19	0.92	2.48
BENZENE, ETHYL-	16.88	23.74	33.71	22.96	18.11	44.44
CYCLOPENTENE, 1-ETHENYL-3-METHYLENE-	44.42	56.30	75.40	68.03	54.70	60.23
2H-PYRAN-2-ONE, TETRAHYDRO-6,6-DIMETHYL-	22.52	32.67	39.92	29.36	21.17	49.30
CYCLOHEXANE, 1,3,5-TRIMETHYL-	5.88	10.45	19.57	9.49	7.18	20.02
BENZENE, 1,4-DIMETHYL-	19.31	32.34	44.37	34.14	22.69	38.75
NONANE	64.91	75.89	105.85	79.74	67.83	118.03
BENZENE, ETHYNYL	5.31	12.47	17.20	13.25	3.87	16.35
BENZENE, ETHENYL	7.54	14.40	26.06	18.89	8.43	25.05
BENZENE, 1-ETHENYL-2-METHYL-	7.44	9.12	17.74	10.70	5.70	15.77
NONANE, 3-METHYL-	11.36	14.66	21.61	17.07	13.45	24.57

Table 21 (continued)

Compounds	Probes (distance from vertical centre in mm)					Hood (dia. mm)
	150	75	0	75	150	300
BENZENE, PROPYL-	16.71	19.75	26.78	18.60	17.16	31.46
BENZALDEHYDE (ACN)(DOT)	2.04	3.12	6.71	2.74	1.70	6.95
BENZENE, (1-METHYLETHYL)-	14.86	24.29	37.09	16.25	13.04	31.27
BENZENE, 1-ETHYL-2-METHYL-	11.20	18.97	24.57	14.87	13.25	27.45
OCTANE, 2,6-DIMETHYL-	4.28	6.84	11.00	6.27	4.60	14.60
BENZENE, 1,3,5-TRIMETHYL-	6.42	9.67	13.89	8.93	5.12	16.47
CYCLOPENTANE, 1-METHYL-3-(2-METHYLPROPYL)-	5.38	7.09	13.89	6.88	5.26	13.71
BENZENE, 1,2,4,-TRIMETHYL-	14.38	15.99	29.32	17.37	10.12	28.42
DECANE	31.26	54.30	74.88	52.45	22.43	86.45
BENZENE, DIETHYL-	2.42	3.35	4.79	2.08	1.13	4.43
NONANE, 4,5-DIMETHYL-	0.88	2.23	4.00	2.93	1.54	3.45
BENZENE, 1-METHYL-2-PROPYL-	2.32	5.17	10.92	5.65	3.39	13.31
CYCLOHEXANE, (2-METHYLPROPYL)-	1.25	5.64	7.64	3.90	1.86	7.23
DECANE, 3-METHYL-	0.64	2.22	4.46	2.62	1.19	4.76
BENZENE, 1,4-DIETHYL-	4.15	7.46	16.97	8.73	4.13	14.43
BENZENE, METHYL(1-METHYLETHYL)-	2.44	4.05	11.68	8.26	3.67	11.32
BENZALDEHYDE, 4-METHYL-	2.76	3.49	9.01	4.35	2.62	8.23
BENZENE, 1,2,3,4-TETRAMETHYL-	1.21	4.10	7.84	3.36	2.92	8.82
BENZENE, 1,2,3,5-TETRAMETHYL-	0.77	1.63	4.54	2.66	1.23	5.74
UNDECANE	1.86	4.01	6.00	3.23	2.41	5.03
BENZENE, 4-ETHYL-1,2-DIMETHYL-	3.52	7.14	12.03	8.87	3.64	15.20
BENZENE, 1,2,4,5-TETRAMETHYL-	0.73	1.17	2.03	1.00	0.58	1.93
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	0.39	0.74	1.43	0.97	0.44	0.90
BENZENE, (1,1-DIMETHYLPROPYL)-	0.13	0.49	0.97	0.36	0.21	1.07
BENZENE, (1-ETHYLPROPYL)-	0.18	0.46	0.99	0.40	0.29	1.21
BENZENE, 1,3-DIETHYL-5-METHYL-	0.15	0.31	0.54	0.27	0.16	0.60
NAPHTHALENE (ACN)(DOT)	26.23	58.49	79.92	56.57	28.84	72.30
DODECANE	1.44	2.34	4.52	3.29	2.63	4.19
NAPHTHALENE, 2-METHYL-	5.05	8.12	12.02	5.07	4.08	14.09
NAPHTHALENE, 1-METHYL-	2.59	5.04	9.15	4.35	2.11	11.47
1,1'-BIPHENYL	2.01	3.02	6.26	2.64	2.03	5.06
BIPHENYLENE	1.67	4.04	5.22	2.93	1.88	4.21
ACENAPHTHYLENE	1.12	2.01	4.29	1.03	0.59	3.82
9H-FLUORENE, 9-METHYLENE-	0.94	2.19	3.04	1.16	0.72	2.05

Table 22. Hydrocarbons identified above a natural gas flame containing 23% condensate vapour, using extraction methods ($\mu g/m^3$).

Compound	Amount
BENZENE, 1-METHYL-2-PROPYL-	2107.0
BENZENE, METHYL(1-METHYLETHYL)-	985.3
BENZENE, 1,2,3,4-TETRAMETHYL-	1279.0
PHENOL, 2-METHYL-	1136.0
BENZENE, 1,2,3,5-TETRAMETHYL-	920.7
BENZENE, 4-ETHYL-1,2-DIMETHYL-	284.9
PHENOL, 4-METHYL-	2859.0
BENZENE, 1,2,4,5-TETRAMETHYL-	536.6
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	741.8
BENZENE, (1-METHYL-1-PROPENYL)-, (E)-	382.0
BENZENE, 2-ETHENYL-1,4-DIMETHYL-	1351.0
PHENOL, 2,5-DIMETHYL-	1310.0
NAPHTHALENE (ACN)(DOT)	1196.0
BENZENE, 1-ETHYL-2,4,5-TRIMETHYL-	837.5
1H-INDENE, 2,3-DIHYDRO-4,7-DIMETHYL-	552.1
BENZENE, (3-METHYL-2-BUTENYL)-	1032.0
1H-INDENE, 2,3-DIHYDRO-1,2-DIMETHYL-	637.2
BENZENE, PENTAMETHYL-	922.2
NAPHTHALENE, 2-METHYL-	334.4
NAPHTHALENE, 1-METHYL-	197.2
1,1'-BIPHENYL	1363.0
TETRADECANE	866.0
NAPHTHALENE, 1,5-DIMETHYL-	247.5
NAPHTHALENE, 2-ETHYL-	221.9
NAPHTHALENE, 2,3-DIMETHYL-	296.4
BIPHENYLENE	185.3
NAPHTHALENE, 1,4-DIMETHYL-	334.3
1,1'-BIPHENYL, 3-METHYL-	145.8
NAPHTHO[2,1-B]FURAN	287.1
NAPHTHALENE, 1,4,5-TRIMETHYL-	180.4
BENZENE, 1-METHYL-2-(PHENYLMETHYL)-	298.4
BENZENE, 1-METHYL-4-(PHENYLMETHYL)-	103.4
NAPHTHALENE, 1,4,6-TRIMETHYL-	174.8
9H-FLUORENE	201.1
BENZENE, 1,1'-METHYLENEBIS[4-METHYL-	139.3
1,1'-BIPHENYL, 2-ETHYL-	234.1
BENZENE, 1-METHYL-2-[(3-METHYLPHENYL)METHYL]-	188.3
BENZENE, 1-METHYL-3-[(4-METHYLPHENYL)METHYL]-	162.4
9H-FLUORENE, 1-METHYL-	112.8
9H-FLUORENE, 2-METHYL-	93.5
9H-FLUORENE, 9-METHYLENE-	567.8
ANTHRACENE	399.1
9H-FLUORENE, 2,3-DIMETHYL-	368.3
BENZENE, 1-METHYL-3-(2-PHENYLETHENYL)-, (E)-	31.1
BENZENE, 1-METHYL-2-(2-PHENYLETHENYL)-	45.5
1,1'-BIPHENYL, (1-METHYLETHENYL)-	34.1
PHENANTHRENE, 3-METHYL-	323.0
ANTHRACENE, 2-METHYL-	327.7
PHENANTHRENE, 2-METHYL-	151.7
NAPHTHALENE, 2-PHENYL-	199.0
PHENANTHRENE, 2,5-DIMETHYL-	209.4
PHENANTHRENE, 3,6-DIMETHYL-	278.9
PHENANTHRENE, 2,3-DIMETHYL-	74.6
FLUORANTHENE	177.5
NAPHTHALENE, 2-(PHENYLMETHYL)-	39.3
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	84.3
PYRENE	317.1
PHENANTHRENE, 2,3,5-TRIMETHYL-	133.7
11H-BENZO[A]FLUORENE	36.7
11H-BENZO[B]FLUORENE	83.4
PYRENE, 4-METHYL-	91.9
NAPHTHALENE, 1-(PHENYLMETHYL)-	22.8
PYRENE, 2-METHYL-	47.7
CHRYSENE	56.8
TRIPHENYLENE	75.3
BENZO[B]THIOPHENE, 3-(2-NAPHTHALENYL)-	176.2
BENZO[E]PYRENE	74.5
BENZO[A]PYRENE	107.3

More evidence of the oxidation reactions that occurred in the burning of this fuel was demonstrated by the presence of the phenolic compounds identified in this fraction. The substituted methyl phenols and dimethyl phenol compounds were detected in concentrations ranging from 1100 to over 2800 $\mu g/m^3$ in these emissions.

The amounts of the individual hydrocarbons identified in this fraction of the emission sample collected above the gas/condensate flame ranged from approximately 20 to nearly 3000 $\mu g/m^3$. Many of these measured concentrations are much higher than comparative hydrocarbon measurements made during any of the previous laboratory testing.

5.2.3 Flaring in Cross-Winds

Open atmosphere flaring was also carried out using the same fuel mixture during cross-wind conditions. Cross-wind velocities during this sampling ranged from 0.5 to approximately 1.0 meter per second. Fuel flows were the same as described in the previous experiments and sampling was carried out using both the multi-probe and hood sampling systems. The samplers were angled according to the average direction of the flame and were placed at the approximate distance of 500 mm from the average visible end of the flame. Results of these investigations are described in the following sections.

5.2.3.1 Emission characterization

Sample collection during the flaring in cross-wind conditions was modified from similar sampling under the more ideal atmospheric conditions. The sampling in this case was only activated while the flame emissions were flowing toward either the sampling probes or the hood samplers. Total sampling time for the collection of samples for the on-site analyses was still approximately 30 seconds, but actually required 2 to 3 minutes to acquire the more representative samples.

The results of the chemical characterization of these simultaneously collected emission samples are contained in Table 23. One of the major effects created by the cross-winds was the overall reduction in combustion efficiencies as measured in these emissions. Efficiency measurements were lower and more variable throughout the samples collected at the different locations across the flame in comparison to values obtained during low wind

Table 23. Chemical characterization of emissions collected 500 mm downwind of a natural gas flame containing 23% condensate vapour from a gas plant. (All values in mg/m^3 except where otherwise noted.)

	Sample Type					
	Probes					Hood (dia mm)
Distance from vertical centre of flame (mm)	150	75	0	75	150	300
Temperature (Celsius)	55	73	98	67	49	107
O_2 (%)	20.4	20.1	19.6	20.1	20.3	19.3
N_2 (%)	76.2	75.9	74.4	76.0	75.7	76.5
H_2	13	18	22	18	12	23
CO	0	6	8	5	0	14
CO_2	3580	3720	4850	3720	3200	12070
Carbon	10	13	16	12	9	20
Methane	9.2	10.3	12.8	9.9	7.7	24.2
Ethylene	0.1	0.2	0.4	0.3	0.1	0.6
Acetylene	0.4	0.8	1.5	1.0	0.5	1.9
Benzene	38	43	67	45	35	101
Toluene	20	28	46	26	22	81
Xylenes	10	14	17	12	8	57
Styrene	7	9	12	10	6	23
Ethynyl Benzene	1	3	3	2	1	12
Naphthalene	36	50	53	46	30	85
Other Hydrocarbons	91	109	126	113	81	241
Combustion Efficiency (%)	84.4	81.6	82.0	81.8	84.3	86.2

conditions. Efficiencies ranged from 82 to 86%, up to 6% lower than what occurs under lower wind conditions.

As in all previous measurements, the primary reason for the low combustion efficiency is the hydrocarbons detected as either unburned condensate components or produced hydrocarbons that survived the outer extremities of the flame and occur in the emissions. The levels of compounds such as benzene, toluene and xylenes were higher in the emissions measured in cross-wind conditions and ranged in concentrations from 10 to 70 mg/m^3.

Another notable difference in the emission measurements during the cross-wind flaring experiments was the results of hood sampling compared to sample probes. Carbon dioxide concentrations for hood sampling were over twice the highest values obtained by sample probes, while hydrocarbon concentrations were slightly less than doubled. The difference in these values may be attributable to the fact that the hood samples were collected at different times and are not directly comparable. Although the levels of the hydrocarbons are much higher in this sample, the measured efficiency of the flame is more favourable at 86% as compared to the average efficiency of 82% from probe samples.

5.2.3.2 Volatile hydrocarbons

Sampling was also carried out on adsorbents for subsequent GC/MS analyses of both volatile and non-volatile fractions. These samples were collected over a one-hour period at a low sampling rate through both hood and probe samplers. A total of 61 compounds were identified in these emission samples, most of which were also identified in the emissions from flares examined under low wind conditions (Table 24). The major difference was in the concentration at which they occurred. The cross-winds produced increases in most of the hydrocarbon concentrations observed. Only the heavier hydrocarbons measured in this fraction, such as naphthalene, were found in similar concentrations to those created in low wind conditions.

Comparison of results of the hood sampling to those obtained from the centre probe revealed relatively similar concentrations. In most cases, differences were small which is more comparable to data obtained by flaring under the lower wind conditions.

Table 24. Hydrocarbons identified in emissions from a natural gas flame containing 23% condensate vapour, in crosswinds and using thermal desorption methods (mg/m^3).

Compounds	Probes (distance from vertical centre in mm)					Hood (dia.mm)
	150	75	0	75	150	300
PENTANE (ACN)(DOT)	1.45	2.18	3.69	2.22	1.15	4.11
3-PENTEN-1-YNE, (Z)-	2.14	2.98	2.97	2.33	1.71	3.16
HEXANE (DOT)	2.61	3.11	6.81	2.79	1.36	5.81
CYCLOHEXANE(DOT	1.85	2.28	4.69	1.91	1.61	4.60
BENZENE (ACN)(DOT)	40.23	47.10	74.35	51.45	34.39	86.04
PENTANE, 3,3-DIMETHYL-	10.52	14.36	25.43	14.49	7.13	24.15
HEXANE, 3-METHYL-	7.60	11.47	17.24	9.26	5.18	17.39
CYCLOPENTANE, 1,2-DIMETHYL-	5.43	6.77	12.11	3.69	3.05	13.48
HEPTANE (DOT)	57.54	70.49	95.66	65.19	28.06	120.67
CYCLOHEXANE, METHYL-	16.35	21.19	34.23	13.40	8.44	44.41
BENZENE, METHYL-	34.97	47.47	71.83	51.33	39.99	82.36
1-HEXENE, 2,5-DIMETHYL-	19.60	24.45	34.67	20.64	14.01	26.85
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	1.55	3.22	11.34	5.21	3.80	13.32
OCTANE (DOT)	70.27	117.30	208.93	115.45	50.61	188.43
HEXANE, 3-ETHYL-	1.50	8.33	11.42	8.23	3.62	12.36
CYCLOHEXANE, ETHYL-	11.32	18.83	25.30	17.85	14.89	24.50
HEPTANE, 3,4-DIMETHYL-	14.50	19.88	20.77	16.67	12.97	20.78
CYCLOHEXANE, 1,2,4-TRIMETHYL-	1.83	3.70	7.09	3.96	3.52	7.55
BENZENE, ETHYL-	13.16	16.72	35.85	19.67	14.11	47.86
CYCLOPENTENE, 1-ETHENYL-3-METHYLENE-	50.30	63.03	85.90	62.60	48.50	71.40
2H-PYRAN-2-ONE, TETRAHYDRO-6,6-DIMETHYL-	25.19	31.10	38.61	36.68	28.96	43.22
CYCLOHEXANE, 1,3,5-TRIMETHYL-	6.13	9.40	16.02	13.32	5.84	15.93
BENZENE, 1,4-DIMETHYL-	25.19	26.95	37.11	27.67	22.21	39.93
NONANE	89.16	117.64	154.84	88.96	70.37	131.96
BENZENE, ETHYNYL-	4.21	6.25	9.46	5.79	3.27	15.74
BENZENE, ETHENYL-	8.00	12.22	18.14	13.56	6.33	22.49
NONANE, 3-METHYL-	15.36	16.40	21.23	17.25	8.24	23.90
BENZENE, 1-ETHENYL-2-METHYL-	7.29	11.16	18.13	9.79	6.71	19.21
BENZENE, PROPYL-	20.78	22.38	34.30	12.63	12.49	29.24
BENZENE, (1-METHYLETHYL)-	17.22	25.07	35.01	19.67	14.30	25.17
BENZENE, 1-ETHYL-2-METHYL-	12.04	18.31	29.13	19.38	13.73	20.44

Table 24 (continued)

Compounds	Probes (distance from vertical centre in mm)					Hood (dia.mm)
	150	75	0	75	150	300
OCTANE, 2,6-DIMETHYL-	7.91	13.35	19.44	13.67	6.64	23.70
BENZENE, 1,3,5-TRIMETHYL-	8.98	14.26	15.85	7.88	4.80	21.13
CYCLOPENTANE, 1-METHYL-3-(2-METHYLPROPYL)-	3.15	7.61	8.25	6.74	3.60	10.40
BENZENE, 1,2,4-TRIMETHYL-	10.39	15.24	20.84	17.38	12.46	20.97
DECANE	64.96	89.61	127.93	73.60	45.19	102.11
BENZENE, DIETHYL-	3.75	3.80	6.78	5.56	1.64	7.10
NONANE, 4,5-DIMETHYL-	1.27	2.41	5.62	4.61	1.32	4.68
BENZENE, 1-METHYL-2-PROPYL-	6.60	11.63	15.07	9.08	5.20	19.06
CYCLOHEXANE, (2-METHYLPROPYL)-	9.87	10.37	16.44	11.40	7.60	18.69
DECANE, 3-METHYL-	2.26	2.84	3.98	2.59	1.93	4.06
BENZENE, 1-ETHYL-2,3-DIMETHYL-	16.79	24.43	24.75	18.85	15.09	20.71
BENZENE, METHYL(1-METHYLETHYL)-	3.66	5.51	12.21	9.69	4.05	18.78
BENZALDEHYDE, 4-METHYL-	4.79	5.44	12.64	8.71	4.73	10.37
BENZENE, 1,2,3,4-TETRAMETHYL-	2.40	3.69	9.66	7.57	2.64	8.88
BENZENE, 1,2,3,5-TETRAMETHYL-	4.16	5.49	9.54	6.02	2.69	12.87
BENZENE, 4-ETHYL-1,2-DIMETHYL-	15.29	22.94	32.88	29.63	15.31	31.77
UNDECANE	1.71	2.59	3.67	2.31	1.77	2.36
BENZENE, 1,2,4,5-TETRAMETHYL-	0.66	0.60	1.67	0.78	0.82	1.78
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	0.91	1.35	1.65	1.47	1.29	1.92
BENZENE, (1,1-DIMETHYLPROPYL)-	0.88	1.01	2.11	1.65	0.71	1.87
BENZENE, (1-ETHYLPROPYL)-	0.60	0.84	2.17	1.39	0.70	1.75
BENZENE, 1,3-DIETHYL-5-METHYL-	0.87	0.86	1.68	1.18	0.39	1.74
NAPHTHALENE (ACN)(DOT)	27.21	46.22	61.88	38.05	25.18	79.95
DODECANE	1.94	3.74	7.86	3.99	1.65	7.40
NAPHTHALENE, 2-METHYL-	5.32	8.15	11.84	6.74	3.20	12.90
NAPHTHALENE, 1-METHYL-	1.55	5.83	6.69	3.42	2.61	7.84
1,1'-BIPHENYL	2.36	5.45	6.47	3.27	2.47	6.14
BIPHENYLENE	1.93	4.20	5.00	2.96	2.72	6.67
ACENAPHTHYLENE	1.62	3.13	3.78	2.23	1.73	3.88
9H-FLUORENE, 9-METHYLENE-	0.91	2.08	3.16	2.01	1.22	3.21

5.2.3.3 Non-volatile hydrocarbons

Extending the analyses of the samples collected on adsorbents to include less volatile components, provided an additional 58 identified hydrocarbons (Table 25). Again, many of these compounds were also identified in the emissions sampled during low wind conditions. The concentrations of these hydrocarbons increased substantially over amounts detected without the cross-wind.

Oxygenated hydrocarbons were detected in larger numbers of compounds as well as in greater concentrations. There were a several more substituted phenols as well as benzoic acid and some diphenoxy-benzene compounds identified in these emissions at concentrations ranging from 100 to nearly 10,000 $\mu g/m^3$. Polycyclic aromatic hydrocarbons were also detected in these emissions and were found at higher concentrations than amounts found in emissions from flames examined without cross-winds.

5.3 Field Studies

The field flare testing program carried out in these investigations was based on industrial scale flaring operations at two oilfield battery sites in Alberta. One site was a sweet oilfield battery with no hydrogen sulfide in any of the produced streams and the other was a sour oilfield battery site that contained approximately 24% hydrogen sulfide in the gaseous stream that was directed to flare. The flares tested at these sites were very basic in design without any combustion enhancements. A more complete description of these sites was provided in section 4 of this report.

5.3.1 Sweet Oilfield Battery Flare Tests

The sweet oilfield battery site chosen contained the necessary equipment to separate the majority of the liquid hydrocarbons from gases, both of which were directed through separate pipelines to respective processing facilities. The flaring system at this site is used primarily for emergency purposes but does have continuous gas flow to the stack to keep the flame going. Flare testing at this site was carried out over a two year period, the first of which included testing with two different gas flows directed to flare, at different distances from the flame, and with two different liquid fuel flows directed to the flare.

Table 25. Hydrocarbons identified in emissions from a natural gas flame containing 23% condensate vapour, in crosswinds and using extraction methods ($\mu g/m^3$).

Compound	Amount
BENZENE, 1,2,3,4-TETRAMETHYL-	4599.0
PHENOL, 2-METHYL-	3047.0
BENZENE, 4-ETHYL-1,2-DIMETHYL-	504.7
PHENOL, 4-METHYL-	9668.0
PHENOL, 2-ETHYL-	794.6
PHENOL, 2,5-DIMETHYL-	3396.0
PHENOL, 3,5-DIMETHYL-	6502.0
NAPHTHALENE (ACN)(DOT)	5145.0
PHENOL, 3,4-DIMETHYL-	2136.0
BENZOIC ACID (ACN)	6749.0
BENZENE, (3-METHYL-2-BUTENYL)-	1634.0
1H-INDENE, 2,3-DIHYDRO-1,2-DIMETHYL-	2267.0
PHENOL, 2-ETHYL-4-METHYL-	1130.0
BENZENE, PENTAMETHYL-	3047.0
NAPHTHALENE, 2-METHYL-	842.5
NAPHTHALENE, 1-METHYL-	457.1
1,1'-BIPHENYL	4413.0
NAPHTHALENE, 1,5-DIMETHYL-	895.1
NAPHTHALENE, 2-ETHYL-	775.2
NAPHTHALENE, 1,7-DIMETHYL-	1254.0
NAPHTHALENE, 2,3-DIMETHYL-	680.2
BIPHENYLENE	931.9
NAPHTHALENE, 1,4-DIMETHYL-	785.2
1,1'-BIPHENYL, 3-METHYL-	349.1
NAPHTHO[2,1-B]FURAN	498.4
NAPHTHALENE, 1,4,5-TRIMETHYL-	558.3
BENZENE, 1-METHYL-2-(PHENYLMETHYL)-	825.5
BENZENE, 1-METHYL-4-(PHENYLMETHYL)-	278.4
NAPHTHALENE, 1,4,6-TRIMETHYL-	380.4
9H-FLUORENE	541.6
BENZENE, 1,1'-METHYLENEBIS[4-METHYL-	431.1
1,1'-BIPHENYL, 2-ETHYL-	661.3
BENZENE, 1-METHYL-2-[(3-METHYLPHENYL)METHYL]-	617.5
BENZENE, 1-METHYL-3-[(4-METHYLPHENYL)METHYL]-	648.1
9H-FLUORENE, 1-METHYL-	398.7
9H-FLUORENE, 2-METHYL-	353.4
9H-FLUORENE, 9-METHYLENE-	1660.0
ANTHRACENE	957.8
9H-FLUORENE, 2,3-DIMETHYL-	1070.0
BENZENE, 1-METHYL-3-(2-PHENYLETHENYL)-, (E)-	94.2
BENZENE, 1-METHYL-2-(2-PHENYLETHENYL)-	125.3
1,1'-BIPHENYL, (1-METHYLETHENYL)-	92.9
PHENANTHRENE, 3-METHYL-	774.2
ANTHRACENE, 2-METHYL-	929.4
4H-CYCLOPENTA[DEF]PHENANTHRENE	471.9
PHENANTHRENE, 2-METHYL-	363.7
PHENANTHRENE, 2,5-DIMETHYL-	583.9
PHENANTHRENE, 3,6-DIMETHYL-	716.8
PHENANTHRENE, 2,3-DIMETHYL-	221.9
FLUORANTHENE	526.9
NAPHTHALENE, 2-(PHENYLMETHYL)-	94.8
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	236.5
PYRENE	825.0
PHENANTHRENE, 2,3,5-TRIMETHYL-	451.3
11H-BENZO[A]FLUORENE	96.2
11H-BENZO[B]FLUORENE	230.3
PYRENE, 2-METHYL-	130.7
2,5-CYCLOHEXADIENE-1,4-DIONE, 2,5-DIPHENYL-	2480.0
CHRYSENE	131.3
TRIPHENYLENE	183.1
BENZENE, 1,2-DIPHENOXY-	94.7
BENZENE, 1,4-DIPHENOXY-	101.4
BENZO[B]THIOPHENE, 3-(2-NAPHTHALENYL)-	667.8
BENZO[E]PYRENE	219.8
BENZO[A]PYRENE	346.1

The second year tests served to verify overall results obtained in the first year and included flare testing with three different liquid fuel levels in the knock-out drum.

5.3.1.1 Effects of gas flow to the flare and sampling distance

Flare testing was carried out at two different gas flows that were directed to the flare. Under normal battery operating conditions, approximately one or more cubic metres per min of solution gas is directed to the flare producing a flame length of approximately 1 metre. Sampling through the heated probe and sampling line was carried out at a distance of 1 to 2 metres beyond the visible end of the flame. Mean wind speed during this sampling period was 3.5 metres per second (m/s) from the NNE with maximum wind speeds to 7.2 m/s. These conditions produced a moderately variable flame blown horizontally by the prevailing winds, and contained a slightly visible amount of carbon particles in the emissions.

The second test was carried out at an increased gas flow to approximately 5 to 6 m^3/min which produced a flame length of about 5 metres. The gas flow at this site was metered, but variation in flows of the amount used is not definitively measured. Sampling of the emissions from this larger flame was carried out at distances from the visible end of the flame of approximately 4 to 5 metres for the first test and 8 to 9 metres for the second test. Mean wind speed during this sampling period was 2.3 m/s producing a flame that was moderately turbulent. The emission plume associated with this flame was more vertical than the previous flame, but a more visible amount of carbon particles were contained within it.

The results of the on-site characterization of the emissions collected above these two flames are shown in Table 26. The measured carbon particulate concentrations and light hydrocarbons from the larger flame were somewhat higher than amounts detected in the emissions at comparable distances from the smaller flame. Doubling the sampling distance from the flame reduced detected levels of most compounds to approximately 30% of the values closer to the flame. The resulting measured combustion efficiencies from the two locations were very comparable, differing by approximately 1%.

Samples were also collected from emissions above these flames over a longer period of time on both adsorbents and the modified PUF samplers for further identification of hydrocarbons by the GC/MS. A total of 71 identified hydrocarbons were found in the

Table 26. On-site characterization of emissions collected above the field flare while flaring at two different solution gas flow rates and at different distances above the flame. (Values in mg/m^3 except where otherwise noted.)

Solution gas flow (m^3/min)	1 to 2	5 to 6	5 to 6
Sampling distance from flame(m)	1 to 2	4 to 5	8 to 9
O_2 %	20.0	19.9	20.5
N_2 %	78.8	78.4	78.8
H_2	20	140	8
CO	7	12	3
CO_2	4400	4710	1660
Carbon	13	52	15
Methane	90	108	37
Ethylene	17	27	9
Acetylene	42	61	19
Benzene	102	136	38
Toluene	16	29	11
Xylenes	46	36	13
Styrene	53	75	25
Ethynyl Benzene	67	57	22
Naphthalene	71	83	32
Other Hydrocarbons	87	101	35
Combustion Efficiency (%)	70.6	67.2	66.1

emissions from the larger flame by thermal desorption methods (Table 27), and 78 by solvent extraction methods (Table 28). Benzene, styrene, ethynyl benzene, naphthalene, and ethynyl-methyl benzene were some of the compounds found in highest concentrations ranging from 100 to 240 mg/m^3. The aromatic hydrocarbons, many with unsaturation in the alkyl side chains attached to them, aliphatic hydrocarbons and a few oxygenated hydrocarbons accounted for the majority of the more volatile hydrocarbons identified in these emissions. Additionally, a number of polycyclic aromatic hydrocarbons were identified ranging to multi-ringed compounds, the largest of which was coronene. The concentrations at which they were found ranged from less than 1 to approximately 80 mg/m^3.

A modified PUF sampler was also used in sampling these emissions to obtain a measure of the polycyclic aromatic hydrocarbons for comparison to systems used by Environment Canada and the Ontario Ministry of Environment and Energy as well as for comparison with the adsorbent tube results. The sampler consisted of two stages, including a glass fibre filter to collect particulates and hydrocarbons associated with the particulates, as well as a polyurethane foam (PUF) plug to collect vapor phase compounds. Sampling was carried out at a much higher flow rate, about 50 times higher than the flow rate used to sample through adsorbents,.

The filter sample contained 31 identified hydrocarbons, ranging from the lower molecular weight substituted benzene compounds to the higher molecular weight polycyclic aromatic hydrocarbon compounds (Table 29). Concentrations of these hydrocarbons ranged from 0.2 to 14 mg/m^3. It was anticipated that only higher molecular weight compounds would be collected by the filter as the lighter ones should have passed through in the vapor phase.

The majority of the hydrocarbons collected by this modified PAH sampler were found on the PUF cartridge. A total of 70 hydrocarbons were identified in the extracts from this cartridge (Table 30), the majority of which were also found by adsorbent sampling. The concentrations of the hydrocarbons detected by this method were also very similar to the levels measured by the adsorbent cartridge technique, varying by about 10 to 20%. The largest variations in concentrations was in the higher molecular weight hydrocarbons.

Table 27. Hydrocarbons identified by thermal desorption methods from emissions above a 5 meter sweet solution gas flame (mg/m^3).

Compound	Amount
CYCLOPENTANE (DOT)	1.8
PENTANE (ACN)(DOT)	10.5
OXIRANE, 2-ETHYL-2-METHYL-	15.3
3-PENTEN-1-OL	48.8
CYCLOHEXANE(DOT	12.7
BENZENE (ACN)(DOT)	241.1
HEXANE, 3-METHYL-	9.8
HEPTANE (DOT)	29.5
1-PENTENE, 2,3-DIMETHYL-	1.8
CYCLOHEXANE, METHYL-	2.3
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	4.2
CYCLOPENTENE, 1,5-DIMETHYL-	1.8
CYCLOPENTENE, 4,4-DIMETHYL-	1.5
BENZENE, METHYL-	70.2
HEXANE, 2,5-DIMETHYL-	7.9
1-HEXENE, 2,5-DIMETHYL-	1.7
CYCLOHEXANE, 1,3-DIMETHYL-, CIS-	1.4
OCTANE (DOT)	19.3
1,3,5-CYCLOHEPTATRIENE	5.3
1H-PYRAZOLE, 1,3-DIMETHYL-	3.1
BENZENE, CHLORO-	1.7
BENZENE, ETHYL-	38.4
BENZENE, 1,3-DIMETHYL-	43.6
NONANE	4.1
BENZENE, ETHYNYL-	94.7
BENZENE, ETHENYL-	147.5
BENZENE, 1,2-DIMETHYL-	80.8
BENZENE, PROPYL-	1.0
BENZENE, (1-METHYLETHYL)-	8.9
BENZENE, 1-ETHYL-2-METHYL-	39.2
BENZENE, 1,3,5-TRIMETHYL-	5.9
OCTANE, 2,6-DIMETHYL-	2.3
BENZENE, 1,2,3-TRIMETHYL-	5.2
BENZENE, 1,2-PROPADIENYL-	0.7
BENZENE, 1-ETHYL-4-METHYL-	34.2
PHENOL (ACN)(DOT)	30.7
DECANE	2.4

Table 27. (continued)

Compound	Amount
BENZENE, 1,2,4-TRIMETHYL-	2.9
BENZENE, 1-ETHENYL-2-METHYL-	1.2
BENZENE, 2-PROPENYL-	2.4
BENZENE, 1-ETHYNYL-4-METHYL	40.1
BENZENE, 1-METHYL-3-PROPYL-	3.5
BENZENE, DIETHYL-	3.5
BENZENE, 1-METHYL-2-PROPYL-	2.1
1,3-CYCLOPENTANEDIONE, 2-ETHYL-	0.8
BENZENE, 1-ETHYL-2,3-DIMETHYL-	2.6
BENZENE, METHYL(1-METHYLETHYL)-	3.6
UNDECANE, 5-METHYL-	4.7
BENZENE, 1,2,3,4-TETRAMETHYL-	0.7
BENZENE, 1,2,3,5-TETRAMETHYL-	1.1
BUTYLAMINE, 1-ETHYL-N,N-DIMETHYL-	1.1
BENZENE, (1-METHYL-1-PROPENYL)-, (Z)-	1.3
1H-INDENE, 3-METHYL-	2.5
BENZENE, (1-METHYLENE-2-PROPENYL)-	3.1
NAPHTHALENE (ACN)(DOT)	127.4
DODECANE	4.1
PYRAZINE, 2-METHYL-6-(METHYLTHIO)-	0.1
NAPHTHALENE, 2-METHYL-	14.9
NAPHTHALENE, 1-METHYL-	1.8
1,1'-BIPHENYL	7.4
BIPHENYLENE	9.6
ACENAPHTHENE	0.7
NAPHTHALENE, 2-ETHENYL-	6.3
ACENAPHTHYLENE	55.2
1,4-EHENONAPHTHALENE, 1,4-DIHYDRO-	2.0
NAPHTHO[2,1-B]FURAN	0.4
1H-PHENALENE	2.8
9H-FLUORENE	32.6
9H-FLUORENE, 9-METHYL-	2.4
9H-FLUORENE, 9-METHYLENE-	1.7
PHENANTHRENE	1.3

Table 28. Hydrocarbons identified by solvent extraction methods in emissions above a 5 meter gaseous flame (mg/m^3).

Compound	Amount
BENZENE, 1,2-DIMETHYL-	5.63
BENZENE, ETHYNYL-	7.51
BENZENE, ETHENYL-	9.45
BENZALDEHYDE (ACN)(DOT)	8.22
BENZENE, (1-METHYLETHYL)-	3.56
BENZENE, 1-ETHYNYL-4-METHYL-	2.28
BENZENE, 1-ETHYL-2-METHYL-	7.20
PHENOL (ACN)(DOT)	8.72
BENZENE, 1,2,4-TRIMETHYL-	2.01
1H-INDENE	51.5
BENZENE, 1-METHYL-2-PROPYL-	2.10
BENZENE, 1-PROPYNYL-	4.54
PHENOL, 4-METHYL-	2.43
BENZENE, 1-METHYL-4-(1-METHYLETHYL)-	1.83
1H-INDENE, 1-METHYLENE-	8.24
BENZENE, 1,3-DIETHENYL-	4.37
BENZENE, (1-METHYL-2-CYCLOPROPEN-1-YL)-	33.69
AZULENE	60.54
NAPHTHALENE (ACN)(DOT)	195.93
2-PROPENAL, 3-PHENYL-	57.30
CINNOLINE, 3-METHYL-	1.54
1H-INDENE, 1-ETHYLIDENE-	3.72
NAPHTHALENE, 2-METHYL-	4.40
NAPHTHALENE, 1-METHYL-	3.57
1,4-METHANONAPHTHALENE, 1,4-DIHYDRO-	8.18
1,1'-BIPHENYL	51.36
BIPHENYLENE	68.19
1,4-ETHENONAPHTHALENE, 1,4-DIHYDRO-	21.43
NAPHTHALENE, 2-ETHENYL-	67.87
ACENAPHTHYLENE	91.40
ACENAPHTHENE	33.75
DIBENZOFURAN	5.36
1,1'-BIPHENYL, 3-METHYL-	4.66
1H-PHENALENE	41.24
9H-FLUORENE	77.39
9H-FLUORENE, 9-METHYL-	3.68
9H-FLUORENE, 1-METHYL-	3.54
BENZALDEHYDE, 4,6-DIHYDROXY-2,3-DIMETHYL-	11.29
BENZALDEHYDE, 2-HYDROXY-4-METHOXY-6-METHYL-	17.75

Table 28. (continued)

Compound	Amount
1,3,7,11-CYCLOTETRADECATETRAENE-5,9,13-TRIYNE	2.21
9H-FLUORENE, 3-METHYL-	21.55
BENZENE, 1,1'-(1,2-ETHYNEDIYL)BIS-	9.56
9H-FLUORENE, 4-METHYL-	18.28
9H-FLUORENE, 9-METHYLENE-	2.89
9H-FLUORENE, 2-METHYL-	3.30
BENZENE, 1,1'-ETHENYLIDENEBIS-	13.13
9H-FLUOREN-9-ONE	18.18
ANTHRACENE	51.54
PHENANTHRENE, 4-METHYL-	0.90
ANTHRACENE, 1-METHYL-	5.11
1H-INDENE, 1-PHENYL-	3.27
ANTHRACENE, 2-METHYL-	6.96
PHENANTHRENE, 2-METHYL-	7.15
1H-PHENALEN-1-ONE	23.04
4H-CYCLOPENTA[DEF]PHENANTHRENE	44.08
NAPHTHALENE, 2-PHENYL-	25.89
1,4-ETHENOANTHRACENE, 1,4-DIHYDRO-	3.10
NAPHTHALENE, 1,8-DI-1-PROPYNYL-	2.28
NAPHTHALENE, 1-PHENYL-	6.11
FLUORANTHENE	63.25
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	23.96
PYRENE	79.14
11H-BENZO[A]FLUORENE	3.79
PYRENE, 4-METHYL-	16.09
TRIPHENYLENE	1.79
PYRENE, 2-METHYL-	14.76
PYRENE, 1-METHYL-	10.06
BENZO[C]PHENANTHRENE	13.11
BENZO[GHI]FLUORANTHENE	44.47
CYCLOPENTA[CD]PYRENE	86.71
BENZENE, 1,2-DIPHENOXY-	17.85
BENZO[K]FLUORANTHENE	11.50
BENZO[E]PYRENE	0.54
BENZO[A]PYRENE	1.18
PERYLENE	1.87
BENZO[GHI]PERYLENE	1.50
DIBENZO[DEF,MNO]CHRYSENE	0.64
CORONENE	0.02

Table 29. Hydrocarbons identified in emissions above a 5 meter sweet solution gas flame and collected on a glass fibre filter (mg/m^3).

Compound	Amount
BENZENE, ETHYL-	3.08
BENZENE, 1,3-DIMETHYL-	2.75
BENZENE, 1,2-DIMETHYL-	3.88
BENZENE, PROPYL-	0.81
BENZENE, (1-METHYLETHYL)-	3.75
BENZENE, 1-ETHYL-2-METHYL-	1.67
BENZENE, 1,3,5-TRIMETHYL-	0.88
BENZENE, 1,2,4-TRIMETHYL-	4.71
BENZENE, 1-METHYL-3-PROPYL-	0.42
BENZENE, DIETHYL-	0.40
BENZENE, 1-METHYL-2-PROPYL-	1.77
FLUORANTHENE	1.26
PYRENE	0.18
11H-BENZO[B]FLUORENE	0.88
PYRENE, 4-METHYL-	0.95
PYRENE, 2-METHYL-	2.87
PYRENE, 1-METHYL-	3.28
BENZO[C]PHENANTHRENE	0.65
BENZO[GHI]FLUORANTHENE	13.70
CYCLOPENTA[CD]PYRENE	5.14
CHRYSENE	0.19
TRIPHENYLENE	1.47
7H-BENZ[DE]ANTHRACEN-7-ONE	12.57
BENZO[K]FLUORANTHENE	0.13
BENZO[E]PYRENE	0.53
BENZO[A]PYRENE	1.21
PERYLENE	3.31
CHRYSIN	2.18
INDENO[1,2,3-CD]PYRENE	9.03
BENZO[GHI]PERYLENE	0.85
DIBENZO[DEF,MNO]CHRYSENE	0.20

Table 30. Hydrocarbons identified in emissions above a 5 meter sweet solution gas flame and collected on a polyurethane foam cartridge (mg/m^3).

Compound	Amount
BENZENE, ETHYL-	1.06
BENZENE, 1,3-DIMETHYL-	2.73
BENZENE, 1,2-DIMETHYL-	2.05
BENZENE, (1-METHYLETHYL)-	6.40
BENZENE, 1-ETHYL-2-METHYL-	2.65
BENZALDEHYDE (ACN)(DOT)	131.60
PHENOL (ACN)(DOT)	10.33
1H-INDENE	46.02
1H-INDENE, 1-METHYLENE-	1.61
BENZENEMETHANOL	136.66
HEXANOIC ACID, 2-ETHYL-	47.62
BENZENE, 1,3-DIETHENYL-	0.60
BENZENE, (1-METHYL-2-CYCLOPROPEN-1-YL)-	5.61
AZULENE	49.65
NAPHTHALENE (ACN)(DOT)	172.64
OCTANOIC ACID	7.18
NONANOIC ACID	3.98
NAPHTHALENE, 2-METHYL-	6.27
NAPHTHALENE, 1-METHYL-	7.85
1H-INDENE, 1-ETHYLIDENE-	2.93
1,1'-BIPHENYL	57.55
DECANOIC ACID	9.52
BIPHENYLENE	99.12
NAPHTHALENE, 2-ETHENYL-	48.59
ACENAPHTHYLENE	139.72
ACENAPHTHENE	60.66
DIBENZOFURAN	3.79
BENZENE, 1,1'-(1,2-ETHANEDIYL)BIS-	1.99
DODECANOIC ACID	7.75
1,1'-BIPHENYL, 3-METHYL-	5.23
1H-PHENALENE	56.08
9H-FLUORENE	95.66
DODECANOIC ACID	4.58
BENZALDEHYDE, 4,6-DIHYDROXY-2,3-DIMETHYL-	18.57
BENZALDEHYDE, 2-HYDROXY-4-METHOXY-6-METHYL-	17.43
1,3,7,11-CYCLOTETRADECATETRAENE-5,9,13-TRIYNE	2.65
PHENANTHRENE	1.22
9H-FLUORENE, 9-METHYLENE-	4.85
9H-FLUORENE, 2-METHYL-	4.34

Table 30 (concluded)

Compound	Amount
BENZENE, 1,1'-ETHENYLIDENEBIS-	12.20
BENZENE, ETHYLPHENOXY-	2.74
TETRADECANOIC ACID	5.66
9H-FLUOREN-9-ONE	18.10
ANTHRACENE	74.18
BENZENE, 1,1'-(1,2-ETHYNEDIYL)BIS-	7.46
9H-FLUORENE, 9-ETHYLIDENE-	1.55
NAPHTHALENE, 1-PHENYL-	7.30
9H-FLUORENE, 9-ETHYLIDENE-	2.45
ANTHRACENE, 2-METHYL-	2.88
PHENANTHRENE, 9-METHYL-	3.78
1H-PHENALEN-1-ONE	25.83
4H-CYCLOPENTA[DEF]PHENANTHRENE	71.39
FLUORANTHENE	50.85
PYRENE	83.57
11H-BENZO[B]FLUORENE	0.86
PYRENE, 4-METHYL-	9.50
PYRENE, 1-METHYL-	8.21
BENZO[C]PHENANTHRENE	16.60
BENZO[GHI]FLUORANTHENE	22.08
CYCLOPENTA[CD]PYRENE	60.96
CHRYSENE	0.11
BENZO[K]FLUORANTHENE	15.84
BENZO[E]PYRENE	1.24
BENZO[A]PYRENE	2.21
CHRYSIN	0.89
PERYLENE	0.25
DIBENZO[DEF,MNO]CHRYSENE	0.32
BENZO[GHI]PERYLENE	0.96
INDENO[1,2,3-CD]PYRENE	0.60
DIBENZO[DEF,MNO]CHRYSENE	0.23
CORONENE	0.12

5.3.1.2 Effects of liquid fuel directed to flare

The second objective of the field flare study was to examine the effect on emissions when additional liquid fuel was directed to the flare along with the solution gas stream. Two different liquid hydrocarbon streams were directed to the flare to examine these effects. The first was directed from the separator where both liquid fuel and some water were contained, and the second was from a location downstream of the separator after the majority of water had been removed. The amount of these liquids directed to the flare could not be measured at the time of testing, but in both cases was sufficient to produce a 5 to 6 metre long flame.

The results of the emission characterization as provided by the on-site analyzers showed very little difference between the emissions created during these two tests. The combustion efficiency measurements were almost identical at 62.2 and 62.7% respectively for the two tests (Table 31). One of the greatest differences was in the larger amount of particulate carbon produced by the liquid hydrocarbon stream containing no water. The carbon content was approximately 33% greater in the emissions from this flame compared to when the liquid fuel stream containing water was directed to the flare. The overall results from these tests were similar to those obtained for emissions when just solution gas was directed to the flare. Combustion efficiencies were however, about 5% better for the solution gas flame and carbon particles were up to 50% lower, than for the worst case encountered when directing the additional liquid hydrocarbons to the flare.

5.3.1.3 Effects of varying liquid fuel levels in the knock-out drum

Flare testing, approximately one year after previous tests were completed, was carried out with three different levels of liquid hydrocarbons contained in the knock-out drum. The liquid levels were governed by an automatic control system used in conjunction with the knock-out drum which allowed level build-up to a maximum depth of 75 cm before pumping it down to the lowest level of approximately 25 cm of liquid. Tests were carried out at liquid levels of 69 cm (considered full), 48 cm (mid-level), and 9 cm (low-level), as measured by the battery operator. The following is a summary of the results obtained while flaring with different levels of hydrocarbons in the knock-out drum. This data also served to compare with what was found in the previous year at this site.

Table 31. On-site characterization of emissions collected above the flame with condensate added from the separator and recovered condensate lines.. (Values in mg/m^3 except where otherwise noted.)

Liquid fuel	From Separator	Condensate Line
O_2 %	19.9	20.1
N_2 %	78.6	78.3
H_2	30	150
CO	30	35
CO_2	4300	4980
Carbon	88	118
Methane	121	144
Ethylene	26	43
Acetylene	22	34
Benzene	141	137
Toluene	22	31
Xylenes	37	44
Styrene	91	102
Ethynyl Benzene	106	96
Naphthalene	102	109
Other Hydrocarbons	95	106
Combustion Efficiency (%)	62.2	62.7

Flare testing in all cases was carried out at an average gas flow of approximately 6 m^3/min which resulted in flame lengths averaging 5 metres. Emission samples were collected over an approximate 30 minute period at distances of 4 to 5 metres beyond the visible end of the flame. Wind speeds averaged between 1.5 to 1.9 m/s during the course of these tests producing moderately turbulent but very luminous flames with visible amounts of carbon particles in the resulting emissions.

During the course of these tests carried out at this site, samples of the vapors from the top of the knock-out drum, not in-line to the flare, were drawn off and analyzed using the equipment contained in the on-site trailer. The results are given in Table 32 which shows that approximately 20 % of the hydrocarbons in this vapor are larger than ethane. A very small trace of hydrogen sulfide was detected in this sample.

Table 32. Composition (%) of solution gas being flared at the sweet oilfield battery site as sampled at the liquid knock-out drum.

Gases		Hydrocarbons	
Hydrogen	0.1	C_1	69.2
Oxygen	0.1	C_2	9.2
Nitrogen	1.1	C_3	5.5
Carbon dioxide	1.6	C_4	4.6
Hydrogen sulfide (ppm)	1.5	C_5	3.5
		C_6	2.0
		C_7	1.3
		C_8	1.0
		C_{9+}	0.8

The on-site chemical characterization of the emissions sampled in the plumes from these flames is contained in Table 33. These results showed that there was very little difference in the composition of the emissions from flare testing while the liquid hydrocarbon level in the knock-out drum was either at the highest or mid-level point. Measured combustion efficiencies were between 64 to 65% during these two tests. These values were very close to those measured in the previous year at this

Table 33. On-site characterization of hydrocarbon emissions from the sweet oilfield battery flare collected 4 to 5 metres from the end of the flame with different liquid HC's levels in the knock-out drum (mg/m^3 except where otherwise noted)

Knock-out levels (cm)	69	48	9
O_2%	20.4	20.8	20.8
N_2 %	78.2	77.9	78.4
H_2	15.0	20.0	10.0
CO	18.3	15.7	9.5
CO_2	5050	4890	4720
Carbon	57.9	54.2	32.2
Methane	109.1	103.8	83.7
Ethylene	31.2	29.0	22.0
Acetylene	48.8	53.7	43.8
Ethane	12.3	9.9	7.0
C_3 HC's	14.7	11.7	8.1
C_4 HC's	7.5	6.4	3.3
Benzene	110.8	116.5	70.6
Toluene	20.0	18.2	10.3
Xylenes	30.9	29.8	17.9
Styrene	82.6	75.5	57.2
Ethynyl benzene	95.3	79.6	59.0
Naphthalene	87.1	77.2	60.7
Other Hydrocarbons	147.5	128.5	109.6
Combustion Efficiency (%)	63.9	65.0	71.0

site (66 to 67%). Methane and benzene were found in the highest concentrations, followed by ethynyl benzene, naphthalene, styrene, and acetylene. Carbon particles were measured at concentrations of between 54 to 58 mg/m^3 in these emissions. In comparison, emissions from the flare test conducted with the lowest level of liquid hydrocarbons in the knock-out drum contained on average, approximately 25% lower concentrations of the measured hydrocarbons and about 40% less carbon particles. This resulted in a combustion efficiency 6 to 7% better than what occurred when flaring with greater amounts of liquid hydrocarbons in the knock-out drum.

Further examination of hydrocarbons contained in these emissions and identified by GC/MS determined that between 80 to 95 compounds were present during any one test. In these samples, benzene, styrene, ethynyl benzene and naphthalene were the most abundant hydrocarbon products found in the emissions during the two tests with the larger amounts of liquid hydrocarbons in the knock-out drum. These products ranged in concentration from 80 to 145 mg/m^3. In the test carried out with the knock-out drum nearer to empty, benzene was no longer the most abundant compound found in the emissions. Ethynyl benzene and styrene were the most abundant, followed by benzene, naphthalene, and toluene, in amounts ranging from 25 to 100 mg/m^3. Tables 34 and 35 contain lists of compounds that were identified by thermal desorption and solvent extraction methods in emissions from the flare tested while the knock-out drum was approximately half full, and are representative of the hydrocarbons identified during all three tests.

5.3.2 Sour Oilfield Battery Flare Tests

The sour oilfield battery site chosen for this testing was estimated to contain between 20 to 25 % hydrogen sulfide. This battery was fed by only two wells, producing oil, sour solution gas, and co-produced water. The major difference in operations at this battery site compared to the sweet battery site was that all gas produced at the sour site was directed to flare, while the majority of gas produced at the sweet site was captured and directed to a gas plant. The solution gas at the sour oilfield battery site was also much drier, i.e. there was no appreciable amount of liquid hydrocarbons that passed from the separator into the knock-out drum. The drum was emptied only once

Table 34. Hydrocarbons identified in emissions from the sweet oilfield battery flare operating with 48 cm of liquid HC's in the knock-out drum and using thermal desorption methods (mg/m³).

Compound	Amount
CYCLOPENTANE (DOT)	2.6
PENTANE (ACN)(DOT)	12.8
3-PENTEN-1-YNE, (Z)-	19.3
HEXANE (DOT)	8.5
CYCLOHEXANE(DOT	9.3
1,3-CYCLOHEXADIENE	9.6
BENZENE (ACN)(DOT)	144.5
HEPTANE (DOT)	7.4
CYCLOHEXANE, METHYL-	1.4
1,5-HEXADIYNE	48.2
BENZENE, METHYL-	27.5
CYCLOHEXANE, 1,4-DIMETHYL-, TRANS-	1.4
CYCLOHEXANE, 1,2-DIMETHYL-, TRANS-	1.2
OCTANE (DOT)	3.6
1,3,5-CYCLOHEPTATRIENE	2.5
BENZENE, ETHYL-	13.7
CYCLOHEXANE, ETHYL-	1.7
CYCLOHEXANE, 1,1,3-TRIMETHYL-	1.4
CYCLOHEXANE, 1,2,3-TRIMETHYL-, (1.ALPHA.,2.ALPHA.,3.BETA.)-	0.9
BENZENE, 1,3-DIMETHYL-	9.3
BENZENE, 1,2-DIMETHYL-	7.4
BENZENE, ETHYNYL-	94.8
BENZENE, ETHENYL-	82.1
NONANE	2.1
BENZENE, (1-METHYLETHYL)-	1.2
1,3,5,7-CYCLOOCTATETRAENE	1.4
BENZENE, 2-PROPENYL-	1.3
BENZENE, PROPYL-	1.3
BENZALDEHYDE (ACN)(DOT)	18.7
BENZENE, 1,2-PROPADIENYL-	1.2
BENZENE, 1-ETHENYL-3-METHYL-	4.9
DECANE	1.0
PHENOL (ACN)(DOT)	26.4
BENZENE, 1-ETHYL-2-METHYL-	2.2
BENZENE, 1-ETHENYL-2-METHYL-	3.1
CYCLOHEXENE, 4-ETHENYL-1,4-DIMETHYL-	1.3
1H-INDENE, 2,3-DIHYDRO-	1.2
BENZENE, 1-ETHYNYL-4-METHYL-	34.5
BENZENE, 1-PROPYNYL-	5.6
BENZENE, 1,2,3-TRIMETHYL-	2.9
AZULENE	6.1
BENZENE, 1,3-DIETHENYL-	2.8
1H-INDENE, 1-METHYLENE-	1.7
BENZENE, (1-METHYL-2-CYCLOPROPEN-1-YL)-	1.8
1H-INDENE, 1-METHYL-	2.6
NAPHTHALENE (ACN)(DOT)	88.7
NAPHTHALENE, 2-METHYL-	6.8
NAPHTHALENE, 1-METHYL-	5.2
1,1'-BIPHENYL	16.1
BIPHENYLENE	19.4
ACENAPHTHENE	1.8
ACENAPHTHYLENE	23.2
9H-FLUORENE	3.8

Table 35. Hydrocarbons identified in emissions from the sweet oilfield battery flare operating with 48 cm of liquid HC's in the knock-out drum and using solvent extraction methods (mg/m^3).

Compound	Amount
NONANE	0.41
BENZALDEHYDE (ACN)(DOT)	0.53
BENZENE, 1-ETHYL-2-METHYL-	0.13
1H-INDENE, 2,3-DIHYDRO-	0.34
DECANE	1.72
BENZENE, 1-ETHYNYL-4-METHYL-	9.83
BENZENE, 1,3-DIETHENYL-	1.27
1H-INDENE, 1-METHYLENE-	0.28
AZULENE	21.20
BENZENE, (1-METHYL-2-CYCLOPROPEN-1-YL)-	11.47
1H-INDENE, 1-METHYL-	1.66
NAPHTHALENE (ACN)(DOT)	99.39
BENZALDEHYDE, O-METHYLOXIME	0.27
1H-INDEN-1-ONE, 2,3-DIHYDRO-	0.74
NAPHTHALENE, 2-METHYL-	9.25
NAPHTHALENE, 1-METHYL-	6.18
1H-INDENE, 1-ETHYLIDENE-	1.22
1,1'-BIPHENYL	58.70
NAPHTHALENE, 2-ETHYL-	1.87
BIPHENYLENE	42.81
NAPHTHALENE, 2-ETHENYL-	7.32
ACENAPHTHYLENE	7.15
ACENAPHTHENE	2.93
DIBENZOFURAN	0.88
1,1'-BIPHENYL, 3-METHYL-	0.31
1H-PHENALENE	21.01
9H-FLUORENE	41.09
9H-FLUORENE, 9-METHYL-	1.07
BENZALDEHYDE, 4,6-DIHYDROXY-2,3-DIMETHYL-	1.16
9H-FLUORENE, 9-METHYLENE-	1.07
9H-FLUORENE, 3-METHYL-	3.05
PHENANTHRENE	10.01
BENZO[C]CINNOLINE	2.06
ANTHRACENE	42.11
1H-INDENE, 1-(PHENYLMETHYLENE)-	1.94
9H-FLUORENE, 9-ETHYLIDENE-	0.89
1H-PHENALEN-1-ONE	1.86
4H-CYCLOPENTA[DEF]PHENANTHRENE	3.50
NAPHTHALENE, 2-PHENYL-	1.98
NAPHTHALENE, 1-PHENYL-	1.82
9,10-ANTHRACENEDIONE	0.94
5H-DIBENZO[A,D]CYCLOHEPTENE, 5-METHYLENE-	0.75
NAPHTHALENE, 1,8-DI-1-PROPYNYL-	1.14
FLUORANTHENE	51.35
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	2.07
PYRENE	32.37
11H-BENZO[A]FLUORENE	2.25
PYRENE, 4-METHYL-	9.13
PYRENE, 1-METHYL-	8.38
BENZO[GHI]FLUORANTHENE	10.16
CYCLOPENTA[CD]PYRENE	29.77
BENZ[A]ANTHRACENE	17.33
CHRYSENE	2.12
BENZENE, 1,2-DIPHENOXY-	1.94
METHANONE, (6-METHYL-1,3-BENZODIOXOL-5-YL)PHENYL-	0.95
BENZO[E]PYRENE	0.71
BENZO[A]PYRENE	1.03
PERYLENE	0.62
INDENO[1,2,3-CD]PYRENE	0.15
BENZO[GHI]PERYLENE	0.26
DIBENZO[DEF,MNO]CHRYSENE	0.15
CORONENE	0.08

per year, which had occurred a week prior to the flare testing. The following is a summary of the results obtained from this site.

5.3.2.1 Flare gas composition

During the course of the tests that were carried out here, samples were also obtained from the top of the knock-out drum prior to being directed to the flare stack. These samples were analyzed using the on-site equipment with the results of these analyses contained in Table 36.

Table 36. Composition of solution gas being flared at the sour oilfield battery site as sampled at the liquid knock-out drum (%).

Gases		Hydrocarbons	
Hydrogen sulfide	22.8	C1	45.4
Hydrogen	0.2	C2	10.7
Oxygen	0.0	C3	5.7
Nitrogen	8.2	C4	2.4
Carbon dioxide	2.0	C5	1.7
		C6	0.5
		C7	0.2
		C8	0.1
		C9+	0.1

5.3.2.2 Emission characterization

The solution gas flow rate at the sour oilfield battery site was constant at approximately 0.45 m^3 per minute. This flow directed through the smaller diameter flare tip produced an average flame length of approximately 1.5 to 2 metres. Sampling was carried out at a distance of 1.5 to 2 metres from the visible end of the flame and over a period of 80 minutes, 60 of which was considered within the plume. During the time of sampling, winds were from the NW at a mean speed of 2 m/s, gusting to a maximum of 5.5 m/s. The resulting flame was almost horizontal and much less visible and slightly more turbulent than flames sampled at the sweet battery site. There was no visible amount of black carbon particles in the plume of this flame however, small amounts of white puffs of smoke could be detected.

The on-site characterization of emissions from this plume consisted of both carbon as well as sulfur-containing compounds. The hydrocarbon characterization of the sour gas flare is contained in Table 37. Carbon containing compounds were found in much lower abundance in these emissions compared to amounts detected in the sweet oilfield battery flare emissions. Aromatic and aliphatic hydrocarbons detected by the on-site analyzers were up to 50% lower than concentrations found in emissions at the sweet battery site. The carbon content of the flame was also close to half, with measured values of 18 mg/m^3. The resulting combustion efficiency of this flame (84%) was approximately 20% higher than values measured at the sweet battery flare. The comparative differences in measurements obtained from the emissions at these two sites is most likely attributable to the differences in the amounts of liquid hydrocarbons that are directed to each of these flares.

The analyses for sulfur compounds by the on-site chromatograph detected compounds such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2), carbon disulfide (CS_2), and lower molecular weight mercaptans and sulfides. The results of these analyses are contained in Table 38. The most abundant sulfur compound found in these emissions, aside from SO_2, was carbon disulfide. It was detected in concentrations of about 480 mg/m^3. The combustion efficiency of this flame as measured by the sulfur mass balance was 82.4%, compared to the 84.1% measured by the carbon mass balance.

Table 37. On-site characterization of hydrocarbon emissions from the sour oilfield battery flare, collected 1.5 to 2 metres from the end of the flame. (Values in mg/m³ except where otherwise noted).

Temperature (ºC)	100-150
O_2 %	19.5
N_2 %	78.1
H_2	150.0
CO	8.0
CO_2	6870.0
Carbon	18.2
Methane	83.1
Ethylene	6.0
Acetylene	36.4
Ethane	4.9
C_3 HC's	5.7
C_4 HC's	2.9
Benzene	24.4
Toluene	12.4
Xylenes	6.7
Styrene	22.7
Ethynyl benzene	18.4
Naphthalene	31.2
Other Hydrocarbons	111.0
Combustion Efficiency (%)	84.1

Table 38. On-site characterization of sulfur compound emissions from the sour oilfield battery flare collected 1.5 to 2 metres from the end of the flame. (mg/m³).

Temperature (ºC)	100-150
Sulfur dioxide	6910
Hydrogen sulfide	126
Carbonyl sulfide	64
Carbon disulfide	482
Others	210
Combustion Efficiency (%)	82.4

5.3.2.3 Volatile hydrocarbons

Emission samples collected from the plume of this flame and on adsorbents, were thermally desorbed and analyzed by the GC/MS system. This fraction contained 31 identified compounds, 9 of which were sulfur compounds (Table 39). The major components of this volatile fraction were carbon disulfide, thiophene, benzothiophene, and benzene, ranging in concentrations from approximately 65 to 450 mg/m³. The majority of the compounds identified were aromatic hydrocarbons, along with the sulfur compounds, nitrogen containing compounds and some oxygenated compounds.

5.3.2.4 Non-volatile hydrocarbons

The adsorbent samples that were solvent extracted contained the less volatile hydrocarbons that were also analyzed by the GC/MS system. The compounds found in this fraction ranged from some substituted benzenes to polycyclic aromatic hydrocarbons, a number of which were sulfur containing compounds. A large number of the hydrocarbons detected here were the same as those found in emissions from flaring of non sulfur-containing fuels.

A total of 54 hydrocarbons were identified in this fraction, 9 of which were also identified in the more volatile fraction (Table 40). The additional 43 compounds identified were mainly polycyclics, sulfur compounds (thiophenes), and oxygenated compounds. Elemental sulfur was detected in the largest concentration at 157 mg/m³, followed by pyrene, dibenzothiophene, biphenyl, and naphthalene, all near 80 mg/m³.

Table 39. Hydrocarbons and sulfur compounds identified in emissions from the sour oilfield battery flare, using thermal desorption methods (mg/m^3).

Compound	Amount
CARBON DISULFIDE (ACN)(DOT)	453.3
THIOPHENE	179.2
BENZENE (ACN)(DOT)	64.3
BENZENE, METHYL-	20.5
THIOPHENE, 3-METHYL-	2.7
2-PROPENOIC ACID, 2-METHYL-, ETHYL ESTER	2.2
BENZENE, ETHYL-	7.1
BENZENE, 1,3-DIMETHYL-	6.5
BENZENE, ETHYNYL-	41.9
BENZENE, ETHENYL-	34.4
BENZENE, METHOXY-	1.4
2(5H)-THIOPHENONE	31.3
2-THIAZOLAMINE	0.9
2H-IMIDAZOLE-2-THIONE, 1,3-DIHYDRO-	1.1
TRICYCLO[4.2.0.02,4]OCT-7-EN-5-ONE	0.2
BENZALDEHYDE (ACN)(DOT)	12.6
BENZONITRILE	1.3
BENZOFURAN	3.6
DECANE	1.2
PHENOL (ACN)(DOT)	12.2
BENZENE, 1-ETHENYL-2-METHYL-	1.7
BENZENE, 1-ETHYNYL-4-METHYL-	13.8
BENZALDEHYDE, 2-HYDROXY-	1.3
BENZENE, BUTYL-	0.9
BENZENE, 1-PROPYNYL-	2.1
ETHANONE, 1-PHENYL-	61.9
1,2,4-TRITHIOLANE	0.9
UNDECANE	0.6
1H-INDENE, 1-METHYLENE-	0.2
NAPHTHALENE (ACN)(DOT)	61.5
AZULENE	34.4
BENZO[B]THIOPHENE	156.6
NAPHTHALENE, 2-METHYL-	1.5
NAPHTHALENE, 1-METHYL-	0.9
1,1'-BIPHENYL	8.0
DIBENZOTHIOPHENE	6.6

Table 40. Hydrocarbons and sulfur compounds identified in emissions from the sour oilfield battery flare, using solvent extraction methods (mg/m^3).

Compound	Amount
BENZENE, ETHENYL-	0.77
BENZALDEHYDE (ACN)(DOT)	0.55
ETHANONE, 1-PHENYL-	0.38
HEXANOIC ACID, 2-ETHYL-	5.04
NAPHTHALENE (ACN)(DOT)	77.11
BENZO[B]THIOPHENE	46.71
BENZOIC ACID (ACN)	6.39
BENZO[B]THIOPHENE, 4-METHYL-	8.85
NAPHTHALENE, 2-METHYL-	14.25
NAPHTHALENE, 1-METHYL-	10.78
PHTHALIC ANHYDRIDE	2.29
1(3H)-ISOBENZOFURANONE	1.51
1,1'-BIPHENYL	77.99
NAPHTHALENE, 1-ETHYL-	6.69
THIOPHENE, 2-PHENYL-	6.97
THIOPHENE, 3-PHENYL-	11.99
NAPHTHALENE, 2,3-DIMETHYL-	5.38
BIPHENYLENE	13.15
INDENE-1,7(4H)-DIONE, 3A,7A-DIHYDRO-5-METHYL-	6.52
ACENAPHTHENE	5.22
NAPHTHALENE, 1-ISOCYANO-	1.82
DIBENZOFURAN	7.12
2H-1-BENZOPYRAN-2-ONE, 7-METHYL-	5.55
1H-INDENE, 5-NITRO-	5.51
DODECANOIC ACID	11.09
9H-FLUORENE	54.21
ETHANONE, 1-(2-NAPHTHALENYL)-	27.98
BENZO[B]THIOPHENE, 2-ETHYL-7-METHYL-	18.55
BENZENE, 1,1'-METHYLENEBIS-	15.65
9H-FLUORENE, 4-METHYL-	1.62
HEXATHIEPANE	28.23
BENZO[C]CINNOLINE	3.81
DIBENZOTHIOPHENE	82.15
PHENANTHRENE	34.09
BENZENE, 1,1'-(1-BUTEN-3-YNE-1,4-DIYL)BIS-	4.00
CINNOLINE, 6-METHYL-3-PHENYL-	5.66
4H-CYCLOPENTA[DEF]PHENANTHRENE	3.21
HEXADECANOIC ACID	4.53
NAPHTHALENE, 2-PHENYL-	3.28
9,10-ANTHRACENEDIONE	1.02
BENZENE, 1,1'-ETHYLIDENEBIS[3,4-DIMETHYL-	2.43
SULFUR, MOL. (S8)	157.35
FLUORANTHENE	14.10
PYRENE	83.26
BENZENE, 1,1'-(1,3-BUTADIYNE-1,4-DIYL)BIS-	5.39
OCTADECANOIC ACID	3.92
BENZO[B]NAPHTHO[2,3-D]THIOPHENE, 9,10-DIHYDRO-7-METHYL-	9.49
CYCLOPENTA[CD]PYRENE	9.66
CHRYSENE	2.40
BENZENE, 1,2-DIPHENOXY-	0.13
DINAPHTHO[2,3-B:2',3'-D]THIOPHENE, 12,13-DIHYDRO-	1.44
BENZO[C]THIOPHENE, 1,3-DIPHENYL-	0.80
BENZO[A]PYRENE	0.46
DINAPHTHO[2,1-B:1',2'-D]THIOPHENE	0.47

6.0 SUMMARY AND CONCLUSIONS

Investigations focused on the characterization of emissions from flaring at oilfield battery sites in Alberta were carried out in three phases with overall objectives to:

- determine the extent to which flared gases are left unburned;
- characterize all products of combustion in the emissions; and
- determine the factors which contribute to incomplete combustion and the extent of their contribution, including the effects of entrained liquids and strong crosswinds.

The research program developed to meet these objectives consisted of laboratory, pilot scale, and field scale studies. The first phase laboratory studies included the development and testing of both flaring and sampling systems as well as the analytical equipment required in the characterization. They also served to identify the types of hydrocarbons that are produced by these flames. The second phase pilot scale studies were used to test these developed systems on a larger scale with more complex fuel mixtures and in cross winds, make modifications where necessary, and substantiate the findings of the laboratory scale studies. The final field phase consisted of flare emissions characterization for both hydrocarbons and sulfur-containing compounds produced from flares operating under various conditions, at two different oilfield battery sites in Alberta.

6.1 Phase 1, Laboratory Studies

The laboratory flare testing program consisted of an evaluation of various gas, liquid, and co-flowing gas/ liquid fuel streams. These pure fuels were flared and tested in a specifically designed chamber, under ideal conditions. The results of these investigations are summarized in the following.

- Methane was found to burn with a very high combustion efficiency, the most efficient of which was under laminar flow (99.98%), followed by the transitional flow (99.91%), and turbulent flow (99.14%). Hydrocarbon concentrations in the emissions above the turbulent flame were approximately double the values detected above the transitional flame and four times amounts above the laminar flame.

- Acetylene, ethylene, and benzene were the major constituents detected within these flames. They represent over 10% of the conversion from the methane fuel prior to combustion. Ethenyl benzene, ethynyl benzene, and naphthalene were also major components while polycyclic aromatic hydrocarbons were detected in lesser concentrations within these flames. The majority of these hydrocarbons produced by the pyrolytic reactions within these flames were effectively destroyed in the outer combustion zone and resulted in high combustion efficiency measurements.
- Propane produced a sooty and less efficient flame under similar conditions used in the methane flame experiments. The carbon particles that were produced along with the higher concentrations of hydrocarbons found in the emissions were the major cause for the reduced efficiency measurements of this flame to approximately 98.3%.
- Laboratory scale flaring of natural gas or industrial gas streams appeared to have little effect on the overall combustion efficiency of the flame when compared to pure methane flames (99.8)%. There were, however, nearly twice as many hydrocarbon compounds identified in samples obtained both from within and above the natural gas flame as compared to the methane flame.
- Flaring of natural gas in the open atmosphere under turbulent conditions reduced the combustion efficiency of the flame to 96%. The reduction was caused primarily by the presence of unburned methane and carbon monoxide in the emissions. The addition of cross-winds to this flame helped to more completely combust the methane and reduce carbon monoxide concentrations, thereby increasing the efficiency to over 99%.
- Pure liquid fuels were much more difficult to burn, resulting in high concentrations of unburned fuel in their emissions. These flames also produced many hydrocarbons that escaped unburned that were found in higher concentrations than those detected in gaseous flare emissions. They also produced higher concentrations of carbon particles and carbon monoxide, particularly while burning toluene.
- Addition of liquid fuels and condensates to pure gas streams has the greatest effect on impairing the ability of the resulting flame to efficiently combust all of the hydrocarbon fuel as well as the hydrocarbons that are produced within these flames.

- The majority of the hydrocarbons identified in emissions from co-flowing gas/liquid fuelled flares were found at much higher concentrations than what was detected in emissions above methane and natural gas flames.
- The degree to which the efficiency of combustion is affected by the addition of liquid fuels to a gaseous stream is dependent on both the amount and type of liquid fuel in the co-flowing stream. The addition of 15% heptane to a pure methane flame reduced the efficiency to between 96 and 98%. At 23% heptane, the efficiency was reduced to 93% and when a 32% mixture with heptane is flared, the measured combustion efficiency was 81%.
- The hydrocarbons produced by reactions within all of the flames examined in the laboratory tests contained a high degree of unsaturation. Ethylene and acetylene were produced in largest concentrations within the flames. Further unsaturation was found in a number of the aliphatic hydrocarbon chains connected to benzene and naphthalene rings, including large quantities of ethynyl and ethenyl benzene. These unsaturated compounds were not found in any significant quantities in the emissions from flaring gaseous fuels, but were found in the emissions from both liquid and co-flowing gas liquid fuelled flames.

6.3 Phase 2, Pilot Scale Studies

Phase 2 of the study consisted of flare testing using a small scale pilot flare in the open atmosphere to examine the effects of slightly larger scale flaring and to address the problems of sampling and analytical procedures that might be encountered in subsequent field testing. Both multi-probes and hood sampling systems were used to examine variability of emission plumes. Natural gas and co-flowing natural gas with a condensate fuel obtained from an oil and gas production facility were primarily used in these tests. The major findings of these tests are contained in the following.

- Flaring of natural gas under very low wind conditions produced a fairly narrow emission plume along the vertical axis from the flame. The emissions from co-flowing natural gas/condensate flames, however were found to diffuse much wider and more rapidly and therefore were more uniform in concentrations across the plume above these flames. Comparison of emission samples collected above this flame using both multi-probe and hood samplers revealed that the results obtained from the hood sampler closely approximated the results obtained from the centre probe.

- Flaring of natural gas in the pilot-sized flare was found to produce higher concentrations of low molecular weight aromatics and other hydrocarbons compared to similar laboratory tests. These higher concentrations of hydrocarbons were associated with combustion efficiency measurements of approximately 98%.
- Combustion efficiencies measured above co-flowing gas/condensate flames were consistently between 88 to 90%, primarily as a result of the presence of unburned hydrocarbons from the condensate along with the higher levels of hydrocarbons produced by reactions within the flames, that escaped into the emissions.
- Cross-winds reduced the combustion efficiency of the co-flowing natural gas/condensate flame by approximately 4 to 6%. The major constituents found in these emissions were the unburned condensate components along with hydrocarbons that were produced within the flame.
- The lower molecular weight aromatics and other hydrocarbons were found in higher concentrations than any comparative levels measured in similar co-flowing flames tested in laboratory experiments.
- A total of 188 hydrocarbons were identified in the emissions above these flames, many of which were polycyclic aromatic hydrocarbons. The concentrations at which they were detected were also greater than levels measured in any of the previous similar laboratory experiments.

6.3 Phase 3, Field Studies

The third phase of these studies was focused on industrial flaring operations at oilfield battery sites, typical of the kind where the majority of solution gas flaring occurs in Alberta. Two different sites were examined; one, a sweet oilfield battery with no hydrogen sulfide in any of the produced streams and the other, a sour site that contained approximately 23 weight % hydrogen sulfide in the gaseous stream that was directed to flare. The majority of the field testing was carried out at the sweet oilfield battery site. The following are some of the major findings that were derived from phase 3.

6.3.1 Sweet battery flare

- Flaring of sweet solution gas at low flow rates, and after it passed through the knock-out drum was found to burn with an efficiency of approximately 71%. The lower efficiency is not only due to the unburned hydrocarbons from the fuel stream that escape into the emissions but also to the higher concentrations of produced hydrocarbons, such as benzene and other low molecular weight aromatics, as well as larger concentrations of higher molecular weight compounds, including many polycyclic aromatic hydrocarbons.
- Increasing the sweet solution gas flow to produce a flame 3 to 4 times longer than that obtained while flaring lower levels, increased the carbon content in the emissions by approximately 5 times, the volatile hydrocarbons by about 33%, and the non-volatiles by up to 3 times the concentrations found in emissions above the smaller flame. This higher volume flame burned with a combustion efficiency of 67%.
- Sampling at twice the distance from this flame found reduced concentrations of all components in these emissions to approximately 30% of values obtained closer to the flame. Combustion efficiency measurements were approximately the same (66%).
- The combustion efficiency as measured in the emissions above these flames was further reduced by 5% to approximately 62% with the addition of more liquid fuel.
- Reducing liquid hydrocarbons contained in the knock-out drum at the sweet oilfield battery site had the effect of increasing the combustion efficiency from 64%, measured when the knock-out was two-thirds full, to 71% when emptied to the lowest attainable level. It also had the effect of reducing hydrocarbon concentrations in the emissions by approximately 25% and carbon particulate levels by about 40%. These tests were carried out in the subsequent year of the studies and were also used to substantiate the overall general findings at this site in the previous year.
- Benzene, styrene, ethynyl benzene, naphthalene, ethynyl-methyl benzenes, toluene, xylenes, acenaphthylene, biphenyl, and fluorene were, in most cases, the most abundant compounds found in any of the emissions examined in the sweet oilfield flare testing. In

the worst case, they were found in concentrations exceeding 300 mg/m^3. These emissions usually contained between 100 and 150 identified hydrocarbons.

- A large amount of the hydrocarbons found in the emissions above these flames are not just unburned hydrocarbons present in the fuel stream, but hydrocarbons produced within the flame by the pyrolytic reactions. This is confirmed by the predominance of unsaturated alkyl side chains attached to aromatic rings in emission samples as opposed to some of the saturated alkyl side chains attached to the aromatics found in the fuel mixture prior to flaring.

6.3.2 Sour battery flare

- Flare testing at the sour oilfield battery site with solution gas containing 23% hydrogen sulfide and much lower amounts of liquid hydrocarbons directed to flare, produced measured combustion efficiencies of 84%, as calculated by the carbon mass balance, and 82.4% as measured by the sulfur mass balance.
- Emissions from this more efficient flame were found to contain over 50% lower concentrations of aromatic hydrocarbons, approximately 20% less aliphatic hydrocarbons, and between 50 to 70% less carbon particles than concentrations detected in emissions from the sweet battery flare.
- The most abundant sulfur compound measured in these emissions other than the sulfur dioxide was carbon disulfide, followed by some thiophenes, hydrogen sulfide, carbonyl sulfide, and other sulfur containing compounds.

6.3.4 Air Quality Modeling and Ambient Monitoring

Additional studies to the flare emission investigations included plume dispersion modeling and some preliminary ground-level monitoring and were carried out at or near the end of this program. A summary of these findings includes the following:

- Based on the results obtained from the two field flare sites, calculations were made to convert stack-top emission concentration values to approximate emission rates and to assess what the theoretical ground level air quality implications of the emissions might be. These approximations and the conclusions of this supplementary study are contained in appendix A.

- An attempt was also made during the field flare emission sampling to carry out ground-level air quality monitoring in the vicinity of the battery sites. Weather conditions and access constraints were the main reasons for the inability to collect meaningful data. In the majority of cases, instruments could not be strategically positioned and/or samples collected for sufficient periods of time, resulting in downwind concentrations no higher than background levels. The one exception occurred at the sour oilfield battery site where sulfur dioxide was detected at ground-level over a few minutes. These readings were within the 1-hour Alberta guideline for sulfur dioxide.

A large amount of information was acquired over the course of these investigations. The laboratory studies definitively established that even the simplest of fuels, methane, produces relatively large quantities of pyrolytic products within the oxygen-void portion of the flame. The amounts that escaped these flames, however were relatively small. Other fuels do not burn quite so efficiently and slightly higher amounts of these produced hydrocarbons as well as some of the unburned fuel could be found in their emissions. The addition of liquids fuel, such as condensates, to gaseous fuel streams was found to have the most profound effect on impairing the ability of the resulting flame to efficiently combust all of the hydrocarbon fuel as well as the hydrocarbons that were produced within these flames.

The hydrocarbons identified in the emissions from each of the two field flares and the concentrations that were measured are specific to each individual flaring operation. Although flaring of all fuels has been shown to produce various levels of hydrocarbons within their respective flames, the amount that escape into the emissions can be very different depending on the composition of the fuel being flared, the flare design itself, and the atmospheric conditions at the time of flaring. The modeling studies carried out additional and subsequent to these studies have determined that predicted ground-level concentrations at these two sites would be low in relation to ambient air criteria or observed values.

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8.0 REFERENCES

Ashworth, J., Carpenter, W., Clark, B., Dabrowski, T., Pharis, H., Tollefson, E., Zukiwsky, R. 1984. “Twin Butte Soils and Water Evaluation Task Force: Executive Summary and Technical Report”. Alberta Environment.

Edwards, J.B. (1974). COMBUSTION Formation and Emission of Trace Species. Ann Arbor Science Publishers Inc. 240 pp.

EUB. (1995). Private communication from R.J. Willard, Drilling and Production, Energy and Utilities Board, Calgary. Alberta Oil and Gas Industry Annual Statistics 95-17.

Galant, S., D. Grouset, G. Martinez, and P. Michean. 1984. Three-dimensional steady parabolic calculations of large scale methane turbulent diffusion flames to predict flare radiation under cross-wind conditions. The Combustion Institute, Pittsburg, PA. 20th International Symposium on Combustion, Ann Arbor, MI, USA, 12 August 1984.

Grouset, D. and P. Plion. 1987. Turbulence and the effects on the environment of off-shore emergency flares. Houille Blanche 42(7-8): 607-616.

Karim, G.A., Rowe, R.D., and Tollefson, E.L. (1985). A review of flaring in the sour gas industry with particular reference to the emission of pollutants. Report to the Environmental Protection Service of Environment Canada under Contract No. OG 84-00242.

Keller, C.D. and T.F. Bidleman. 1984. Collectionof airborne polycyclic aromatic hydrocarbons and other organics with a glass fiber filter - polyurethane foam system. Atmos. Environ. 18(4): 837.

Legge, A.H., M. English, T. Guidotti, and H.S. Sandhu. 1992. A vision of clean air. Journal of the Air and Waste Management Association. 42(7): 888-891.

McCrillis, R.C. 1988. Flares as a means of destroying volatile organic and toxic compounds. Final Report 1980-87. Air and Energy Engineering Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA/600/D-88/106. 28 pp.

McDaniel, M. 1983. Flare efficiency study. Industrial Environmental Research Laboratory, Research Triangle Park, NC. Report No. EPA 600/2-83-052. 145 pp.

Pohl, J.H. and N.R. Soelberg. 1985. Evaluation of the efficiency of industrial flares: Flare head design and gas composition. Final Report October 82-December 84, Energy and Environsmental Research Corporation, Irvine, CA, Report No. PB-86-100559/XAB. 140 pp.

Pohl, J.H. and N.R. Soelberg. 1986. The combustion and destruction of sour gas mixtures in flare flames. Combustion Institute, Pittsburg, PA. 21st International Symposium on Combustion, Munich, Federal Republic of Germany, 3 August 1986.

Pohl, J.H. and N.R. Soelberg. 1986a. Evaluation of the efficiency of industrial flares: H_2S gas mixtures and pilot-assisted flares. Final Report April 1984-July 1986. Energy and Environmental Research Corporation, Irvine, CA, Report No. PB-87-102372/XAB. 105 pp.

Pohl, J.H., J. Lee, R. Payne, and B. Tichenor. 1986. Combustion efficiency of flares. Combustion Science and Technology 50: 217-231.

Sandhu, H.S., H.P. Sims, R.A. Hursey, W.R. MacDonald, and B.R. Hammond. 1980. Environmental sulfur research in Alberta: A review. Staff Report #4 to Research Secretariat, Alberta Department of Environment. 89 pp.

Strosher, M.T. 1984. Twin Butte source and ambient air evaluation study. Final Report to the Twin Butte Soil and Water Evaluation Task Force under Alberta Environment Contract No. 84-9111. 37 pp.

Strosher, M., P. Samuel, and G.A. Karim. 1992. Investigations of flare gas emissions In Alberta: Phase I: Laboratory studies. Report to Environment Canada, the Energy Resources Conservation Board, and the Canadian Petroleum Association. Alberta Research Council.

Strosher, M. and P. Samuel. 1993. Investigations of flare gas emissions in Alberta. Report to Environment Canada, the Energy Resources Conservation Board, and the Canadian Association of Petroleum Producers. Alberta Research Council.

Strosher, M. 1994. Investigations of flare gas emissions in Alberta: Pilot scale studies. Report to Environment Canada, the Energy Resources Conservation Board, and the Canadian Association of Petroleum Producers. Alberta Research Council.

Strosher, M. 1995. Investigations of flare gas emissions in Alberta: Field Studies. Report to Environment Canada, the Energy and Utilities Board and the Canadian Association of Petroleum Producers. Alberta Research Council.

Strosher, M. 1996. Investigations of flare gas emissions in Alberta: Phase 3- Field Studies. Report to Environment Canada, the Energy and Utilities Board and the Canadian Association of Petroleum Producers. Alberta Research Council.

Yamasaki, H., K. Kuwata and H. Miyanoto. 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 16(4): 189.

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ESTIMATED GROUND LEVEL CONCENTRATIONS OF PRODUCTS OF INCOMPLETE COMBUSTION (PIC) ASSOCIATED WITH FLARING ACTIVITIES AT TWO SITES IN ALBERTA

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ABSTRACT

The Alberta Research Council (ARC) has conducted laboratory-based and field-based observational studies on flaring for purposes of measuring Products of Combustion, including Products of Incomplete Combustion (PIC). These include volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH). A wide range of these products were observed in the plumes, indicating inefficient combustion associated with flaring activities. The ARC studies included measurements of flare emissions at both a sweet and a sour oil battery site.

The purpose of this present study was to assess the ground level concentrations that could occur in association with the observed PIC. For this purpose observed plume concentrations (mg m^{-3}) of selected VOC and PAH were converted to associated flare stack emission rates (mg s^{-1}) using theoretical equations established in accordance with mass and momentum conservation requirements. Emission rates were then applied in a plume dispersion model using meteorological data, considered to be representative of central Alberta, to assess potential ground level concentrations that could be associated with flaring inefficiencies at the two sites sampled during the ARC study.

Theoretical modelling calculations showed that routine flaring activities should result in the occurrence of the largest concentrations of air contaminants within a distance of several hundred meters from the flare stack. The largest magnitudes of predicted VOC concentrations associated with the sweet oil battery flare are relatively small, while those of PAH are comparable to values found in large industrial cities of North America and the United Kingdom. Maximum predicted annual average concentrations of non-polar compounds, which include PAH, associated with emissions from the sour oil battery flare were about 80 percent of those associated with the sweet oil battery flare. Predicted maximum daily average concentrations of both VOC and PAH decreased to 20 percent of their largest values at distances of about three and one km from the flares associated with sweet and sour gas emissions respectively.

1.0 INTRODUCTION

The Alberta Research Council (ARC) has completed laboratory-based and field-based observational studies relating to the constituents of gaseous plumes emitted from flare stacks. The investigations included field measurements at a single sweet oil battery flare and at a single sour oil battery flare. Investigations of the sweet gas flare were conducted with the liquids knock-out drum two-thirds full, half-full, and near empty. Investigation of the sour gas flare was conducted with the liquids knock-out drum near empty. Analyses of plume constituents were made for a wide range of hydrocarbon compounds for both the sweet and sour gas plumes. Measurements were also conducted for sulphur compounds in the plume downwind of the sour gas flare.

If the flared gases were being completely combusted within the flame, then only water vapour and carbon dioxide would have existed downwind of the sweet gas flares. The gaseous plume downwind of the sour gas flare would contain only these gases plus sulphur dioxide. Observations however revealed a wide range of Products of Incomplete Combustion (PIC) containing Volatile Organic Compounds (VOC) and Polycyclic Aromatic Hydrocarbons (PAH).

The purpose of this report is to put plume concentrations of PIC measured near the stack-top in perspective in terms of potential ground level concentrations. Estimates of ground level concentrations have been achieved by using measured plume concentration data for air contaminants together with information concerning wind speed, stack exit velocity, plume temperature, stack diameter and downwind measuring distance from the stack to estimate their emission rates. A plume dispersion model developed by the United States Environmental Protection Agency was then used together with representative meteorological data obtained from the Edmonton International Airport to estimate daily and annual average ground level contaminant concentrations that might result from these emissions. Estimated ground level concentrations of selected VOC and PAH were compared to relevant ambient air quality criteria and observational data reported in the published literature.

2.0 OBSERVED AMBIENT CONCENTRATIONS OF TOXIC AIR POLLUTANTS

Air quality concerns in Canada have traditionally been focused on concentrations of five pollutant categories for which ambient air quality criteria have been promulgated: Sulphur Dioxide, Carbon Monoxide, Nitrogen Oxides, Suspended Particulate Matter and Ozone. These are the pollutants to which people are the most widely exposed. Over the last ten years there has been a growing awareness of potential hazards due to a wide range of toxic pollutants such as those associated with incomplete combustion. As effects of these "new" pollutants are still being debated, there have been only a few jurisdictions in which ambient standards have been established. It is more customary to regulate these toxic/hazardous (i.e. non-criteria) pollutants through emission standards rather than ambient air quality guidelines (standards). While there are only five traditional pollutants there are now over 800 hazardous pollutants for which emission standards have been set by various jurisdictions (Godish 1991).

Because studies of hazardous pollutants are usually only of local interest and are expensive to conduct, there have been only a few studies published as to observed ambient concentrations of selected compounds. These studies are often limited to Benzo(a)Pyrene (BaP) and Benzene which are viewed as surrogates for PAH and VOC respectively. Perhaps the most ambitious study of toxic pollutants has been that conducted as part of the Airborne Toxic Element and Organic Substances (ATEOS) project in New Jersey (Lioy and Daisey 1987). Table 1 presents geometric means of ambient concentrations of selected PAH observed during the ATEOS study as measured during winter and summer seasons in two New Jersey communities: Newark and Ringwood. The Newark site was located in an industrial - residential zone of a large city while the Ringwood observational site was in a rural setting. As expected, concentrations tended to be much higher in Newark as compared to Ringwood. Concentrations were higher during winter months because of the greater intensity and persistence of ground based temperature inversions which occur during this season. The highest annual average BaP concentration to which people in the United States are exposed has been estimated to be about 20 ng m^{-3} (U.S. Environmental Protection Agency 1991). This value is much larger than concentrations given in Table 1.

More detailed studies were conducted by the ATEOS personnel into daily average observed concentrations of BaP and Cyclo-hexane extractables (CX). These last compounds consist of the non-polar Cyclo-hexane soluble fractions of material collected by the air sampler, which contain polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, nitro-PAH and other unidentified non-polar compounds. Concentration values for CX should be indicative of the total concentrations of PAH and other non-volatile compounds which may occur in urban areas as a result of incomplete combustion of fossil fuels. The mean of daily average values of BaP and CX observed in 27 New Jersey cities were 0.5 and 6,490 ng m^{-3} respectively. The largest observed values were respectively 7.9 and 46,100 ng m^{-3}.

Results of an observational study of PAH have been reported for Birmingham U.K. (Harrison et al. 1996) in which 12 of the measured compounds were also found during the ARC study. These compounds together with average concentrations observed during summer and winter months are shown in Table 2. Concentrations tended to be much higher in winter months because of the greater frequency of ground based inversion. Pyrene and Phenanthrene had the largest concentrations of the observed PAH, while Benzo(a)Pyrene had the least.

Table 3 presents average daily concentrations of 13 PAH compounds measured at downtown sites in Toronto and Montreal during the period 01 January 1994 to 31 December 1995 (Dann 1996) which were also observed in plumes downwind of the two flares sampled during the ARC study. Observed PAH concentration values tended to be larger in Montreal than in Toronto. Phenanthrene and Fluoranthene were the most commonly observed PAH in both cities, while Perylene was the least commonly observed.

Table 1 **Geometric Means of Daily Average Polycyclic Aromatic Hydrocarbons (ng m^{-3})* Observed in Newark and Ringwood, New Jersey During Winter and Summer 1982 Unless Otherwise Indicated**

Compound	Newark		Ringwood	
	Summer	Winter	Summer	Winter
Benz(a)Anthracene	0.15	1.36	0.02	0.42
Benzo(a)Pyrene	0.21	1.63	0.04	0.32
Benzo(e)Pyrene	0.16	2.38	0.03	0.35
Benzo(g,h,i)Fluoranthene	0.20	1.31**	0.07	0.20**
Benzo(g,h,i)Perylene	0.62	2.74	0.02	0.59
Chrysene	0.52	4.94	0.12	1.32
Coronene	0.37	0.52**	0.07	0.19**
Indeno(1,2,3-cd)Pyrene	0.37	2.90	0.10	0.79
Perylene	0.01	0.01	0.01	0.09
Pyrene	0.35	2.77**	0.08	0.43**

* 1 ng = 10^{-9} g

** Winter 1983

Table 2 **Average Concentrations of Polycyclic Aromatic Hydrocarbons (ng m^{-3})* Observed in Birmingham, United Kingdom During 1992**

Compound	Summer	Winter
Acenaphthene	4.23	13.46
Acenaphthylene	2.72	15.40
Anthracene	0.61	4.49
Benz(a)Anthracene	0.34	5.59
Benzo(a)Pyrene	0.25	0.81
Benzo(g,h,i)Perylene	0.76	1.97
Chrysene	0.61	6.49
Coronene	0.27	1.03
Indeno(1,2,3-cd)Pyrene	0.42	1.96
Phenanthrene	3.84	24.11
Pyrene	3.33	38.04

* 1 ng = 10^{-9} g

Table 3 **Average Concentrations (ng m^{-3})* of Polycyclic Aromatic Hydrocarbons (PAH) Observed in Downtown Toronto and Montreal (01 January 1994 to 31 December 1995)**

Compound	**Toronto**	**Montreal**
Acenaphthene	1.67	2.12
Acenaphthylene	3.12	3.33
Anthracene	0.99	0.91
Benz(a)Anthracene	0.31	0.68
Benzo(a)Pyrene	0.23	0.47
Benzo(e)Pyrene	0.32	0.90
Benzo(g,h,i)Fluoranthene	0.44	0.55
Benzo(g,h,i)Perylene	0.61	0.81
Fluoranthene	4.18	5.92
Indeno(1,2,3-cd)Pyrene	0.37	0.58
Perylene	0.04	0.08
Phenanthrene	17.78	23.94
Pyrene	3.23	4.03

* 1 ng = 10^{-9} g

Mean annual BaP concentrations measured for residential areas of Calgary and Edmonton are about 0.05 and 0.20 ng m^{-3} respectively (Myrick 1995).

Observations of ambient concentrations of volatile organic compounds such as those measured during the ARC flare emissions studies are also comparatively rare. Table 4 presents maximum annual averages of nine relevant VOCs observed in the city of Basel, Switzerland during 1988 (Organization of Economic Co-operation and Development [OECD] 1995). It also presents average concentrations of VOC observed in Edmonton, Alberta over about a 3 ½ year period (18 May 1991 to December 22, 1994) (Myrick 1996). Benzene and Toluene were the most commonly observed VOC in Basel, while in Edmonton the most commonly observed VOC were Toluene, Acetylene and Xylenes.

Data concerning daily average concentrations of Benzene have been routinely collected in Canada at over 30 urban and rural monitoring sites since 1987 (Dann and Wang 1995). The composite average of all data collected over the years from 1989 to 1993 was 3600 ng m^{-3}. The highest over all 24 hour average daily concentration of 126,300 ng m^{-3} was observed in Montreal. The highest daily average benzene concentrations observed in Calgary and Edmonton were 16,800 and 19,300 ng m^{-3} respectively.

While national ambient criteria for toxic pollutants are relatively rare, some local jurisdictions such as the Ontario Ministry of the Environment and Energy (OMEE) have adopted standards for a very wide range of potentially hazardous gases. Table 5 presents OMEE ambient air quality criteria for nine of the pollutants observed by ARC personnel during their investigations into flare gas emissions.

3.0 ESTIMATES OF CONTAMINANT EMISSIONS RATES

Results of the ARC study gave contaminant concentrations (mg m^{-3}) as measured in the plume adjacent to and downwind from the top of two active flare stacks. These concentrations must be converted to associated stack emission rates (mg s^{-1}) in order that estimates of ground level concentrations may be obtained using standard plume dispersion models.

3.1 Theory

It was assumed, following Leahey and Schroeder (1987) that plumes immediately downwind of a flare stack will have a "top hat" crosswind profile, that is a variable will have a constant value inside the plume, another value outside the plume and a discontinuity at the plume boundary. It follows from mass conservation that

$$C = \frac{4\,Q}{\pi\,U\,D^2} \qquad (1)$$

Table 4 **Annual Average Concentrations (ng m^{-3})* of Indicated Volatile Organic Compounds As Observed in the City of Basel, Switzerland (1988) and Edmonton, Alberta (18 May 1991 to December 22, 1994)**

Component	Concentration (ng m^{-3})	
	Basel	Edmonton
Acetylene	-	8520
Benzene	10,000	3670
Decane	1100	4410
Heptane	2500	1170
Hexane	5000	2450
Napthalene	-	430
Nonane	1100	510
Octane	1000	490
Styrene	700	500
Toluene	27,000	9400
1,3,5 Trimethylbenzene	2500	780
Xylenes	-	8340

* 1 ng = 10^{-9} g

Table 5 Ambient Air Quality Criteria (ng m^{-3})* Established by the Ontario Ministry of the Environment and Energy (OMEE) for the Indicated Toxic Pollutants

Compound	Daily Average Concentration (ng m^{-3})
Acetylene	56,000,000
Carbon Disulphide	330,000
Ethylene	40,000
Hexane	12,000,000
Napthalene	22,500
Octane	15,300,000
Styrene	400,000
Toluene	2,000,000
Xylenes	2,300,000

* 1 ng = 10^{-9} g

where C = contaminant concentrations in plume (mg m^{-3})
Q = contaminant emission rate (mg s^{-1})
U = wind speed (m s^{-1})
D = plume diameter (m)

It was additionally assumed that

$$D = 2\ \beta h \tag{2}$$

where β, h are the plume entrainment parameter and plume rise respectively.

Conservation of momentum and mass requirements can be applied to the plume to show that (Briggs 1975):

$$h = \left(\frac{3}{4\ \beta^2}\right)^{1/3} \left(\frac{D_o}{R}\right)^{2/3} \left(\frac{\rho}{\rho_o}\right)^{1/3} X^{1/3} \tag{3}$$

where D_o = stack diameter
X = downwind distance (m)
R = U/V
V = stack exit velocity (m s^{-1})
ρ_o, ρ = ambient air and plume density respectively (kg m^{-3})

The entrainment constant β is a function of ρ_o, ρ and R. Both experimental evidence (Ricou and Spalding 1961) and theory (Morton 1965, Townsend 1966) show that

$$\beta = \beta_o \left(\frac{\rho}{\rho_o}\right)^{1/2} \tag{4}$$

where β_o = entrainment constant for a plume with density equal to that of ambient air. Briggs (1975) has shown that it is related to R:

$$\beta_o = (0.4 + 1.2\ R) \tag{5}$$

Flared gas may be emitted at relatively high speed into the atmosphere where flames will maintain high temperatures in the immediate vicinity of the flare stack exit. Gases leaving the flare stack will be subjected to forces created by dynamic pressures and heating. It was assumed that the effective density of exiting gases will be equal to flame gas densities. Because of rapid mixing, the molecular weight of the flame gas will be close to that of air. It follows that:

$$\frac{\rho}{\rho_0} \cong \frac{T_0}{T} \qquad (6)$$

where T_0 and T are the temperatures of the air and flare plume, respectively.

The relationship between gas emission rate Q (mg s^{-1}) and measured plume concentrations C (mg m^{-3}) may now be derived from manipulation of Equations (1)-(6):

$$Q = \pi \left(\frac{3}{4}\beta_0\right)^{2/3} \left(\frac{D_0}{R}\right)^{4/3} \left(\frac{T_0}{T}\right) X^{2/3}\, U\, C \qquad (7)$$

3.2 Calculation Results

Table 6 presents stack, emission and measured plume parameters for sweet and sour gas flares studied by the ARC. Parameters for the sweet gas flare apply to the measurements conducted when the liquid knock out drum was half full. The flare stack diameter and exit velocities for the sweet gas flare were significantly larger than those for the sour gas flare. Effluent gas volumes were correspondingly an order of magnitude larger for the sweet than for the sour gas flare. Flame temperatures of 1273 K were assumed based upon results of independent studies discussed by Leahey and Schroeder (1987). Downwind distances to the measurement point were about twice the flame length. Plume temperatures shown in Table 6 are those measured at the downwind distance shown in the table.

Analytical techniques adopted in the ARC study differed from those used by the ATEOS project in so far as Hexane rather than Cyclo-hexane solvents was used to extract non-polar compounds from material collected by the air sampler. Results of the two extraction methods however should be comparable (Strosher 1996).

Table 7 presents measured plume concentrations and associated estimated stack emission rates for 15 PAH compounds which were selected from the many observed in the ARC study because representative ambient concentrations were available in the published literature. It also presents comparable information for Total Hexane Extractables. The greatest estimated emission rates of PAH were for Fluoranthene, Anthracene and Pyrene.

Table 8 shows measured plume concentrations and associated estimated stack emission rates for 13 VOC and one sulphur compound. The largest emission rates for VOC were for Benzene, Napthalene, and Acetylene.

Table 6 **Stack, Emission and Measurement Parameters Associated with the Two Gas Flares Sampled in the ARC Study**

Parameter	Sweet Gas Flare	Sour Gas Flare
Stack Height (m)	12.0	15.0
Stack Diameter (m)	0.200	0.076
Stack Exit Velocity (m s^{-1})	3.2	1.65
Gas Effluent Rate (m^3 s^{-1})*	0.1000	0.0075
Ambient Temperature (K)	288	288
Flame Temperature (K)	1273	1273
Flame Length (m)	4.5	1.75
Measured Plume Temperature (K)	373	398
Wind Speed (m s^{-1})	1.9	2.0
Total Measurement Time (min)	40	80
Measurement Time in Plume (m)	30	60
Downwind Distance to Measurement Point (m)	9.0	3.5

* at 288° K and 101.325 kPa.

Table 7 **Observed Plume Concentrations (mg m^{-3})* and Estimated Emission Rates (mg s^{-1}) for Selected PAH Compounds Associated with the Two Flares Observed During ARC Investigations. Values for Total Hexane Extractables Are Also Shown**

Component	Sweet Gas Flare		Sour Gas Flare	
	Measured Plume Concentration (mg m^{-3})	Estimated Stack Emission Rate (mg s^{-1})	Measured Plume Concentration (mg m^{-3})	Estimated Stack Emission (mg s^{-1})
Acenaphthene	2.93	5.6	5.22	0.8
Acenaphthylene	23.2	44.1	-	-
Anthracene	42.11	80.0	-	-
Benz(a)Anthracene	17.3	32.5	-	-
Benzo(a)Pyrene	1.03	2.0	0.46	0.1
Benzo(e)Pyrene	0.71	1.4	-	-
Benzo(g,h,i)Fluoranthene	10.16	19.1	-	-
Benzo (g,h,i) Perylene	0.26	0.5	-	-
Chrysene	2.12	4.0	2.4	0.4
Coronene	0.08	0.2	-	-
Fluoranthene	51.35	97.6	14.1	2.1
Indeno(1.2.3-cd)Pyrene	0.15	0.3	-	-
Perylene	0.62	1.2	-	-
Phenanthrene	-	-	34.09	5.1
Pyrene	32.37	60.7	83.26	12.5
Hexane Extractables	596.3	1133.0	761.6	114.2

* 1 mg = 10^{-3} g

Table 8 Observed Plume Concentrations (mg s^{-3})* and Estimated Emission Rates (mg s^{-1}) for Selected VOC Compounds Associated with the Two Flares Observed During ARC Investigations. Data Relating to Carbon Disulphide Are Also Shown

Component	Sweet Gas Flare		Sour Gas Flare	
	Measured Plume Concentration (mg m^{-3})	Estimated Stack Emission Rate (mg s^{-1})	Measured Plume Concentration (mg m^{-3})	Estimated Stack Emission (mg s^{-1})
VOC				
Acetylene	53.7	102.0	36.4	5.5
Benzene	144.5	274.6	64.3	9.7
Decane	1.0	1.9	1.2	0.2
Ethylene	29.0	55.1	6.0	0..9
Heptane	7.4	13.9	-	-
Hexane	8.5	16.0	-	-
Napthalene	99.4	188.9	77.1	11.6
Nonane	2.1	4.0	-	-
Octane	3.6	6.8	-	-
Styrene	75.5	141.6	22.7	3.4
Toluene	18.2	34.1	12.4	1.9
1,3,5 Trimethyl Benzene	2.9	5.5	-	-
Xylenes	29.8	55.9	6.7	1.0
Sulphur Compounds				
Carbon Disulphide	-	-	453.3	68.0

* 1 mg = 10^{-3} g

With the obvious and expected exception of carbon disulphide, emission rates of contaminants associated with sour gas flaring were much less than those for sweet gas. This is partly attributable to the fact that the amount of sour gas being flared was an order of magnitude less than the amount of sweet gas.

4.0 PLUME DISPERSION MODELLING

A plume dispersion model was employed to predict maximum ground level contaminant concentrations that might occur as the result of emissions associated with incomplete combustion at the two flare sites. It was assumed that the terrain surrounding the sites was flat. Dispersion calculations were made using five years of meteorological data collected at the Edmonton International Airport which should be generally representative of meteorological conditions observed in central Alberta.

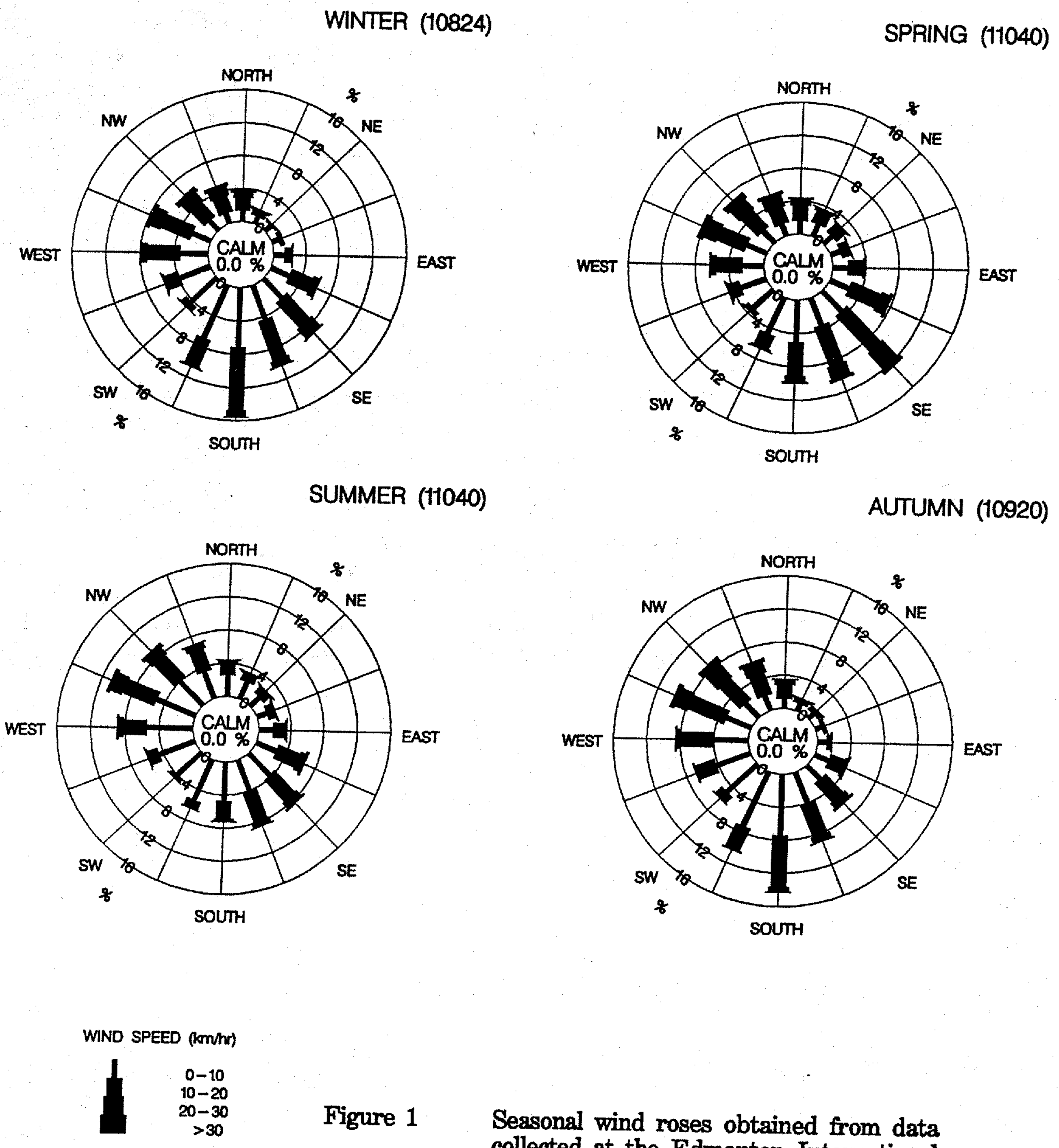
The Industrial Source Complex (ISC3) Model, developed by the United States Environmental Protection Agency was adopted for use in estimating plume dispersion effects. This model which is used and accepted by Alberta Environmental Protection is based upon the assumption of a Gaussian shaped plume. Use of the model requires a knowledge of source emissions parameters and hourly meteorological data relating to wind speeds, wind directions, mixing height and atmospheric stability categories.

The ISC3 plume model accepts hourly meteorological data records to define the conditions of transport and diffusion. It may be used to estimate ambient concentrations of contaminants as a function of downwind distances from point sources for each hour of input meteorology. Results of the calculations may then be subsequently used to estimate daily and annual average values.

Further details as to the ISC3 model may be found elsewhere (U.S. Environmental Protection Agency 1995).

4.1 Meteorological Data Inputs

Wind rose information collected at the Edmonton International Airport over a five year period (01 November 1990 to 31 October 1995) is presented in Figure 1 for winter (December, January, February), spring (March, April, May), summer (June, July, August) and autumn (September, October, November) seasons. The number of hourly data which the roses represent is shown in brackets. Wind roses are an efficient and convenient means of presenting wind data. The length of the radial barb gives the total percent frequency of winds from the indicated direction while portions of the barb of different widths indicate the frequency of associated wind speed categories. Thus, for example, Figure 1 shows that south winds occurred at the International Airport in winter about 16 percent of the time while south winds of less than 10 km h^{-1} occurred about seven percent of the time. A perusal of Figure 1 shows that there is a general tendency for winds to be either from the northwest or southeast. This tendency is most notable during the spring and summer seasons.



WINTER (10824)

SPRING (11040)

SUMMER (11040)

AUTUMN (10920)

Figure 1 Seasonal wind roses obtained from data collected at the Edmonton International Airport from 01 November 1990 to 31 October 1995.

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Estimates of atmospheric mixing heights for use in the ISC3 model were obtained from ambient temperature data collected at the Edmonton International Airport and from upper air information collected by the Canadian Atmospheric Environment Service at Stony Plain, Alberta which lies about 40 km west of Edmonton. Diurnal variations in median seasonal mixing heights are shown in Figure 2. Maximum mixing heights which occurred during mid afternoon hours for spring, summer and autumn seasons were about 1250, 1700, 750 m respectively. Mixing heights tended to remain constant during winter days with values of about 400 m.

The ISC3 plume dispersion model estimates plume dispersion according to stability categories which range from extremely unstable through neutral to extremely stable. Estimated seasonal frequencies of the stabilities categories as derived from using the Pasquill (1961) method which relies upon wind speed and cloud cover are shown in Table 9. Extremely unstable atmospheric conditions which are associated with strong solar heating seldom occur in Alberta. Neutral atmospheric stabilities which are associated with cloudy skies and/or strong winds are the most common of the categories. Extremely stable atmospheres which occur at night under clear skies and the low winds are, as expected, most common during the winter season.

4.2 Source Emission Parameters

The ISC3 plume dispersion model was employed for emission sources with sensible heat emissions equal to those of the two observed flares. These were, in accordance with the finding of Leahey and Davies (1984) calculated as being equal to 45 percent of the heating value of the emitted gas ($M\,J\,s^{-1}$) estimated using gas compositions shown in Table 10 together with gas flow rates previously presented in Table 6. The remainder (55%) of the heat content of the emitted gases was assumed to be radiated to atmosphere.

Other source emission parameters used to estimate ground level contaminant concentrations (e.g. stack heights, contaminant emission rates) have been presented in Tables 6, 7 and 8.

5.0 CALCULATION RESULTS FOR GROUND LEVEL CONCENTRATIONS OF PRODUCTS OF INCOMPLETE COMBUSTION

Ground level concentrations of a given contaminant are directly proportional to its mass emission rate. Thus ground level concentrations of a contaminant will double if its emission rate is doubled. Figures 3 and 4 present isopleths of the largest daily and annual average ground level concentrations, associated with the sweet gas flare as predicted on a relative basis. Comparable information for the sour gas flare is shown in Figures 5 and 6.

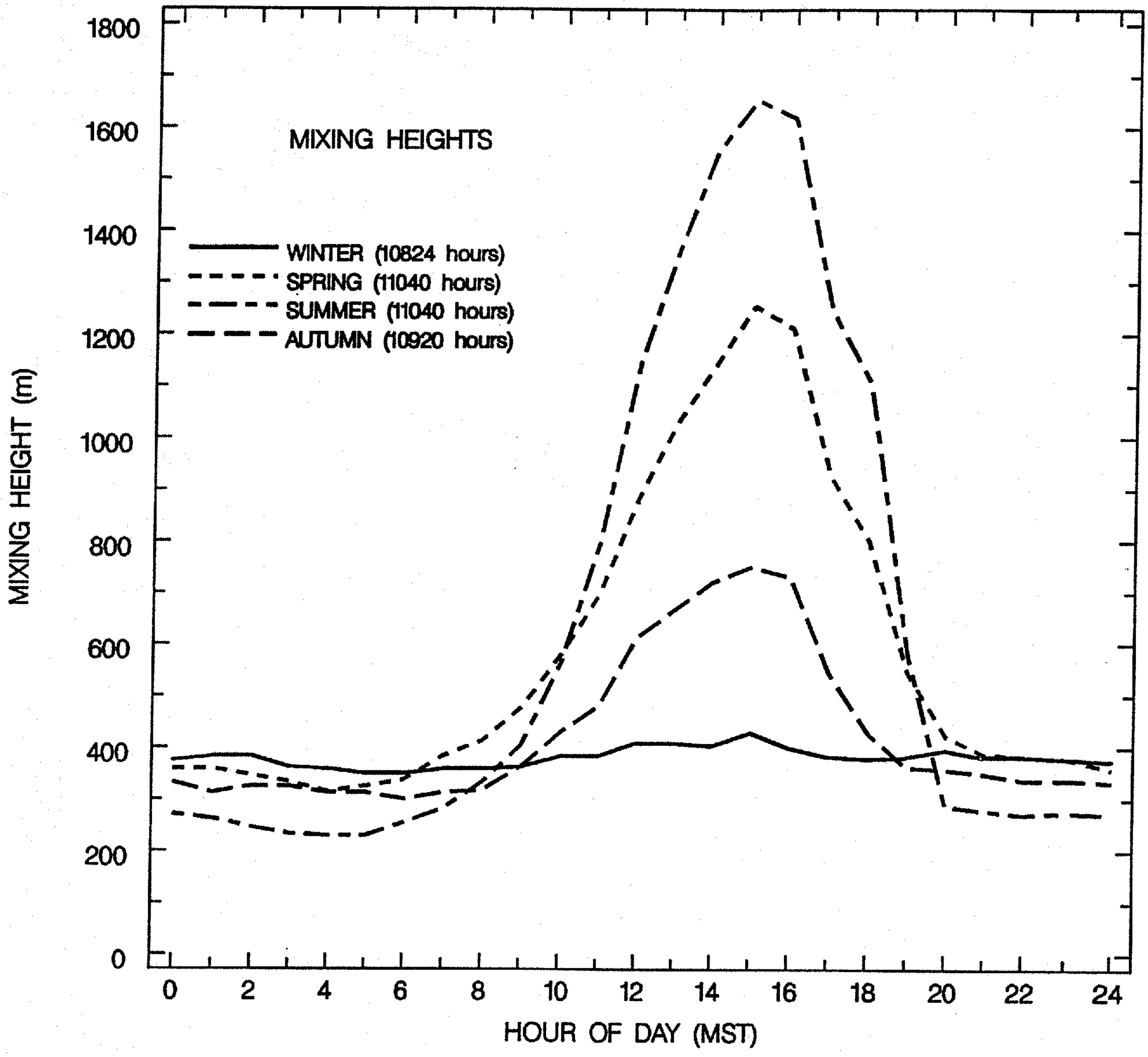

Figure 2 Seasonal median hourly mixing heights calculated from ambient temperature data collected at the Edmonton International Airport and from upper air data at Stony Plain, Alberta, for the period 01 November 1990 to 31 October 1995.

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Table 9 **Estimated Percent Frequency of Occurrence of the Indicated Stability Category**

Category	Season				
	Winter	Spring	Summer	Autumn	Annual
Extremely Unstable	0.00	0.16	0.40	0.05	0.15
Moderately Unstable	1.34	6.64	13.26	3.46	6.21
Slightly Unstable	7.89	14.98	19.95	11.99	13.73
Neutral	49.70	46.20	36.00	43.25	43.75
Slightly stable	19.46	14.95	13.09	18.59	16.50
Moderately stable	15.55	12.20	12.04	16.45	14.04
Extremely stable	6.06	5.05	5.26	6.21	5.61

Table 10 **Percent Flammable Composition of Gas Combusted at the Two Observed Flares. Heating Value of Each Gas (M J m^{-3}) Is Also Shown**

Component	Sweet Gas Flare	Sour Gas Flare
Butane	4.6	2.4
Ethane	9.2	10.7
H_2S	0.0	22.8
Methane	69.2	45.4
Pentane	8.6	2.6
Propane	5.5	5.7
Heating Value (M J m^{-3})*	51.3	38.5

* at 15° C and 101.325 kPa.

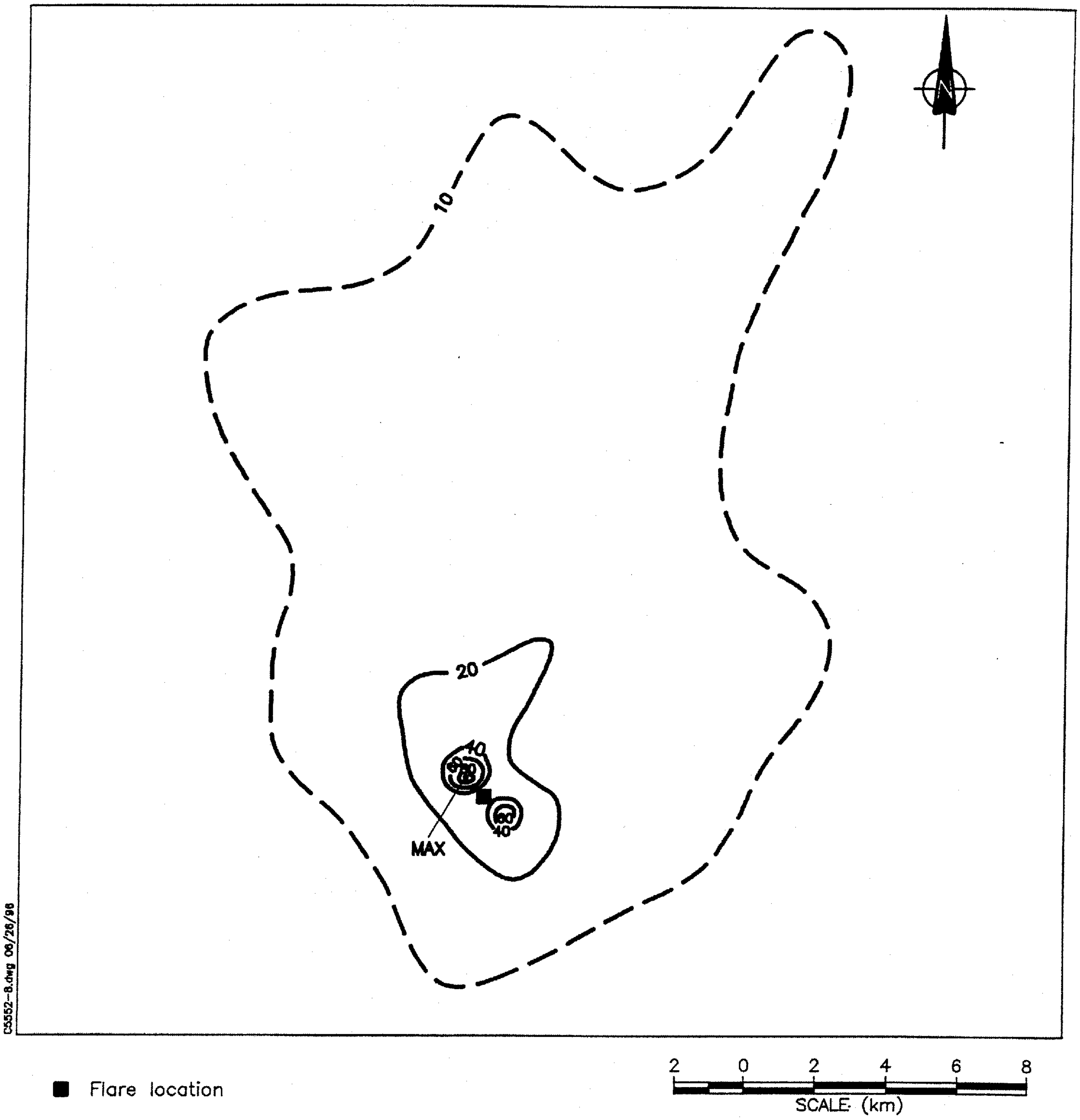

Figure 3 Isopleths of relative maximum daily average ground level pollutant concentrations (%) associated with the sweet gas flaring.

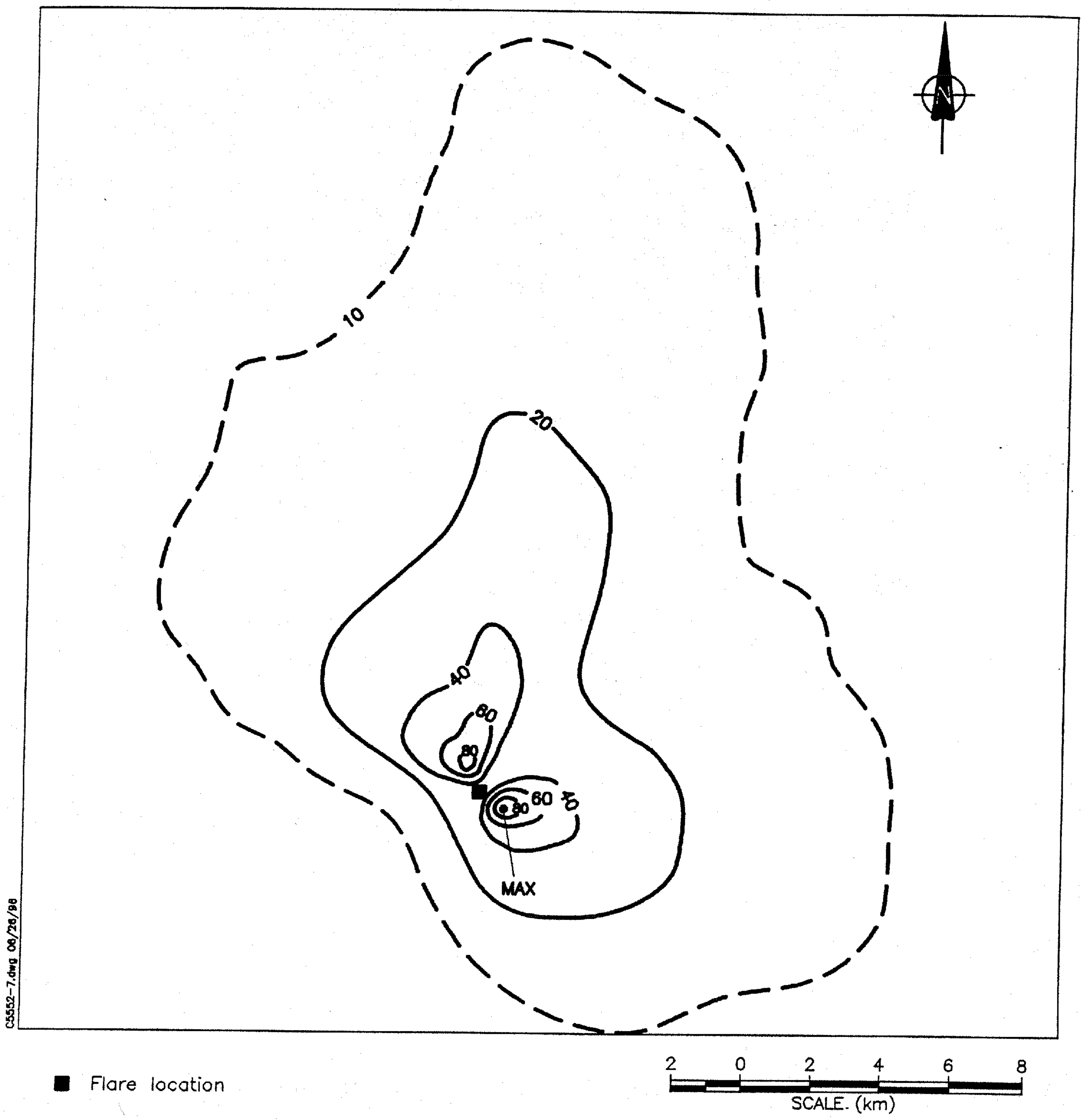

Figure 4 Isopleths of relative maximum annual average ground level pollutant concentrations (%) associated with sweet gas flaring.

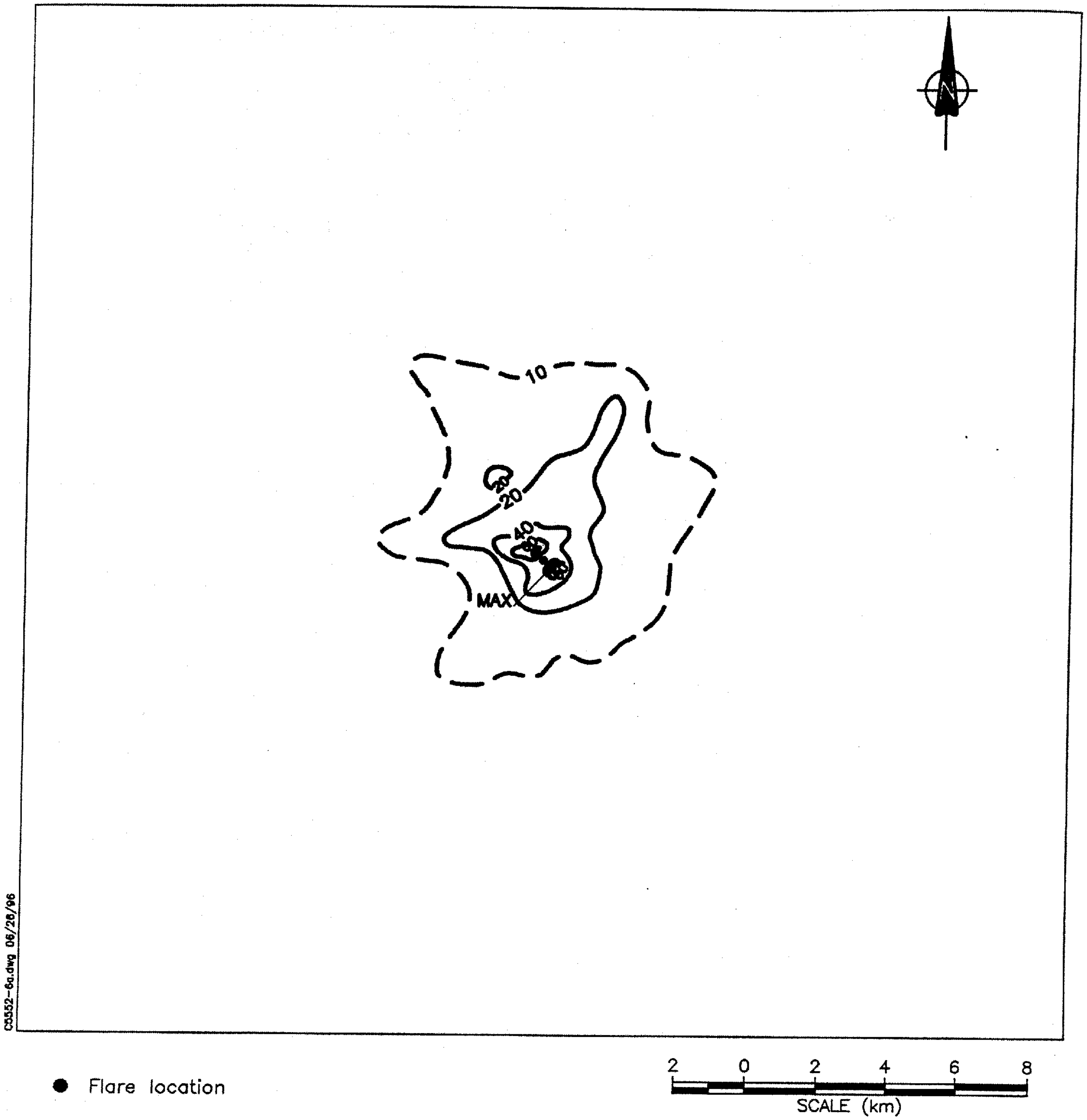

Figure 5 Isopleths of relative maximum daily average ground level pollutant concentrations (%) associated with sour gas flaring.

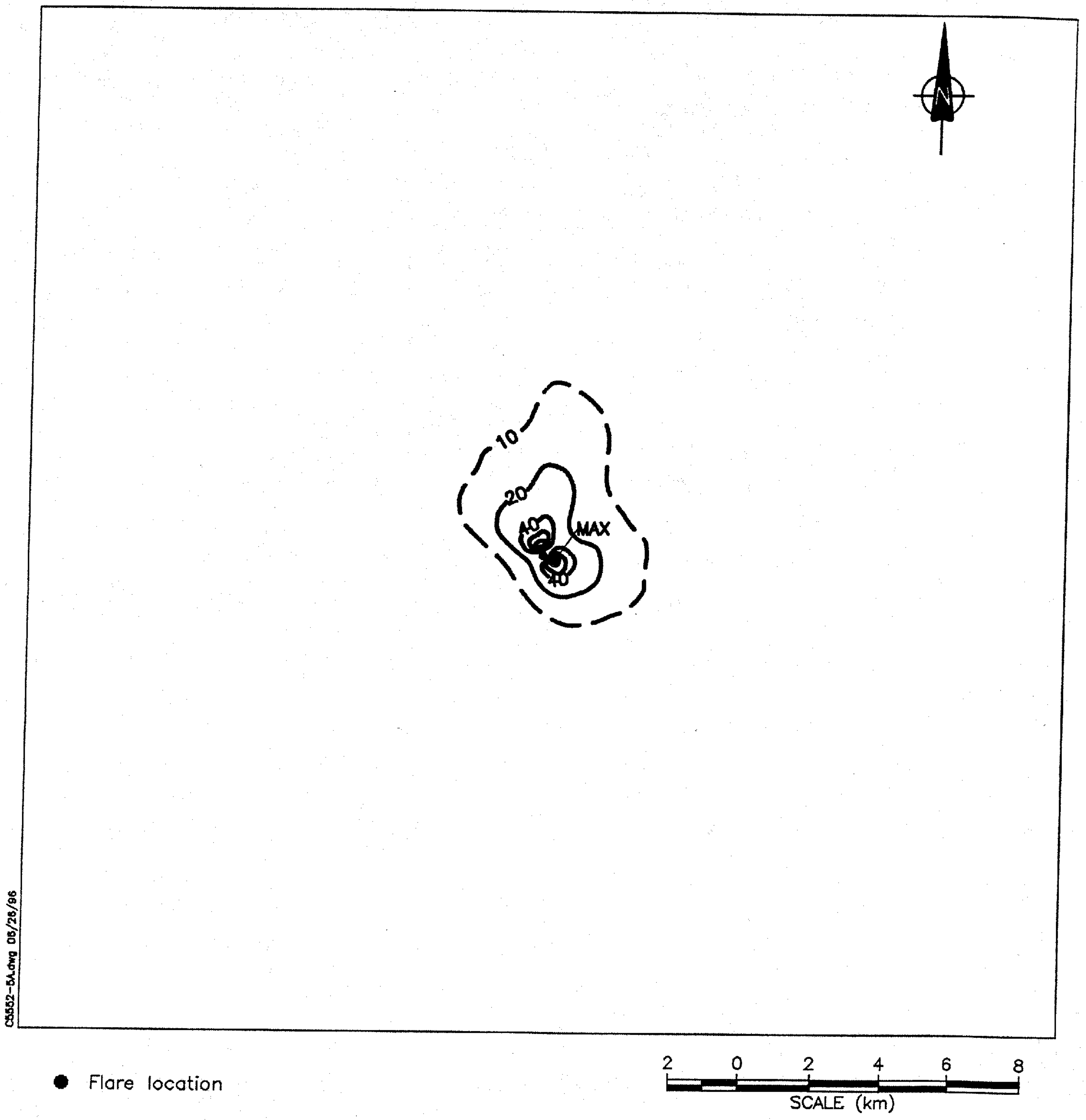

Figure 6 Isopleths of relative maximum annual average ground level pollutant concentrations (%) associated with sour gas flaring.

Figure 3 shows, for example, that the maximum daily average ground level pollutant concentrations associated with sweet gas flaring should occur within a few hundred meters of the flare. Concentrations initially drop off very rapidly with distance and are generally about 20 percent of the over all maximum concentration at distances of about three km from the flare site.

A perusal of Figures 3 and 6 shows that the area influenced by the sweet gas emissions (i.e. the air quality "imprint") is much greater for the sweet gas than for the sour gas flare. This was expected as emissions from the sweet gas flare exceed those from the sour gas flare by an order of magnitude. Isopleth patterns tend to lie along a general NW-SE axis. This reflects the pattern shown by wind roses in Figure 1. Relatively large pollutant concentrations are very localized. For daily averages they decline to 20 percent of their maximums at distances from the flare of about 3 and 1½ km for sweet and sour gas respectively. The corresponding distances for annual averages are about six and two km.

Table 11 shows predicted largest daily maximum and annual average ground level concentrations of PAH compounds associated with the two facilities investigated by the ARC. They are given in units of ng m^{-3} and parts per billion (ppb). Most of the predicted annual average concentrations of the seven PAH compounds associated with the sour gas flaring site are comparable to or greater than concentrations of the same PAH associated with the sweet gas flare. The maximum predicted annual average concentration for Hexane Extractables associated with sour gas flaring is about 80 percent of that associated with sweet gas flaring.

Table 12 shows a comparison between annual predicted maximum PAH concentrations and values observed in Newark, Birmingham, Toronto and Montreal. Observed concentrations for Newark and Birmingham were taken as the average of summer and winter values shown in Tables 1 and 2. A perusal of Table 12 indicates that maximum predicted annual average concentration values for PAH constituents in the vicinity of the two sites sampled in the ARC study are often similar to or greater than concentrations of the same PAH species observed in Urban areas. Care however should be taken in comparing maximum predicted PAH concentrations, which are representative of very localized areas, with observed urban values which are presumably representative of large regions.

Table 13 presents maximum predicted daily and annual average ground level concentrations of VOC and Carbon Disulphide associated with the sites sampled during the ARC study. A perusal of Table 13 shows that predicted maximum daily average values for VOC and Carbon Disulphide concentrations are very small when compared to OMEE (Table 5) criteria or observed values (Table 4).

Table 11 Largest Maximum Predicted Ground Level Concentrations of PAH Compounds Associated with Sweet and Sour Gas Flaring

Component	Mol wt.	Sweet Gas Flare				Sour Gas Flare			
		Daily Average		Annual Average		Daily Average		Annual Average	
	(g/mol)	(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)
PAH									
Acenaphthene	154.2	47.0	0.00745	1.7	0.00027	23.8	0.0037	1.9	0.00029
Acenaphthylene	152.2	370.0	0.05944	13.5	0.00217	-	-	-	-
Anthracene	178.2	671.2	0.09209	24.5	0.00336	-	-	-	-
Benz(a)Anthracene	228.3	272.7	0.02921	9.9	0.00107	-	-	-	-
Benzo(a)Pyrene	252.3	16.8	0.00163	0.6	0.00006	3.0	0.0002	0.2	0.00002
Benzo(e)Pyrene	252.3	11.7	0.00114	0.4	0.00004	3.0	0.0002	0.2	0.00002
Benzo(g,h,i)Fluoranthene	252.3	160.2	0.01553	5.8	0.00057	-	-	-	-
Benzo(g,h,i)Perylene	276.3	4.2	0.00037	0.2	0.00002	-	-	-	-
Chrysene	228.3	33.6	0.00359	1.2	0.00013	11.9	-	0.9	0.00010
Coronene	300.4	1.7	0.00014	0.1	0.00000	-	-	-	-
Fluoranthene	202.3	818.9	0.09900	29.9	0.00361	62.4	0.0075	4.9	0.00059
Indeno(1.2.3,-cd)Pyrene	202.3	2.5	0.00030	0.1	0.00001	-	-	-	-
Perylene	252.3	10.1	0.00098	0.4	0.00004	-	-	-	-
Phenanthrene	178.2	-	-	-	-	151.6	0.0208	11.8	0.00162
Pyrene	202.3	509.3	0.06157	18.6	0.00225	371.5	0.0449	29.0	0.00351
Hexane Extractables		9505.6	-	346.0	-	3394.0	-	264.9	-

* 1 ng = 10^{-9} g

Table 12 Comparison Between Largest Maximum Predicted Annual Average Ground Level Concentrations (ng m^{-3})* for Selected PAH Associated with the Two Flares Sampled by ARC and Average Concentrations Observed in Newark, Birmingham, Toronto and Montreal

PAH	Sweet Gas Flare	Sour Gas Flare	Newark	Birmingham	Toronto	Montreal
Acenaphthene	1.7	1.9	-	8.8	1.7	2.1
Acenaphthylene	13.5	-	-	9.1	3.1	3.3
Anthracene	24.5	-	-	2.6	1.0	0.9
Benz(a)Anthracene	9.9	-	0.8	3.0	0.3	0.7
Benzo(a)Pyrene	0.6	0.2	0.9	0.5	0.2	0.5
Benzo(e)Pyrene	0.4	0.2	1.3	-	0.3	0.9
Benzo(g,h,i)Fluoranthene	5.8	-	0.8	-	0.4	0.6
Benzo(g,h,i)Perylene	0.2	-	1.7	1.4	0.6	0.8
Chrysene	1.2	0.9	2.7	3.6	-	-
Coronene	0.1	-	0.4	0.7	-	-
Fluoranthene	29.9	4.9	-	-	4.2	5.9
Indeno(1.2.3,-cd)Pyrene	0.1	-	1.6	1.2	0.4	0.6
Perylene	0.4	-	0.0	-	0.0	0.1
Phenanthrene	-	11.8	-	14.0	17.8	23.9
Pyrene	18.5	29.0	1.6	20.7	3.2	4.0
Hexane Extractables	346.0	264.9	10,920**	-	-	-

* 1 ng = 10^{-9} gm

** Cyclo-hexane extractables

Table 13 Largest Maximum Predicted Ground Level Concentrations of VOC and Carbon Disulphide Associated with Sweet and Sour Gas Flaring

Component	Mol wt. (g/mol)	Sweet Gas Flare				Sour Gas Flare			
		Daily Average		Annual Average		Daily Average		Annual Average	
		(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)	(ng m^{-3})*	(ppb)
VOC									
Acetylene	26.0	855	0.80417	30	0.02819	165	0.15492	15	0.01404
Benzene	78.1	2300	0.72000	85	0.10263	290	0.09077	25	0.00782
Decane	142.3	15	0.00258	0	0.00000	5	0.00086	0	0.00000
Ethylene	28.0	460	1.18675	15	0.01310	25	0.02179	0	0.00000
Heptane	100.2	115	0.98628	5	0.00400	-	-	-	-
Hexane	86.2	135	0.03832	5	0.00366	-	-	-	-
Napthalene	128.2	1585	0.30240	60	0.01145	345	0.06581	25	0.00477
Nonane	128.3	35	0.00666	0	0.00000	-	-	-	-
Octane	114.2	55	0.01176	0	0.00000	-	-	-	-
Styrene	104.2	1190	0.27939	45	0.03441	100	0.02349	10	0.00234
Toluene	92.2	285	0.07563	10	0.02663	55	0.01459	5	0.00133
1,3,5 Trimethyl Benzene	120.2	45	0.02625	0	0.00000	-	-	-	-
Xylenes	196.2	470	0.16261	15	0.00187	30	0.00374	0	0.00000
Carbon Disulphide	76.1	-	-	-	-	2020	0.64878	160	0.05139

* 1 ng = 10^{-9} g

6.0 SUMMARY

This report presents results of a theoretical evaluation of ground level concentrations for Products of Incomplete Combustion (PIC) measured in the plumes of flares by the Alberta Research Council at both a sweet and sour oil battery site. The amount of gas being combusted in the sweet gas flare was an order of magnitude larger than that associated with the sour gas flare. The main results of the theoretical calculations are as follows:

- Maximum ground level concentrations of PIC associated with emissions from the two sites sampled are localized and expected to occur within several hundred meters of the flare stack.
- Calculated concentrations of PIC decrease very rapidly with distance from the maximum. Daily average values, for example, are generally about 20 percent of the over all maximum concentration at distances of about 3 and 1½ km from the flare for sweet and sour gas emissions respectively.
- Largest maximum calculated annual average ground level concentrations of Hexane Extractables associated with the sour battery flare are about 80 percent of those associated with the sweet battery site.
- Largest maximum calculated ground level concentrations of volatile organic compounds (VOC) and Carbon Disulphide associated with the two flares are much lower than OMEE ambient criteria.
- Largest maximum calculated ground level concentrations of some Polycyclic Aromatic Hydrocarbons (PAH) associated with the sweet and sour gas flaring are comparable to those observed in large industrial cities.

REFERENCES

Briggs G.A. (1975) Plume rise predictions. *Lectures on Air Pollution and Environmental Impact Analyses*, pp. 59-111. American Meteorological Society, 34 Beacon Street, Boston, MA, 02108, U.S.A.

Dann T.F. 1996. Tables of PAH Observed in Montreal and Toronto (personal communication). Environment Canada Technology Development Branch, 3439 River Road, Ottawa, Ontario K1A 0H3.

Dann T.F. and D.K. Wang 1995. "Ambient Air Benzene Concentrations in Canada (1989-1993): Seasonal and Day of Week Variations, Trends, and Source Influences". *J. Air & Waste Mgmt. Assoc.* **45**, 695-702.

Environment Canada, 1989. Polycyclic Aromatic Hydrocarbons in the Ambient Air of Toronto, Ontario and Montreal, Quebec. Technology Development and Technical Services Branch, Pollution Measurement Division.

Godish 1991. *Air Quality* 2nd Edition. Lewis Publishers, 121 South Main Street, Chelsea, Michigan 48118 pp. 294.

Harrison R.M., D.J.T. Smith and L. Luhana 1996. Source Appointment of Atmospheric Polycyclic Aromatic Hydrocarbons Collected from an Urban Location in Birmingham, U.K. *Envir. Sci. & Tech.* **30** (3) 825-832.

Leahey D.M. and M.B. Schroeder 1987. Observations and Predictions of Jet Diffusion Flame Behaviour *Atmospheric Environment* **21** pp. 777-784.

Leahey D.M. and Davies M.J.E. (1984). Observations of plume rise from sour gas flares. *Atmospheric Environment*, **18**, pp. 917-922.

Lioy P.J. and J.M. Daisey 1987. *Toxic Air Pollution: A Comprehensive Study of Non-Criteria Pollutants.* Lewis Publishers Inc., 121 South Main Street, Chelsea, Michigan 48118.

Morton B.R. (1965). Modeling fire plumes. *Tenth Symposium (International) on Combustion*, pp. 973-982.

Myrick R.H. 1995: *Air Quality Monitoring Report for Alberta 1993.* Air Issues and Monitoring Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, 9820 - 106th Street, 6th Floor, Oxbridge Place, Edmonton, Alberta T5K 2J6.

Myrick R.H. 1996. Maximum 24-hour and Period Average VOC Concentrations at Edmonton and Calgary Stations (personal communications). Air Issues and Monitoring Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, 9820 - 106th Street, 6th Floor, Oxbridge Place, Edmonton, Alberta T5K 2J6.

Organization for Economic Co-operation and Development (OECD) 1995. *Control of Hazardous Air Pollutants in OECD Countries*. OECD Publications, 2 rue Andre' Pascal, 75775, Paris Cedex 16, pp. 235.

Pasquill, F., 1961: The Estimation of the Dispersion of Windborne Material. *Meteorol. Mag.*, **90**(1063): 33-49.

Ricou F.P. and Spalding D.B. (161). Measurements of Entrainment by Axisymmetrical Turbulent Jets. *J. Fluid Mech.* **9**, pp. 21-32.

Strosher M. 1996. Personal Communication. Research Officer, Air Quality Assessment and Modelling Group, Environmental Research and Engineering, Alberta Research Council.

Townsend A.A. (1966). The Mechanism of Entrainment in Free Turbulent Flows. *J. Fluid Mech.* **26**, pp. 689-697.

U.S. Environmental Protection Agency. 1995. *User's Guide for the Industrial Source Complex (ISC3) Dispersion Models: Volume II - Description of Model Algorithms*. Office of Air Quality Planning and Standards Emissions, Monitoring and Analysis Division, Research Triangle Park, NC 27711.

United States Environmental Protection Agency. 1991. Office of Toxic Substances, *Toxics in the Community*. The 1989 Toxics Release Inventory National Report. EPA 560/4-91-014, Washington, D.C.