

REPORT NO. **FRA.80-1**
FRA/ORD-80/08
REFERENCE USE ONLY

FIRE BEHAVIOR OF TRANSFORMER DIELECTRIC INSULATING FLUIDS

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JANUARY 1980

FINAL REPORT

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Prepared for
U.S. DEPARTMENT OF TRANSPORTATION
FEDERAL RAILROAD ADMINISTRATION
Office of Research and Development
Washington DC 20590

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1. Report No. FRA/ORD-80/08		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle FIRE BEHAVIOR OF TRANSFORMER DIELECTRIC INSULATING FLUIDS				5. Report Date January 1980	
				6. Performing Organization Code	
7. Author(s) A. Tewarson, J.L. Lee, and R.F. Pion				8. Performing Organization Report No. DOT-TSC-FRA-80-1 J.I. OEON2. RC 332-0021 FLB	
9. Performing Organization Name and Address Factory Mutual Research Corporation 1151 Boston-Providence Turnpike Norwood MA 02062				10. Work Unit No. (TRAIS) RR030 /R0350	
				11. Contract or Grant No. DOT-TSC-1703	
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Railroad Administration Office of Research and Development Washington DC 20590				13. Type of Report and Period Covered Final Report Apr - Sep 1979	
				14. Sponsoring Agency Code	
15. Supplementary Notes *Under contract to:		U.S. Department of Transportation Research and Special Programs Administration Transportation Systems Center Cambridge MA 02142			
16. Abstract This report presents results for the fire behavior of pure and askarel-contaminated fluids which are candidates for use as railroad transformer dielectric insulating fluids. In the study a hydrocarbon and a dimethyl-siloxane fluid were examined. The fire behavior of the fluids was examined on the basis of parameters obtained in the FM Laboratory-Scale Flammability Apparatus. The measured flash point, fire point and boiling point of the hydrocarbon fluid were lower than those of dimethyl-siloxane fluid both in the presence and absence of the askarel. There was some noticeable decrease in the flash and fire points when the amount of askarel in the mixture was increased from about 5 percent to 7 percent by weight. The analyses of the results indicated that: 1) Ignition and surface flame spread for the hydrocarbon fluid are expected to be about one and a half times as fast as for the dimethyl-siloxane fluid in larger-scale fires (the ignition and surface flame spread for red oak are expected to be about three times as fast as for the hydrocarbon fluid). Askarel contamination of hydrocarbon and dimethyl-siloxane fluids is expected to have insignificant effect on ignition and surface flame spreads of the fluids in larger-scale fires. 2) The heat release rate in the combustion of heptane, hydrocarbon and dimethyl-siloxane fluid in larger-scale fires is expected to be in the ratio of about 20:10:1 respectively. Askarel contamination of the hydrocarbon and dimethyl-siloxane fluid is expected to have insignificant effect on the heat release rate in larger-scale fires involving these fluids. The parameters from the FM Flammability Apparatus were found to be useful to predict satisfactorily the fire behavior of fluids expected in larger-scale fires.					
17. Key Words Railroad Transformer Dielectric Insulating Fluids Askarel Contamination Fire Behavior Flash, Fire, Boiling Points			18. Distribution Statement Ignition, Surface Flame Spread Heat Release Rates Pyrolysis and Combustion DOCUMENT IS AVAILABLE TO THE PUBLIC THROUGH THE NATIONAL TECHNICAL INFORMATION SERVICE, SPRINGFIELD, VIRGINIA 22161		
19. Security Classif. (of this report) UNCLASSIFIED		20. Security Classif. (of this page) UNCLASSIFIED		21. No. of Pages 74	22. Price

PREFACE

This document presents the results of DOT/TSC Contract - 1703. Mr. I. Litant was the Technical Monitor for this project. The contract was conducted by the Factory Mutual Research Corporation, Norwood, Massachusetts from April 1979 through August 1979. The purpose of this contract was to evaluate 1) the fire behavior of a hydrocarbon fluid and a dimethyl-siloxane fluid which are candidates for use in the retro-filling of askarel-filled railroad transformers, and 2) to investigate the effect of askarel on the fire behavior of the replacement fluids.

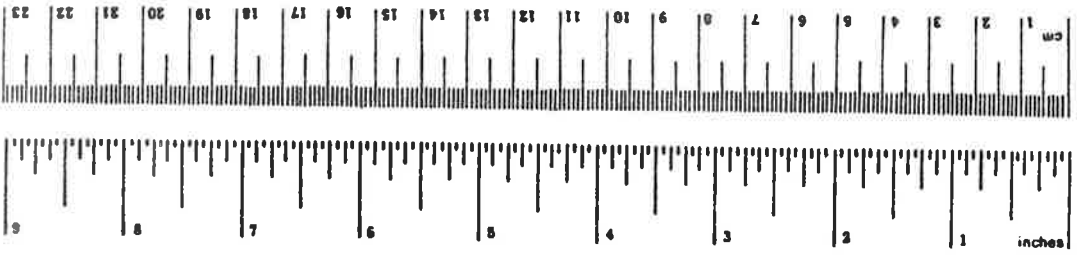
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
in ²	square inches	6.5	square centimeters	cm ²
ft ²	square feet	0.09	square meters	m ²
yd ²	square yards	0.8	square meters	m ²
mi ²	square miles	2.6	square kilometers	km ²
acres	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons	0.9	tonnes	t
			(2000 lb)	
VOLUME				
teaspoon	teaspoons	5	milliliters	ml
Tablespoon	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cup	0.24	liters	l
pt	pint	0.47	liters	l
qt	quart	0.95	liters	l
gal	gallon	3.8	liters	l
ft ³	cubic feet	0.03	cubic meters	m ³
yd ³	cubic yards	0.76	cubic meters	m ³
TEMPERATURE (exact)				
	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm ²	square centimeters	0.16	square inches	in ²
m ²	square meters	1.2	square yards	yd ²
km ²	square kilometers	0.4	square miles	mi ²
ha	hectares (10,000 m ²)	2.5	acres	acres
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	short tons
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m ³	cubic meters	35	cubic feet	ft ³
m ³	cubic meters	1.3	cubic yards	yd ³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



** on p. 2-54 (exact). For other exact conversions and more data see tables, see NBS Misc. Publ. 286, U.S. Dept. of Weights and Measures, Price 92.25, SD Catalog No. C-13 70 286.

$kW = kJ/s$
 $BTU = 1.055 kJ$
 $BTU/lb = 0.00233 kJ/g$
 $BTU/ft^2-min = 0.1892 kW/m^2$

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LIST OF ABBREVIATIONS AND SYMBOLS

a	Fuel surface area (m^2)
C_p	Specific heat of air (kJ/gK)
ΔC_i	Product concentration difference (volume percent)
D	Optical density per unit path length (m)
E_{eff}	Energy required to generate and maintain flammable fuel vapor/air mixture near the surface (kJ/m^2)
E_T	Total external energy supplied to the fuel to generate and maintain flammable fuel vapor/air mixture near the surface, defined as ignition/flame spread parameter of the fuel (kJ/m^2)
H_A	Actual heat of combustion per unit mass of the fuel or the ratio of actual heat release rate to vaporization rate of the fuel (kJ/g)
H_C	Convective heat of combustion per unit mass of the fuel or the ratio of convective heat release rate to vaporization rate of the fuel (kJ/g)
H_R	Radiative heat of combustion per unit mass of the fuel or the ratio of radiative heat release rate to vaporization rate of the fuel (kJ/g)
H_T	Net complete heat of combustion per unit mass of the fuel (kJ/g)
I	Optical transmission through the mixture of product and ambient air (mv)
I_o	Optical transmission through ambient air (mv)
k_{O_2}	Stoichiometric mass oxygen to fuel ratio
ℓ	Optical path length (m)
L_g	'Actual' heat of vaporization of the fuel (kJ/g)
\dot{m}''_b	Vaporization rate of the fuel in combustion per unit fuel surface area (g/m^2s)
\dot{m}''_p	Vaporization rate of the fuel in pyrolysis per unit fuel surface area (g/m^2s)
\dot{M}''_i	Generation (or depletion) rate of the product i per unit fuel surface area (g/m^2s)
\dot{M}''_T	Total mass flow rate of the mixture of hot products and air through the sample duct per unit fuel surface area (g/m^2s)

OC	Ratio of optical density per unit path length to fuel vapor concentration (m^2/g)
p_a	Ambient pressure (atm)
Δp_d	Pressure difference between inside and outside of the sample duct (atm)
Δp_m	Pressure difference across the orifice plate in the sample duct (atm)
\dot{q}''_e	External heat flux incident on the fuel (kW/m^2)
\dot{q}''_{fc}	Convective heat flux from the flame supplied to the fuel (kW/m^2)
\dot{q}''_{fr}	Radiative heat flux from the flame supplied to the fuel (kW/m^2)
\dot{q}''_o	Fuel surface reradiation loss (kW/m^2)
\dot{Q}''_A	Actual heat release rate in the combustion of the fuel per unit fuel surface area (kW/m^2)
\dot{Q}''_C	Convective heat release rate in the combustion of the fuel per unit fuel surface area (kW/m^2)
\dot{Q}''_R	Radiative heat release rate in the combustion of the fuel per unit fuel surface area (kW/m^2)
S	Vaporization sensitivity of the fuel to external heat flux or the ratio of vaporization rate of the fuel to external heat flux applied to the fuel (g/kJ)
t_{ig}	Time to piloted ignition of fuel vapor/air mixture (s)
T_d	Gas temperature in the sample duct (K)
T_a	Ambient temperature (K)
Y_{CO}	Yield of CO or the ratio of generation rate of CO to vaporization rate of the fuel
Y_{CO_2}	Yield of CO_2 or the ratio of generation rate of CO_2 to vaporization rate of the fuel
ϵ	Surface absorptivity or fraction of supplied energy absorbed by the fuel surface
χ_a	Fraction of external energy supplied and/or removed from the fuel surface by sources other than external heat source
δ_i	Density ratio of product i and air
ϕ	Ratio of flow rate of oxygen to vaporization rate of the fuel divided by stoichiometric mass oxygen to fuel ratio

SUMMARY

This report presents results for the fire behavior of pure and askarel-contaminated fluids which are candidates for use as railroad transformer dielectric insulating fluids. The fluids used in the study were a high temperature hydrocarbon fluid and a dimethyl-siloxane fluid. The amount of askarel in the mixture was varied from 0 to 7 percent by weight. The fire behavior of the fluids was examined on the basis of parameters obtained in the FM Laboratory-Scale Flammability Apparatus.

The following summary presents the results:

1. The heat release rate in larger-scale fires of hydrocarbon fluid is expected to be about ten times the rate of dimethyl-siloxane fluid under stagnant pool conditions. Askarel contamination of hydrocarbon fluid is expected to have insignificant effect on the heat release rate in the larger-scale fires of the hydrocarbon fluid. Askarel contamination of dimethyl-siloxane fluid is expected to show some decrease in the heat release rate in larger-scale fires. The heat release rate in larger-scale fires of hydrocarbon and dimethyl-siloxane fluids is expected to be about one-half and one-twentieth the rate for heptane. The heat release in larger-scale fires of heptane is expected to be about $2,700 \text{ kW/m}^2$.
2. In larger-scale fires, heptane, hydrocarbon and dimethyl-siloxane fluids are expected to vaporize in the ratio of about 20:10:1 respectively. Askarel contamination of the hydrocarbon fluid is expected to have insignificant effect on the vaporization rates of the hydrocarbon fluid in larger-scale fires. Askarel contamination of the dimethyl-siloxane fluid is expected to result in some decrease in the vaporization rate of dimethyl-siloxane fluid in larger-scale fires. The formation of a solid crust at the surface of dimethyl-siloxane fluid in larger-scale fires in stagnant pools is expected to be beneficial in maintaining low vaporization rate.
3. The boiling point of dimethyl-siloxane is 39°C higher than the boiling point of hydrocarbon fluid. The boiling point of askarel is considerably lower than dimethyl-siloxane and hydrocarbon fluids (175°C lower and 136°C lower respectively). Thus, mixtures of dimethyl-siloxane and hydrocarbon with askarel subjected to heat are expected to generate askarel-rich vapors.

4. The flash and fire points of hydrocarbon/askarel mixtures are lower than those of dimethyl-siloxane/askarel mixtures by about 28°C and 61°C respectively. The flash and fire points of hydrocarbon/askarel and dimethyl-siloxane/askarel mixtures decrease slightly as the amount of askarel is increased in the mixture; the decrease is especially noticeable for dimethyl-siloxane for the flash point above about 5 percent by weight of askarel.

5. The ignition and surface flame spread for hydrocarbon under larger-scale fire conditions are expected to be about one and a half times as fast as that of dimethyl-siloxane fluid in the presence or absence of askarel. The ignition and surface flame spread in larger-scale fire conditions are expected to increase somewhat as the amount of askarel is increased in the mixtures with dimethyl-siloxane and hydrocarbon fluids. Ignition and surface flame spread for red oak in the larger-scale fires are expected to be about three times as fast as for the hydrocarbon fluid.

6. Under certain conditions, a fluid exposed to an exposure fire (i.e., external heat flux) can generate vapors without burning, which is defined as a non-flaming fluid fire (or pyrolysis) in this report. Under these conditions dimethyl-siloxane fluid is expected to vaporize at a lower rate than the hydrocarbon fluid at lower external heat flux values. However, at higher external heat flux values dimethyl-siloxane is expected to vaporize about twice as fast as the hydrocarbon fluid. Askarel contamination of hydrocarbon fluid is expected to have insignificant effect on the vaporization rate of the hydrocarbon fluid in the non-flaming fires. Askarel contamination in dimethyl-siloxane fluid in non-flaming fires, however, is expected to be beneficial in reducing the vaporization rate of pure dimethyl-siloxane fluid below that of the hydrocarbon fluid for higher external heat flux values.

7. The FM Flammability Apparatus is useful in evaluating the fire behavior expected in larger-scale fires of pure and contaminated transformer dielectric insulating fluids.

On an overall basis, for stagnant pool fire conditions, the fire hazard of dimethyl-siloxane fluid is expected to be less than that of the hydrocarbon. In this study, hazards associated with human physiological responses to fire products, as described in Ref 8, have not been assessed.

1. INTRODUCTION

OBJECTIVE

The objective of this study was to evaluate 1) the fire behavior of a high-temperature hydrocarbon fluid and a dimethyl-siloxane fluid which are candidates for use in the retro-filling of askarel-filled railroad transformers, and 2) to investigate the effect of askarel on the fire behavior of the fluids.

In this report the high-temperature hydrocarbon fluid is designated as hydrocarbon fluid. A high-temperature hydrocarbon fluid made by a different manufacturer and used in larger-scale fire tests was also used in this study for quantitative correlation. This fluid is designated as hydrocarbon fluid-2.

2. BACKGROUND

The fire behavior of a fuel depends on the following parameters⁽¹⁾:

- 1) Ease of ignition/rate of surface flame spread;
- 2) Rate with which fuel vaporizes in pyrolysis and in combustion.

Pyrolysis is defined as a process occurring without burning and combustion is defined as a process occurring with burning;

- 3) Heat release rates;
- 4) Generation rates of pyrolysis and combustion products considered toxic;
- 5) Magnitude of optical transmission through pyrolysis and combustion products, i.e., reduction in visibility through the products;
- 6) Ease of extinction of pyrolysis and combustion processes.

The above parameters are dependent on the physical and chemical properties, size, shape and configuration of the fuel, and the fuel environment.

Hydrocarbon and dimethyl-siloxane fluids are very dissimilar in their physical and chemical properties. It is known that in larger-scale pan fires the heat release rate from a hydrocarbon fluid is about 14 times the rate from a dimethyl-siloxane fluid.⁽²⁾ The flash point of dimethyl-siloxane is reduced considerably as the amount of askarel in the mixture is increased up to 5 percent by weight.⁽³⁾ These results indicate that retrofilling of askarel-filled railroad transformers by hydrocarbon and dimethyl-siloxane fluids, where some askarel contamination of the fluids is expected, could present an increased degree of fire hazard. This study, therefore, was undertaken to evaluate the fire behavior of hydrocarbon and dimethyl-siloxane fluids in the presence and absence of different amounts of askarel. The fire behavior was evaluated on the basis of the first three cited parameters. The parameters were obtained by using the FM Laboratory-Scale Flammability Apparatus.⁽¹⁾

3. PARAMETERS FOR THE EVALUATION OF FIRE BEHAVIOR OF FUELS

In this study the parameters considered for the evaluation of fire behavior of fuels included 1) expected ease of ignition and rate of surface flame spread; 2) vaporization rate in the pyrolysis and combustion of the fuel; and 3) heat release rates in the combustion of fuel. The parameters were either measured directly or derived from the measured properties utilizing simple principles.

3.1 IGNITION AND SURFACE FLAME SPREAD

Ignition is defined as a process of generation and maintenance of a flammable fuel vapor/air mixture near the surface. Flame spread is defined as a series of consecutive ignitions at the surface. Ignition and flame spread are sustained at the surface when there is a balance between the energy supplied to the surface and the energy required to generate and maintain the flammable fuel vapor/air mixture near the surface. The energy can be supplied to the surface by external heat sources as well as by the flame of the fuel vapor/air mixture present near the surface. Some of the energy supplied, however, is taken away by surface heat losses when the surface temperature is higher than ambient.

In the FM Flammability Apparatus, the external energy is supplied to the fuel surface by radiant heaters. If \dot{q}_e'' is the external heat incident on the fuel surface and t_{ig} is the time to ignition, then the total external energy supplied to the fuel is $\dot{q}_e'' \cdot t_{ig}$. This total energy can be defined as an ignition/flame spread parameter, E_T . If the energy required to generate and maintain flammable fuel vapor-air mixture near the surface is expressed as E_{eff} , then the following relationship can be derived:⁽⁴⁾

$$\frac{E_{eff}}{E_T} = \epsilon (1 + \chi_a) \quad , \quad (3-1)$$

where ϵ = surface absorptivity or, fraction of supplied energy absorbed by the fuel surface; χ_a = fraction of external energy supplied and/or removed from the surface by sources other than the external heat source (such as energy supplied by the flame and energy removed by surface heat losses). Three conditions can be described from eq (3-1):

1) When the magnitude of external heat flux is very high.
Under this condition $\chi_a \ll 1.0$, and if $\epsilon \approx 1.0$,

$$E_T \approx E_{\text{eff}} \quad (3-2)$$

Under this condition an increase in external heat flux will result in a proportional decrease in time to ignition such that their product, which is defined as energy, remains constant irrespective of the magnitude of external heat flux. Under this condition ignition and surface flame spread are governed by fuel surface properties alone and energy supplied by the flame or removed by surface losses are unimportant.

2) When the energy supplied by the flame of fuel vapor/air mixture is negligibly small and surface heat losses are large.

Under this condition, χ_a is negative and E_T is greater than E_{eff} . In this case E_T will continue to increase as external heat flux is decreased until the critical heat flux is reached at or below which ignition and flame spread cannot occur.

3) When the energy supplied by the flame of fuel vapor/air mixture is large, surface heat losses are small and surface absorptivity is close to unity.

Under this condition, χ_a could be positive or negative depending on the magnitude of the energy supplied by the flame and surface heat losses. If χ_a is positive, E_T is less than E_{eff} ; less energy is needed from external sources for ignition and flame spread.

The smaller the value of E_T , the faster are the ignition and surface flame spread expected in larger-scale fires. The larger the value of E_T , the slower are the ignition and surface flame spread expected in larger-scale fires. The smaller magnitude of E_T could be due to: 1) higher external heat flux values; 2) fuels with low surface heat losses; 3) significant flame radiation resulting in a higher magnitude of energy supplied to the fuel; and 4) surface absorptivity is close to unity, i.e., all the energy supplied to the surface is absorbed. Thus, the relative magnitudes of ignition/surface flame spread parameter, E_T , for different fuels, which are expected to be different in larger-scale fires, could be obtained in the laboratory-scale apparatus by simple measurement of time to ignition at different heat flux values expected in larger-scale fires. This is one of the principles of operation of the FM Flammability Apparatus and was used to examine the fluids in this study.

3.2 VAPORIZATION RATE OF THE FUEL

The rate with which a fuel vaporizes depends on heat flux supplied to fuel, heat losses by the fuel and the heat required to vaporize the fuel. In pyrolysis, which is defined as a vaporization process occurring without flaming, the heat is predominantly supplied to the fuel by external heat sources. In combustion, defined as a process occurring with flaming, in addition to heat supplied by external source, the flame of the fuel vapor/air mixture present near the surface also supplies heat to the fuel.

In the FM Flammability Apparatus, the radiant heaters are used as external heat sources and the vaporization rate of the fuel in pyrolysis and combustion is measured directly.

The ratio of fuel vaporization rate to external heat flux applied to the fuel is defined as the vaporization sensitivity of the fuel to external heat flux, S . S is defined as the amount of fuel vaporized per unit amount of external energy incident to the fuel surface and is expressed as⁽⁴⁾:

$$S = \frac{\epsilon}{L_g} (1 + \chi_a) \quad , \quad (3-3)$$

where ϵ = surface absorptivity as defined in eq (3-1); L_g = 'actual' heat of vaporization of the fuel; and χ_a = fraction of external energy supplied and/or removed from the surface by sources other than the external heat source (i.e., energy supplied by the flame and energy removed by surface heat losses).

In pyrolysis, because there is no flame, χ_a is negative. In combustion the energy supplied by the flame is not zero and χ_a can be positive or negative depending on the amount of energy supplied by the flame and energy removed by surface losses. The higher the value of S , higher is the amount of fuel vaporized per unit amount of external energy supplied and, thus, higher are the magnitudes of parameters, such as heat release rate, toxic product and "smoke" generation rates.

The following conditions can be described on the basis of eq (3-3):

1) The magnitude of external heat flux is very high.

Under this condition, $\chi_a \ll 1.0$, and if $\epsilon \approx 1.0$

$$S \approx 1/L_g \quad . \quad (3-4)$$

Thus, the inverse of the sensitivity is the 'actual' heat of vaporization of the fuel. Under this condition energy supplied by the flame or removed from the surface is unimportant.

2) The energy supplied from the flame is large, the energy removed from the surface is small, and surface absorptivity is close to unity. Under this condition χ_a can be positive or negative. If χ_a is positive, S is larger than in case 1. This condition is generally present in larger-scale fires where flames are highly radiating.

3) Flame is absent, i.e., pyrolysis occurs. Under this condition χ_a is negative and S is smaller than under conditions 1) and 2). From S as a function of external heat flux L_g/ϵ and surface heat losses can be calculated.

In larger-scale fires, different fuels are expected to have different S values. Fuels with high S values are expected to present a higher degree of fire hazard than fuels with low S values. In fact, fuels could be arranged in decreasing order of S which would be expected to represent a decreasing order of degree of fire hazard. The higher value of S could be due to: 1) small value of the actual heat of vaporization of the fuel, L_g ; 2) low values of surface heat losses; 3) highly radiating flame, i.e., higher values of energy supplied to the fuel; and 4) the surface absorptivity, ϵ , close to unity, i.e., all the energy supplied is absorbed by the surface. The sensitivity, S, expected in larger-scale fires of different fuels can be obtained by simple measurements of vaporization rates at different external heat flux values expected in larger-scale fires. This is one of the principles of operation of the FM Flammability Apparatus and was used to examine the fluids in this study.

3.3 HEAT RELEASE RATE

Heat release rate is defined as a product of vaporization rate and the heat of combustion of the fuel. The heat of combustion of the fuel is the actual heat of combustion rather than complete heat of combustion, because fuel vapors usually do not burn completely in fires. Thus,

$$\dot{Q}_A'' = \dot{m}_b'' \cdot H_A \quad , \quad (3-5)$$

where \dot{Q}_A'' = actual heat release rate from the combustion of the fuel per unit fuel surface area (kW/m^2); \dot{m}_b'' = vaporization rate of the fuel in combustion per unit fuel surface area ($\text{g/m}^2\text{s}$); H_A = actual heat of combustion per unit mass of the fuel (kJ/g).

In the FM Flammability Apparatus used in this study, the actual heat release rate, \dot{Q}_A'' , was obtained by using the technique of oxygen depletion, which has recently been developed at the Factory Mutual Research Corporation (FMRC) and is described in Appendix A. Since \dot{Q}_A'' and \dot{m}_b'' are obtained in the experiments, H_A can be calculated, which is the ratio of \dot{Q}_A'' to \dot{m}_b'' from eq (3-5).

The convective heat release rate is measured directly in the FM Flammability Apparatus as described in Section 4.6.2, and can be expressed as:

$$\dot{Q}_c'' = \dot{m}_b'' \cdot H_c \quad , \quad (3-6)$$

where \dot{Q}_c'' = convective heat release rate from the combustion of the fuel per unit fuel surface area (kW/m^2); \dot{m}_b'' = vaporization rate of the fuel in combustion per unit fuel surface area ($\text{g/m}^2\text{s}$); H_c = convective heat of combustion per unit mass of the fuel (kJ/g). Since \dot{Q}_c'' and \dot{m}_b'' are obtained in the experiments, H_c , the ratio of \dot{Q}_c'' to \dot{m}_b'' from eq (3-6), can be calculated.

When flame radiation is equal to zero, $H_A = H_c$. When flame radiation is not zero, as is the case in larger-scale fires, and heat losses are negligibly small,

$$H_R = H_A - H_c \quad (3-7)$$

and,

$$\dot{Q}_R'' = \dot{Q}_A'' - \dot{Q}_c'' \quad , \quad (3-8)$$

where, H_R = radiative heat of combustion per unit mass of the fuel (kJ/g); \dot{Q}_R'' = radiative heat release rate from the combustion of the fuel per unit fuel surface area (kW/m^2). H_R and \dot{Q}_R'' , thus, can be calculated by difference. This principle is used in the FM Flammability Apparatus, because the apparatus has been designed such that heat losses are negligibly small.

Fires of different fuels can occur under different conditions where mass loss rates and heat of combustion can vary significantly. The heat release rates, thus, are not expected to be constant in fires if conditions are variable. Thus, in the FM Flammability Apparatus, mass loss rate, heat of combustion and heat release rate for fuels are obtained under wide variations of experimental conditions expected in real fires.

The higher the rate of heat release in larger-scale fires, the higher is the degree of fire hazard expected. These principles have been used to examine the fluids in this study.

4. EXPERIMENTAL APPARATUS AND PROCEDURES

The FM Flammability Apparatus shown in Figures 4-1 and 4-2 was used in this study because the apparatus has been designed to obtain generalized parameters to describe the fire behavior of liquids and solids under wide variations of conditions expected in larger-scale fires.⁽¹⁾ In addition, encouraging correlations have been obtained between data from the apparatus and larger-scale fire tests.

4.1 FUEL SAMPLE CONTAINER

The fuel container was about 0.007 m^2 in area and about 0.02 m deep and was made from two sheets of heavy-duty aluminum foil. The container was supported in a horizontal configuration on four pins (No. 10 in Figure 4-2).

4.2 AIR SUPPLIED TO THE FUEL

The fuel in the container was surrounded by a quartz tube (No. 9 in Figure 4-2) about 0.17 m in diameter and 0.61 m long. Air with a flow rate of about $1.4 \times 10^{-3} \text{ m}^3/\text{s}$ was introduced at the bottom of the quartz tube. This condition is defined as forced air flow condition. The experiments were also performed without the quartz tube, where fuel was burned in the open (defined as natural air flow condition).

4.3 EXTERNAL HEAT FLUX APPLIED TO THE FUEL

Four high-density radiant heaters each containing six tungsten quartz lamps (No. 13, in Figure 4-2) were used coaxially for the application of external heat flux to the fuel. The output of all four radiant heaters was controlled by a single controller.

The external heat flux to the fuel surface was calibrated by using a heat flux gauge (Model No. 16-10-GTW63, Medtherm Corporation, Huntsville, Alabama). The heat flux gauge was traversed horizontally and vertically within the range of the fuel dimension. Each radiant heater was adjusted by forward and backward or upward and downward movements and by varying the angle of inclination until the heat flux within the range of fuel dimension was reasonably uniform. For each controller setting, the heat flux gauge was placed at about 100 locations within the range of fuel dimension, and the steady-state output of the heat flux

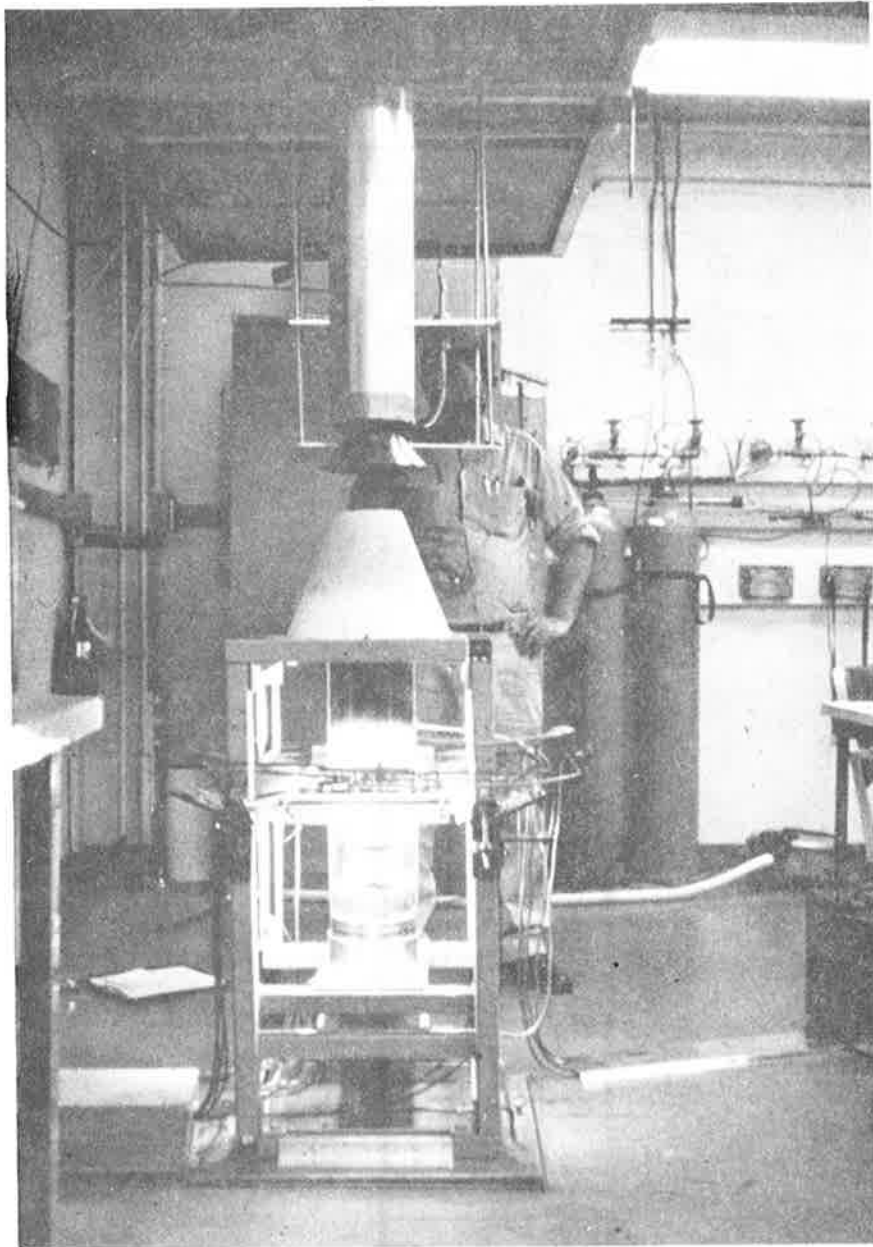


FIGURE 4-1 FM FLAMMABILITY APPARATUS

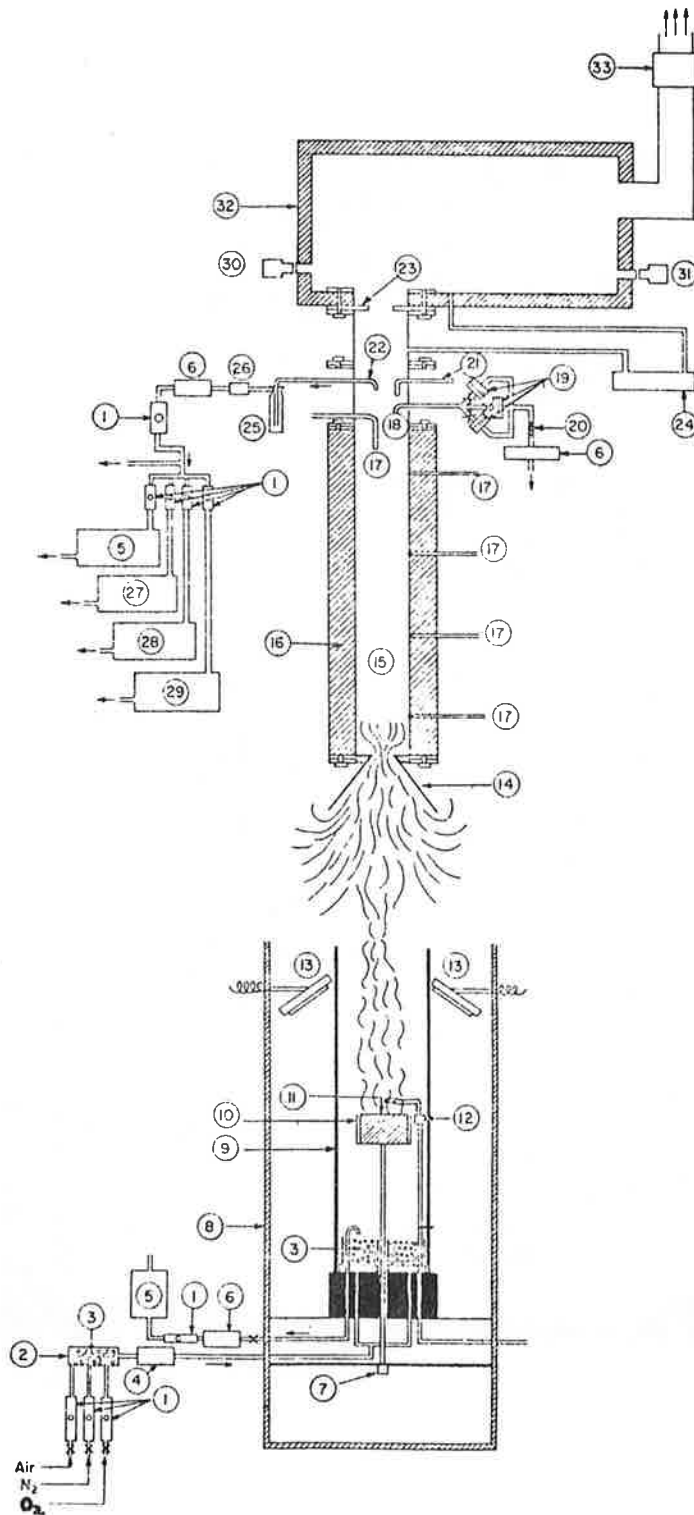


FIGURE 4-2 LABORATORY-SCALE FLAMMABILITY APPARATUS

LIST OF COMPONENTS FOR EXPERIMENTAL APPARATUS

1. Calibrated Flow Meters - Matheson Gas Products, Lynchurst, New Jersey
2. Steel Gas Mixer, 0.076 m ID, 0.24 m in length
3. Glass Beads (1.5 mm in diameter)
4. Flow Meter - Model 2012, Thermo System Inc., St. Paul, Minnesota
5. Continuous Oxygen Paramagnetic Analyzers: Models F-3 and 755,
Beckman Instruments, Inc., Fullerton, California
6. Pumps
7. Water-cooled Universal Transducing Cell, Model No. UC3,
Statham Instruments, Inc., Oxnard, California
8. Uni-strut Frame
9. Quartz Tube, 0.61 m in length and 0.17 m in diameter (internal)
10. Aluminum Sample Holder, ~0.10 m in diameter (internal)
and ~0.02 to 0.05 m deep
11. Fuel
12. Pilot Flame
13. High-density Radiant Heaters (four, only two are shown) Model 5208,
Research Inc., Minneapolis, Minnesota
14. 0.0016 m stainless steel funnel, internal diameter of stem hole, 0.0310 m
15. 0.00018 m stainless steel duct, ID 0.10 m, 0.61 m long
16. Fiberglass Insulation, 0.1 m thick, 0.61 m long
17. Thermocouples - Type TAS, exposed junction Chromel-Alumel, United Sensor
and Control Corporation, Watertown, Massachusetts, and Chromel-Alumel
Ribbon Thermocouples, 36FF, ISA Type K, Nannac Corporation, Framingham,
Massachusetts
18. 0.001 m ID Stainless Steel Particulate Probe
19. Aerosol Filter Holders, Model XX50-04700, containing filters and
attached to tubes containing charcoal, Tenex, P2O₅, CaSO₄, etc. for
collecting liquid products
20. Limiting orifice, Model XX50-000-00, Millipore Corporation,
Bedford, Massachusetts
21. Probe attached to a cell (not shown) to measure the concentration of
inorganic products (HCl, HCN, etc.)
22. 0.001 m ID Stainless Steel Gas Sampling Probe
23. 0.05077 m Orifice Plate, 0.0032 m thick stainless steel
24. Inclined-vertical Manometer, Model 424-5, Dwyer Instruments Inc.,
Michigan City, Indiana
25. Traps (two, only one is shown) for condensible compounds immersed in a
cooling bath
26. Drier (Anhydrous Ca SO₄), W.A. Hammond Drierite Company, Xenia, Ohio
27. Continuous CO IR-Analyzer, Model 315A, Beckman Instruments, Inc.,
Fullerton, California
28. Continuous CO₂ IR-Analyzer, Model 315A, Beckman Instruments, Inc.,
Fullerton, California
29. Continuous Hydrocarbon Flame-Ionization Analyzer, Model 400,
Beckman Instruments Inc., Fullerton, California
30. Light Source
31. Photo-Cell
32. 0.025 m thick steel box, 0.61 m long, 0.30 m wide, and 0.30 m high
33. Blower

gauge was recorded for each location. All the output values were averaged and multiplied by the calibration constant of the gauge (supplied by the Medtherm Corporation). The deviation between various values was about ± 5 percent of the average value. This procedure was repeated for different controller settings covering the range up to about 70 kW/m^2 at the fuel surface. A calibration curve for the radiant heaters was then constructed where the average heat flux values at the fuel surface were plotted as functions of the controller settings. In the experiments, the calibration curve then was used to determine the heat flux value being applied to the fuel by noting the controller setting.

In all the experiments, the radiant heaters were stabilized by keeping them on for 300 s prior to exposing the fuel to the external heat flux. During this period the fuel was protected by a water-cooled shield completely surrounding the quartz tube and the fuel. At the end of 300 s, the shield was removed quickly to expose the fuel to the external heat flux.

The accuracy of the external heat flux to the fuel surface was determined by measuring the mass vaporization rate of distilled water with experimental conditions identical to those used for the fuels. Table 4-1 lists the data, where excellent agreement between measured and calculated values of the mass vaporization rate of distilled water confirms the accuracy of the external heat flux calibration.

The maximum value of external heat flux that could be applied to the fuel in the apparatus was about 70 kW/m^2 .

4.4 IGNITION OF FUEL VAPOR/AIR MIXTURE

For the piloted ignition of the fuel vapor-air mixture, a premixed ethane/air flame, about 0.03 m in length and about 0.010 m above the fuel surface was provided (No. 12 in Figure 4-2). The flame was tilted upward slightly and was close to the edge of the fuel surface. The heat flux from the flame to the surface was negligibly small.

4.5 VAPORIZATION RATE OF THE FUEL

A water-cooled load cell (No. 7 in Figure 4-2) was used to measure the vaporization rate of the fuel. The load cell was calibrated by using standard weights.

TABLE 4-1
 VAPORIZATION RATE FOR DISTILLED WATER IN NORMAL AIR^a

External Heat Flux (kW/m ²)	Natural Air Flow ^b		External Heat Flux (kW/m ²)	Forced Air Flow ^c	
	Vaporization Rate (g/m ² s)			Vaporization Rate (g/m ² s)	
	Measured	Calculated		Measured	Calculated
16.4	5.9	5.9	26.5	9.7	9.8
26.5	10.4	9.8	32.0	12.4	12.0
33.9	12.9	12.7	38.9	14.7	14.6
44.3	17.3	16.7	45.0	17.4	17.0
59.7	23.4	22.7	52.3	20.1	19.8
			59.7	22.8	22.7

^a From Ref. (1).

^b In the open without the quartz tube.

^c Inside the quartz tube; air flow rate $\sim 1.3 \times 10^{-4} \text{ m}^3/\text{s}$.

4.6 HEAT RELEASE RATE AND GENERATION RATES OF PRODUCTS

For the measurement of heat release rate and generation rate of products, all the products diluted by room air were captured in a sampling duct (Nos. 14 and 15 in Figure 4-2). The sampling duct was designed so that heat losses were minimal and the velocity, temperature, and concentration profiles in the measuring section, were flat across the duct so that single point measurements could be made.

4.6.1 Total Mass Flow Rate of the Mixture of Hot Products and Air

The total mass flow rate of the mixture of hot products and air through the sampling duct was calculated from the following equation:

$$\dot{M}''_T = 9.16 \times [(p_a - \Delta p_d) \cdot \Delta p_m / T_d]^{1/2} \cdot \frac{1}{a}, \quad (4-1)$$

where \dot{M}''_T = total mass flow rate of the mixture of hot products and air through the sampling duct per unit fuel surface area ($\text{g}/\text{m}^2\text{s}$); p_a = measured ambient pressure (atm); Δp_d = measured pressure difference between inside and outside of the sampling duct (atm); Δp_m = measured pressure difference across the measuring orifice plate in the sampling duct, No. 23 (atm); T_d = measured gas temperature in the sampling duct, No. 17 (K); a = fuel surface area taken as the area of the container (m^2).

4.6.2 Convective Heat Release Rate

The convective heat release rate was calculated from the following equation:

$$\dot{Q}''_C = [\dot{M}''_T \cdot C_p(T) \cdot (T_d - T_a)]_{\text{Exp}} - [\dot{M}''_T \cdot C_p(T) \cdot (T_d - T_a)]_{\text{Blank}}, \quad (4-2)$$

where \dot{Q}''_C = convective heat release rate per unit fuel surface area (kW/m^2); C_p = specific heat of air ($\text{kJ}/\text{g K}$); $(T_d - T_a)$ = measured gas temperature rise in the sampling duct above ambient temperature (K); Exp = combustion experiments; Blank = identical blank experiment in the absence of the fuel.

4.6.3 Generation (or Depletion) Rates of Gaseous Products

The concentrations of CO , CO_2 and O_2 were measured by Beckman analyzers (Nos. 5, 27, 28 in Figure 4-2).

The sample of the mixture of products and air was taken from location No. 22, and, before it was introduced into the analyzers, it was passed through two traps, (No. 25) in series, immersed in a cooling bath maintained at -30°C . The traps contained glass beads on top of which glass wool was placed. After leaving the traps, the sample was introduced into a drying tube (No. 26) (anhydrous CaSO_4), and finally was passed through a filter paper (type LS, $5\ \mu\text{m}$). The sampling rate was about $2 \times 10^{-4}\ \text{m}^3/\text{s}$.

The delay time (response time of the analyzer plus time for the sample to reach the analyzer) for each analyzer was measured by creating an appropriate gas environment near location No. 22, and by measuring the time taken by the analyzer for 90 percent of the full response; time zero was the time at which sampling was started.

For the calibration of individual analyzers, gas environments of known concentrations of the calibration gas and pure dry N_2 were created separately near location No. 22.

Before starting an experiment, data for the background concentrations of gases were measured. The generation rates of the products or depletion rate of O_2 were calculated from the following equation:

$$\dot{M}''_i = \Delta C_i \cdot \dot{M}''_T \cdot \delta_i \quad , \quad (4-3)$$

where \dot{M}''_i = generation (or depletion) rate of the product per unit fuel surface area ($\text{g}/\text{m}^2\text{s}$); ΔC_i = difference between initial and final concentration of the product (volume fraction); δ_i = ratio of the density of the product to the density of air.

4.7 OPTICAL TRANSMISSION THROUGH THE MIXTURE OF PRODUCTS AND AIR

The optical transmission, for a fixed path length of 0.749 m, was measured in the flow direction of the mixture of hot products and air (Nos. 30 and 31 in Figure 4-2). The light source used was a tungsten lamp; the light was received by a vacuum phototube (RCA 1P39). The collimating windows were fabricated from a plano-convex lens (Melles Griot 01LP XIII).

In order to reduce the deposition of products on the windows of the optical system, air was introduced at the windows, at a rate of about $2 \times 10^{-5}\ \text{m}^3/\text{s}$, (which was very small compared to the value of about $0.04\ \text{m}^3/\text{s}$ for the volumetric flow rate of the mixture of products and air flowing through the system).

The optical density per unit path length was calculated by the following equation:

$$D = \frac{1}{\ell} \ln (I_o/I) , \quad (4-4)$$

where D = optical density per unit optical path length (m^{-1}); ℓ = optical path length (m); I_o = optical transmission through ambient air (mv); I = optical transmission through the mixture of products and ambient air (mv).

4.8 FUELS

The fuels used in the experiments were:

- 1) a 50 - Centistoke dimethyl-siloxane fluid specified for use as a transformer coolant;
- 2) a high-temperature commercial hydrocarbon fluid specified for use as a transformer coolant. (In this report this fluid is designated as hydrocarbon fluid. Another high-temperature hydrocarbon fluid which was used for correlation with larger-scale fire tests is designated as hydrocarbon fluid-2);
- 3) Askarel, believed to be 30 percent trichlorobenzene and 70 percent polychlorinated diphenyl ($C_{12} H_5 Cl_5$).

4.9 DATA ACQUISITION AND ANALYSIS

The data were collected through Hewlett-Packard Computer Data Acquisition System (Model 7970B Digital tape unit and Model 2114B Computer). The data were collected every second for the entire duration of each experiment (each of the collected data was an average of three readings). The data were analyzed through the IBM-370 Computer.

4.9.1 Time to Piloted Ignition of Fuel Vapor/Air Mixture

The time to piloted ignition of fuel vapor/air mixture was measured as a function of external heat flux applied to the fuel.

4.9.2 Vaporization Rate in the Pyrolysis of the Fuel

The vaporization rate was measured as a function of external heat flux applied to the fuel in the nitrogen environment.

4.9.3 Vaporization Rate in the Combustion of the Fuel in Normal Air

The vaporization rate in the combustion of the fuel in normal air was measured as a function of external heat flux applied to the fuel under natural air flow condition.

4.9.4 Heat Release Rate in the Combustion of the Fuel in Normal Air

The heat release rate was obtained as a function of external heat flux applied to the fuel under natural air flow condition. The convective heat release rate was obtained by using eq (4-2). The actual heat release rate was obtained by using the technique of oxygen depletion which has recently been developed at FMRC and is described in Appendix A. The radiative heat release rate was then obtained by difference between actual and convective heat release rates, because heat losses in the apparatus are negligibly small.

4.9.5 Mass Generation Rates of Products in the Combustion of Fuel in Normal Air

Limited data for the mass generation rates of CO and CO₂ were obtained as functions of external heat flux applied to the fuel under natural air flow condition using eq (4-3).

4.9.6 Optical Transmission through Products Generated in the Combustion of Fuel in Normal Air

Limited data for optical transmission as a function of external heat flux were obtained in the study under natural air flow condition.

4.9.7 Boiling, Flash, and Fire Points of the Fuels

The flash and fire points of the fuels were measured by using the "Cleveland Open Cup" method (ASTM D92). The boiling points of the fuels were measured using the technique given in Reference (5).

5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 FUEL DENSITY

The following densities were measured for the fuels:

<u>Fuel</u>	<u>Density (kg/m³)</u>
Hydrocarbon fluid	770.0
Dimethyl-siloxane fluid	960.8
Askarel	1448.8

5.2 FUEL BOILING POINTS*

The boiling points of the fuels, measured by the technique described in Ref (5), are listed in Table 5-1 and shown in Figure 5-1. The boiling point of dimethyl-siloxane fluid is 39°C higher than the boiling point of hydrocarbon fluid. The boiling point of askarel is considerably lower than dimethyl-siloxane and hydrocarbon fluids (175°C lower and 136°C lower, respectively). The boiling points of dimethyl-siloxane/askarel and hydrocarbon/askarel mixtures decrease rapidly as the amount of askarel is increased to 6 percent by weight. Because of boiling point differences it is expected that, as the mixtures are heated, the vapors will be richer in askarel. The vapors will continue to be richer in askarel until most of the askarel has been distilled from the mixture and the boiling point of the fluid is close to the boiling point of pure dimethyl-siloxane and hydrocarbon fluid. The data in Table 5-1 indicate that the boiling points of dimethyl-siloxane/askarel and hydrocarbon/askarel mixtures containing similar amounts of askarel are very similar.

5.3 FLASH AND FIRE POINTS OF FUELS

The measured data for flash and fire points are listed in Table 5-2 and shown in Figure 5-2, where data from Ref (3) are also included. The data measured in this study show higher values of both flash and fire points than the data reported in Ref (3). The data reported in Ref (3) indicate a more rapid decrease in the flash point with increase in the amount of askarel than found in this study.

* Boiling is defined as the appearance of bubbling within the liquid, which possibly could involve chemical decomposition.

TABLE 5-1
 BOILING POINTS OF DIMETHYL-SILOXANE/ASKAREL
 AND HYDROCARBON/ASKAREL MIXTURES^a

Wt % of Askarel in the Mixture	Boiling Point (°C) ^b	
	Dimethyl-Siloxane/ Askarel	Hydrocarbon/ Askarel
0	422	383
4.0	295	292
5.0	278	280
6.0	274	275
7.0	271	272
100.0	247	247

^a Measured by the technique described in Ref (5).

^b For the first appearance of boiling; temperature constant for about 20 s.
 The temperature increases as liquid starts boiling vigorously.

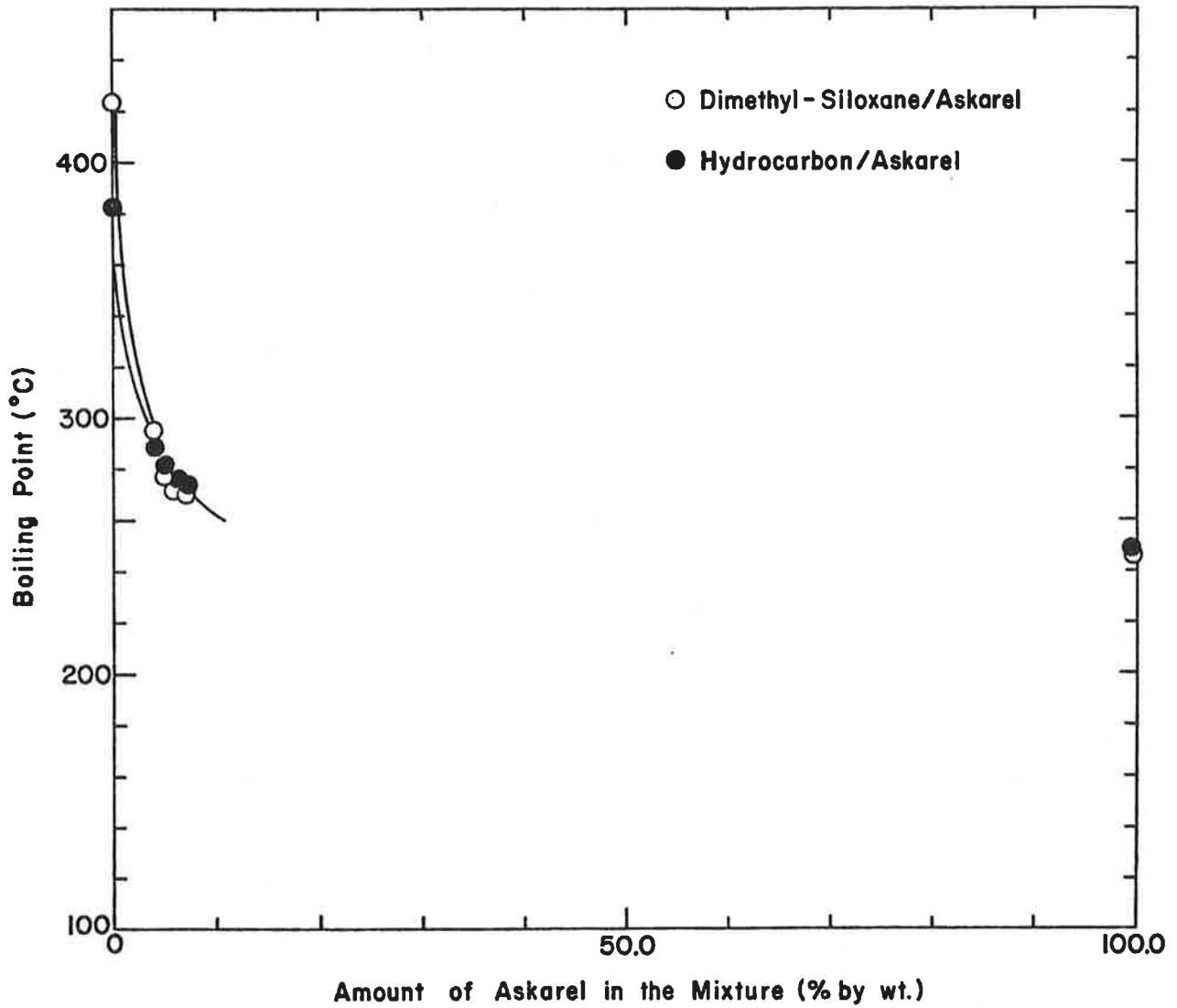


Figure 5-1. Boiling Points of Dimethyl-Siloxane/Askarel and Hydrocarbon/Askarel Mixtures as Functions of Amount of Askarel in the Mixture

TABLE 5-2
FLASH AND FIRE POINTS OF DIMETHYL-SILOXANE/ASKAREL AND HYDROCARBON/ASKAREL MIXTURES^a

Wt % of Askarel in the Mixture	Dimethyl-Siloxane/Askarel Mixture		Hydrocarbon/Askarel Mixture	
	Flash Point (°C) This Study	Fire Point (°C) This Study	Flash Point (°C) Ref (3)	Fire Point (°C) Ref (3)
0	310	374	288	343
0.5	310	366	277	349
1.0	307	371	260	349
2.0	-	-	-	-
3.0	304	366	216	352
4.0	304	377	204	349
5.0	301	374	193	346
6.0	282	366	193	349
7.0	266	363	199	352
			282	271
			277	271
			271	268
			271	268
			271	266
			313	302
			304	302
			304	302
			304	302

^a Measured by using "Cleveland Open Cup" method (ASTM D-92).

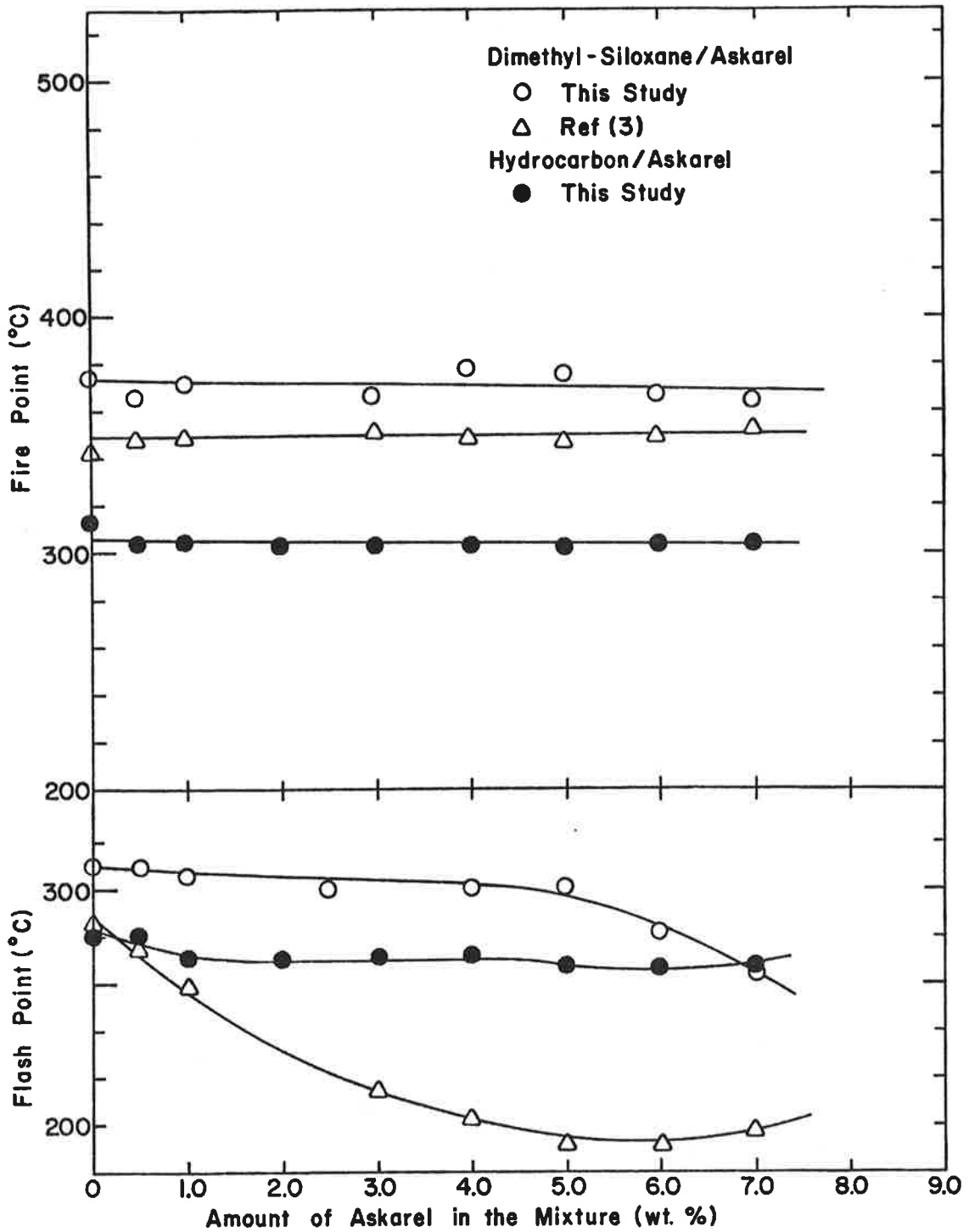


Figure 5-2. Flash and Fire Points of Dimethyl-Siloxane/Askarel and Hydrocarbon/Askarel Mixtures as Functions of the Amount of Askarel in the Mixture

The results of this study indicate lower flash and fire points for the hydrocarbon/askarel mixtures than the dimethyl-siloxane/askarel mixtures. The flash and fire points of both the hydrocarbon/askarel and the dimethyl-siloxane/askarel mixtures decrease slightly with increase in the amount of askarel; the decrease, however, is noticeable above about 5 percent by weight of askarel.

The flash point is that temperature at which the liquid fuel will ignite in air when a pilot flame is passed near and at a fixed distance above the fuel surface. It is the temperature, less than the boiling point, at which the liquid can exert a vapor pressure so that a mixture of fuel vapor/air will be just within the flammability limits. The flash point will vary somewhat according to the position of the ignition source. The further the source from the liquid surface, the higher the flash point.

The fire point is the temperature at which the liquid will not only ignite but will continue to burn. The fire point, which is less than the boiling point, is a temperature that will create a mixture ratio near the surface so that rate of energy release due to combustion will be at least equal to the rate of energy required for the evaporation of the liquid for maintaining a flammable vapor/air mixture near the surface.

Table 5-3 lists the ratio of the flash and fire points to the boiling points of the mixtures.

Both flash and fire points are lower than the boiling point for pure dimethyl-siloxane and hydrocarbon in Table 5-3 as expected. However, the ratios of flash and fire points to the boiling point for the mixtures in Table 5-3 are greater than or close to unity. This indicates that substantial amounts of askarel are distilled off without ignition before the establishment of flash or fire point.

5.4 IGNITION AND SURFACE FLAME SPREAD

The data measured for time to piloted ignition of fuel vapor/air mixture as a function of external heat flux applied to the fuel are listed in Tables 5-4 and 5-5. These measurements were made in the FM Flammability Apparatus where experimental conditions are different than those used in the Cleveland Open Cup method for flash and fire points (ASTM D92). The forced air flow condition corresponds to the condition where the fuel is inside the quartz tube with air entering the tube at the bottom at some known rate. The natural air flow condition corresponds to fuel in the open without the quartz tube (see Section 4.2).

TABLE 5-3
 RATIOS OF FLASH AND FIRE POINTS TO BOILING POINTS OF
 DIMETHYL-SILOXANE/ASKAREL AND HYDROCARBON/ASKAREL MIXTURES

Wt % of Askarel in the Mixture	<u>Flash Point</u> <u>Boiling Point</u>		<u>Fire Point</u> <u>Boiling Point</u>	
	Dimethyl- Siloxane/ Askarel	Hydrocarbon/ Askarel	Dimethyl- Siloxane/ Askarel	Hydrocarbon/ Askarel
0	0.73	0.74	0.89	0.82
4.0	1.03	0.93	1.28	1.03
5.0	1.08	0.96	1.35	1.08
6.0	1.03	0.97	1.34	1.10
7.0	0.98	0.98	1.34	1.11

5.4.1 Ignition/Flame Spread Parameter for Pure Dimethyl-Siloxane and Hydrocarbon Fluids

Figure 5-3 is a plot of ignition/flame spread parameter, E_T , as a function of external heat flux for dimethyl-siloxane and hydrocarbon fluids. E_T , defined in Section 3.1, decreases as external heat flux is increased. Thus, as the heat flux is increased, ignition and surface flame spread are expected to be faster in larger-scale fires.

Under natural or forced air flow condition, the value of E_T for methyl-siloxane fluid is higher than for the hydrocarbon fluid. Thus, the ignition and surface flame spread in larger-scale fires are expected to be faster for the hydrocarbon fluid than for the dimethyl-siloxane fluid.

The value of E_T under natural air flow condition is considerably lower than under forced air flow condition. This is probably due to increased convective cooling under forced air flow condition, i.e., increased surface heat losses; this is condition 2) in Section 3.1. The values of E_T , thus, suggest that ignition and surface flame spread are expected to be faster under natural air flow condition than under forced air flow condition for dimethyl-siloxane and hydrocarbon fluids in larger-scale fires.

The data in Figure 5-3 also suggest that, at lower external heat flux values, E_T is strongly dependent on the external heat flux; E_T continues to increase as external heat flux is continued to be decreased. In this fashion it is possible to reach a critical heat flux value at or below which ignition and surface flame spread cannot occur, a condition also equivalent to flame extinction. For this condition, the critical value of E_T can be defined.

As the external heat flux is increased, E_T decreases and tends to approach a constant value for forced air flow condition as expected from condition 1 in Section 3.1.

5.4.2 Ignition/Flame Spread Parameter for Dimethyl-Siloxane/Askarel Mixtures

Figure 5-4 is a plot of ignition/flame spread parameter, E_T , as a function of amount of askarel in mixtures with dimethyl-siloxane fluid. E_T decreases with increase in the amount of askarel in dimethyl-siloxane fluid. Thus, increased contamination of dimethyl-siloxane fluid by askarel is expected to result in faster ignition and surface flame spread in larger-scale fires. As external heat flux is increased, E_T decreases and, thus, ignition and surface

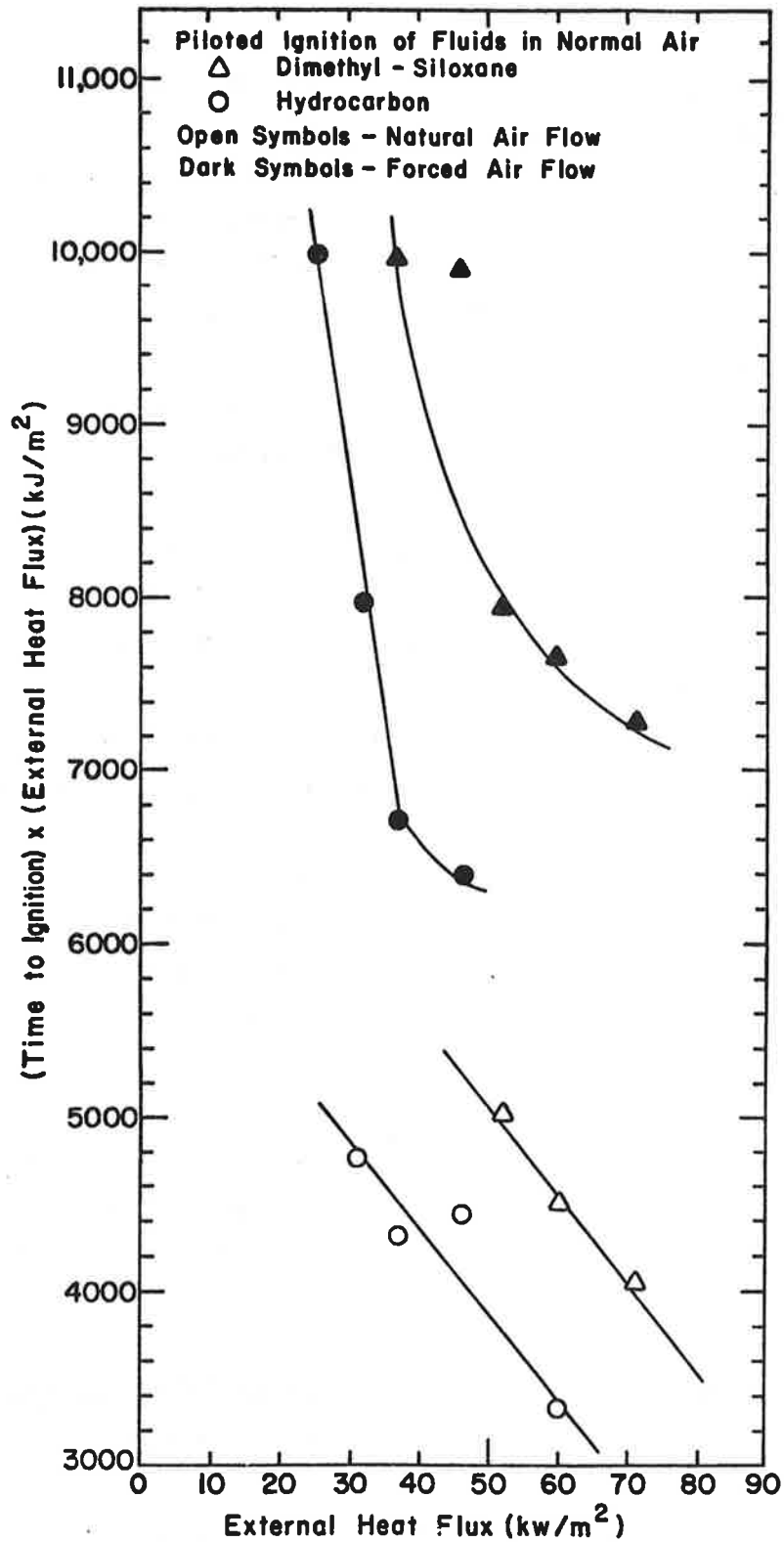


Figure 5-3. Ignition/Flame Spread Parameter for Pure Dimethyl-Siloxane and Hydrocarbon Fluids as a Function of External Heat Flux Under Forced and Natural Air Flow Conditions

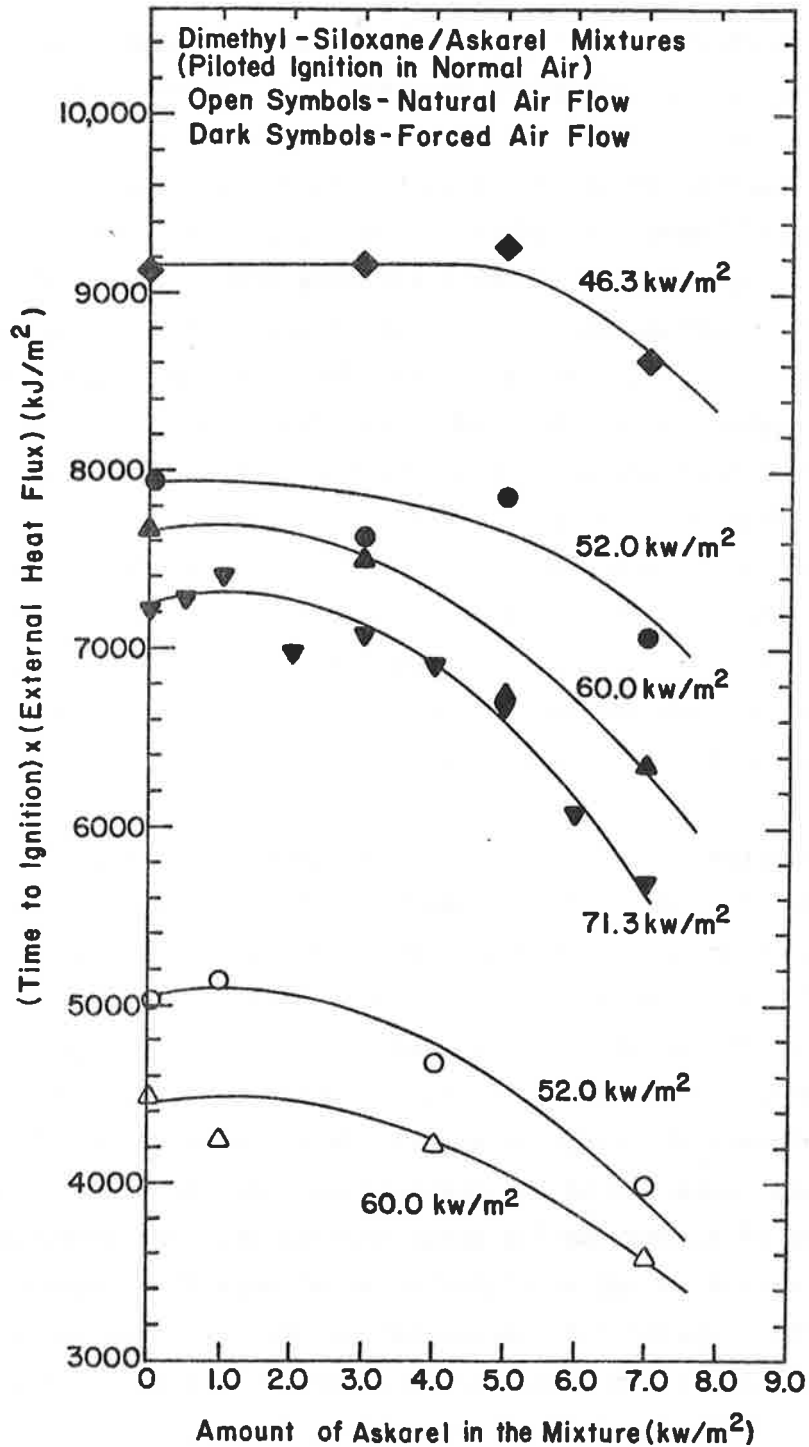


Figure 5-4. Ignition/Flame Spread Parameter for Dimethyl-Siloxane/Askarel Mixtures as a Function of Amount of Askarel in the Mixture

flame spread in dimethyl-siloxane/askarel mixtures are expected to be faster. The value of E_T is smaller under natural air flow condition than under forced air flow condition. Thus, ignition and surface flame spread for dimethyl-siloxane/askarel mixtures are expected to be faster under natural air flow condition than under the forced air flow condition.

For fixed external heat flux value, the decrease in the value of E_T by increasing the amount of askarel, according to eq (3-1) could be due to: 1) chemical interaction of dimethyl-siloxane and askarel such that the energy required to generate and maintain the flammable fuel vapor/air mixture near the surface, E_{eff} , and surface heat losses are decreased; and/or 2) interaction of askarel with the flame resulting in an increase in flame radiation and, thus, higher energy supplied to the fuel surface by the flame. Askarel is an approximate mixture by weight of 70 percent polychlorinated biphenyl and 30 percent trichlorobenzene. Our studies with various other types of fuels show that addition of chlorinated-aromatic type compounds to fuels increases flame radiation.⁽⁴⁾ Thus, it appears that increase in flame radiation may be one of the dominant factors in decreasing the value of E_T as the amount of askarel is increased in dimethyl-siloxane fluid.

5.4.3 Ignition/Flame Spread Parameter for Hydrocarbon/Askarel Mixtures

Figure 5-5 is a plot of ignition/flame spread parameter, E_T , as a function of amount of askarel in mixtures with hydrocarbon fluid. In Figure 5-5 the value of E_T shows some variations as the amount of askarel in hydrocarbon fluid is increased. The decrease in E_T value, however, becomes noticeable above 4 percent by weight of askarel. Thus, increased contamination of hydrocarbon fluid above 4 percent by weight of askarel is expected to result in faster ignition and surface flame spread in larger-scale fires of hydrocarbon/askarel mixtures. The values of E_T are smaller under natural air flow condition than under forced air flow condition and at higher external heat flux values. Thus, ignition and surface flame spread for hydrocarbon/askarel mixtures are expected to be faster under natural air flow condition than under forced air flow condition and for higher external heat flux values.

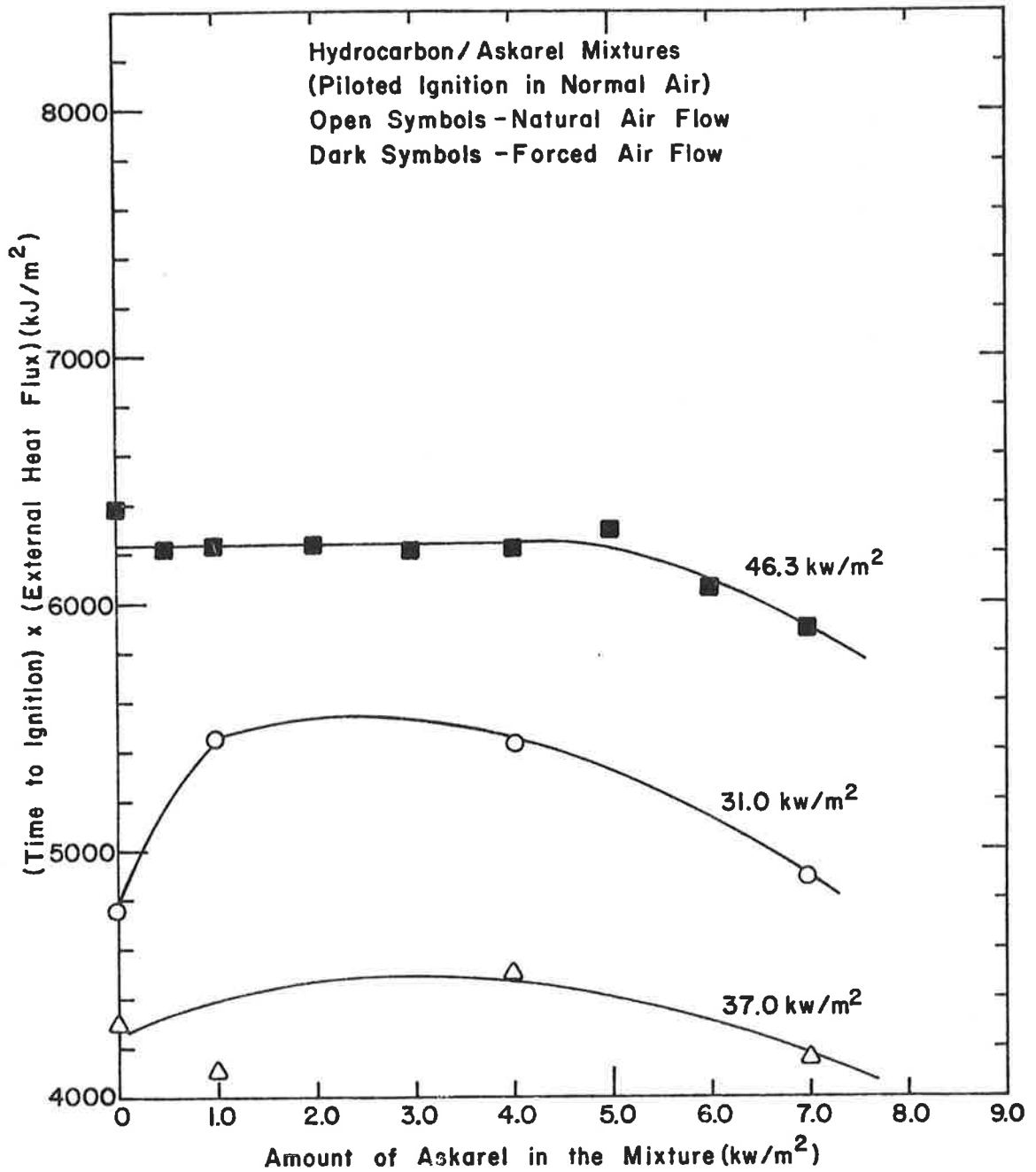


Figure 5-5. Ignition/Flame Spread Parameter for Hydrocarbon/Askarel Mixtures as a Function of Amount of Askarel in the Mixture

Hydrocarbon flames in air are very luminous and generate significant amounts of flame radiation;⁽⁴⁾ the effect of flame radiation in lowering the value of E_T may not be as important (as it is in dimethyl-siloxane) until the amount of askarel in hydrocarbon fluid is increased above about 4 percent by weight.

5.4.4 Relative Magnitudes of Ignition and Surface Flame Spread of Dimethyl-Siloxane and Hydrocarbon Fluids in the Presence and Absence of Askarel

The smaller the value of ignition/flame spread parameter, E_T , the faster are the ignition and surface flame spread expected in larger-scale fires. The magnitude of ignition and surface flame spread is, thus, inversely proportional to E_T . The values of $1/E_T$ can be used for a comparison of magnitudes of expected ignition and surface flame spread for various fuels using red oak as a reference. In our other studies, the ignition/flame spread parameter for red oak was obtained by using conditions identical to those used for the fluids in the FM Flammability Apparatus. The reference point used corresponds to an arbitrarily selected inverse ignition/flame spread parameter equal to 100 for red oak at 31.0 kW/m^2 of external heat flux. The data calculated for relative magnitudes of ignition and surface flame spread are listed in Table 5-6. An examination of the data in the table reveals:

- 1) The expected magnitude of ignition and surface flame spread for red oak increases by a factor of five if external heat flux is increased from 31.0 to 71.3 kW/m^2 .
- 2) For pure or askarel-contaminated dimethyl-siloxane and hydrocarbon fluids, the increase in the magnitude of ignition and surface flame spread is by a factor of about three.
- 3) The ignition/surface flame spread of hydrocarbon/askarel exposed to larger-scale fire conditions is expected to be about one and a half times as fast as those of dimethyl-siloxane/askarel mixtures.
- 4) Under larger-scale fire conditions ignition and surface flame spread for red oak are expected to be about five times as fast as for dimethyl-siloxane/askarel mixtures and about three times as fast as for hydrocarbon/askarel mixtures.
- 5) The magnitude of ignition and surface flame spread is expected to increase insignificantly as the amount of askarel is increased in dimethyl-siloxane and hydrocarbon fluids under larger-scale fire conditions.

TABLE 5-6
RELATIVE MAGNITUDES OF IGNITION AND SURFACE FLAME SPREAD FOR
DIMETHYL-SILOXANE/ASKAREL AND HYDROCARBON/ASKAREL MIXTURES USING RED OAK AS A REFERENCE^a

External Heat Flux (kW/m ²)	Red Oak	Dimethyl-Siloxane/Askarel		Hydrocarbon/Askarel	
	Relative Ignition/ Surface Flame Spread	Wt % of Askarel	Relative Ignition/ Surface Flame Spread	Wt % of Askarel	Relative Ignition/ Surface Flame Spread
25.9	-	0.0	26	0.0	62
	-	-	-	7.0	65
31.0	100	-	-	0.0	78
		-	-	7.0	83
37.0	203	0.0	63	0.0	92
46.3	329	0.0	68	0.0	97
		3.0	68	0.5	100
		5.0	67	1.0	99
		7.0	72	2.0	99
		-	-	3.0	100
		-	-	4.0	100
52.0	339	0	78	0	103 ^b
		3.0	81	-	-
		5.0	79	-	-
		7.0	87	7.0	111 ^b
		0	81	0	108 ^b
		3.0	82	-	-
60.0	492	5.0	93	-	-
		7.0	98	7.0	117 ^b
		0	85	0	113 ^b
		0.5	85	-	-
71.3	475	1.0	84	-	-
		2.0	89	-	-
		3.0	87	-	-
		4.0	90	-	-
		5.0	93	-	-
		6.0	102	-	-
		7.0	109	7.0	123 ^b
		-	-	-	-
		-	-	-	-

^a Reference point corresponds to the inverse of ignition/flame spread parameter equal to 100 for red oak
^b Estimated values, at 31.0 kW/m²

From the data, the following conclusions can be drawn for larger-scale fires:

1) Ignition and surface flame spread for the hydrocarbon fluid are expected to be about one and a half times as fast as for the dimethyl-siloxane fluid. This also holds for mixtures with askarel.

2) Askarel contamination of the hydrocarbon and dimethyl-siloxane fluids is not expected to have any significant effect on ignition and surface flame spread of the fluids in larger-scale fires.

3) Ignition/surface flame spread for red oak is expected to be about three and five times as fast as for hydrocarbon/askarel and dimethyl-siloxane mixtures respectively.

5.5 VAPORIZATION RATE OF THE FUEL

The vaporization rate in pyrolysis was measured in a nitrogen environment as a function of external heat flux under forced nitrogen flow condition. The vaporization rate in combustion was measured in normal air under natural air flow condition.

5.5.1 Vaporization Rate of the Fuel in Pyrolysis

Tables 5-7 and 5-8 list the data for the vaporization rate in the pyrolysis of dimethyl-siloxane/askarel and hydrocarbon/askarel mixtures respectively. The vaporization rates are average steady state (maximum) values per unit fuel surface area.

5.5.1.1 Vaporization Rate in the Pyrolysis of Pure Dimethyl-Siloxane and

Hydrocarbon Fluids - Figure 5-6 is a plot of vaporization sensitivity of the fuel to external heat flux, S , in pyrolysis as a function of inverse of external heat flux for dimethyl-siloxane and hydrocarbon fluids. Note the sudden change in the value of S for dimethyl-siloxane in Figure 5-6. Data for hydrocarbon fluid-2* are also included in the figure. The vaporization sensitivity of the fuel to external heat flux, S , is defined as the ratio of vaporization rate to external heat flux.

The higher the value of S , the higher is the degree of fire hazard. In Figure 5-6, for lower external heat flux values (higher values of inverse heat flux), the value of S is higher for hydrocarbon fluids than for dimethyl-siloxane fluid. At higher external heat flux values (lower values of inverse heat flux),

*Hydrocarbon fluid-2 is from a different source than the high temperature hydrocarbon fluid used in this study.

TABLE 5-7
 VAPORIZATION RATE IN THE PYROLYSIS OF
 DIMETHYL-SILOXANE/ASKAREL MIXTURES IN NITROGEN^a

External Heat Flux (kW/m ²)	31.0	37.0	46.3	52.0	60.0	71.3
Wt % of Askarel in the Mixture						
0	1.0	1.6	39.1	70.9	111.0	159.0
0.5	-	-	2.0	-	48.6	85.0
1.0	-	-	-	-	-	64.2
2.0	-	-	-	-	-	60.1
3.0	-	-	1.9	-	30.0	49.0
4.0	-	-	-	-	-	45.7
6.0	-	-	-	-	-	50.9
7.0	-	-	10.6	-	33.6	52.1
8.0	-	-	-	-	-	55.1
9.0	-	-	-	-	-	57.6

^a Average steady state (maximum) values of the vaporization rate per unit fuel surface area (g/m²s); sample = 5×10^{-5} m³ in aluminum dish, ~ 0.007 m² in area, ~ 0.02 m deep inside the quartz tube; nitrogen flow $\sim 1.4 \times 10^{-3}$ m³/s.

TABLE 5-8
 VAPORIZATION RATE IN THE PYROLYSIS OF
 HYDROCARBON/ASKAREL MIXTURES IN NITROGEN^a

External Heat Flux (kW/m ²)	37	46.3	52.0	60.0	71.3
Wt % of Askarel in the Mixture					
0	16.9	39.1	43.4	57.3	71.5
1.0	-	25.1	38.4	-	71.0
3.0	-	-	-	-	74.2
4.0	-	25.4	46.1	-	74.0
5.0	-	-	-	-	74.3
7.0	14.2	28.3	38.5	-	69.9

^a Average steady state (maximum) values of vaporization rate per unit fuel surface area (g/m²s); sample = 5 x 10⁻⁵ m³ in aluminum dish, ~0.007 m² in area, ~0.02 m deep inside the quartz tube; nitrogen flow ~1.4 x 10⁻³ m³/s.

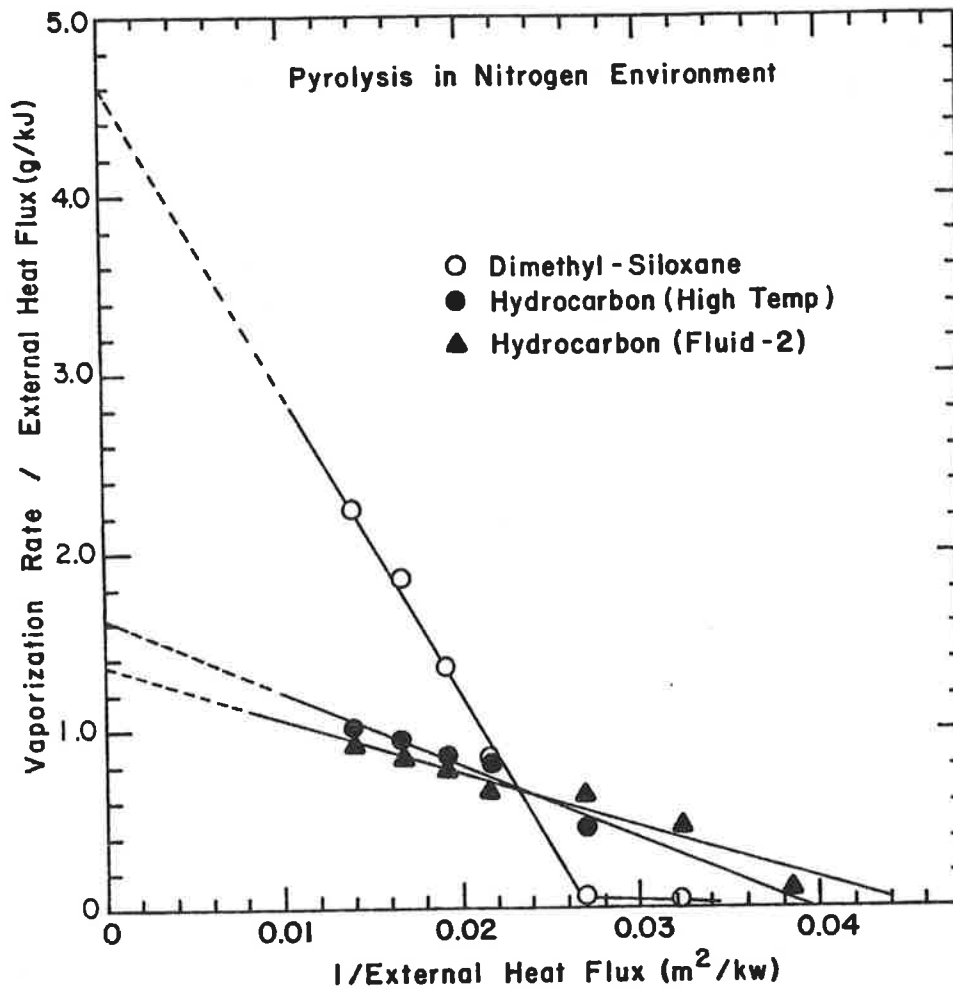


Figure 5-6. Vaporization Sensitivity of the Fuel to External Heat Flux in Pyrolysis for Dimethyl-Siloxane and Hydrocarbon Fluids as a Function of Inverse of External Heat Flux

the value of S for dimethyl-siloxane fluid is considerably higher than for the hydrocarbon fluids. Thus, in pyrolysis, hydrocarbon fluid is expected to vaporize faster than dimethyl-siloxane fluid at low values of external heat flux applied to the fluid. At higher external heat flux values, however, dimethyl-siloxane fluid is expected to vaporize about twice as fast as the hydrocarbon fluid and, in this respect, the dimethyl-siloxane fluid is expected to present a higher degree of fire hazard than the hydrocarbon fluid.

The relationship in Figure 5-6 can be expressed as follows using eq (3-3),

$$\frac{\dot{m}''_p}{\dot{q}''_e} = \frac{\epsilon}{L_g} - \left(\frac{\epsilon}{L_g} \cdot \dot{q}''_o \right) / \dot{q}''_e \quad , \quad (5-1)$$

where \dot{m}''_p = vaporization rate in pyrolysis per unit fuel surface area ($\text{g}/\text{m}^2\text{s}$); \dot{q}''_e = external heat flux applied to the fuel (kW/m^2); \dot{q}''_o = surface heat loss, predominantly due to surface reradiation (kW/m^2). The intercept in Figure 5-6 is thus equal to ϵ/L_g , and the slope is equal to $\epsilon \cdot \dot{q}''_o / L_g$ from which \dot{q}''_o can be calculated. If ϵ is known, the 'actual' heat of vaporization, L_g , can be calculated. The data calculated from least squares analysis are listed in Table 5-9. In the table L_g/ϵ is defined as the 'effective' heat of vaporization and \dot{q}''_o as surface reradiation loss. When $\epsilon \approx 1.0$, the 'effective' heat of vaporization is equal to 'actual' heat of vaporization. When $\epsilon < 1.0$, the 'effective' heat of vaporization is greater than the 'actual' heat of vaporization.

The two hydrocarbon fluids have approximately similar values of 'effective' heat of vaporization and surface reradiation loss. The 'effective' heat of vaporization of dimethyl-siloxane fluid, however, is about one third the value for hydrocarbon fluids. The sensitivity of fuel to external heat flux, S, is thus higher for dimethyl-siloxane fluid than the hydrocarbon fluids at higher heat fluxes as expected from eq (3-3), where χ_a is small or surface reradiation loss is less important.

The surface reradiation loss for dimethyl-siloxane fluid is higher than for the hydrocarbon fluids in Table 5-9. As the external heat flux is decreased, the surface reradiation loss becomes important or χ_a in eq (3-3) increases. Thus, S for dimethyl-siloxane fluid becomes smaller than for the hydrocarbon fluids at lower heat flux values.

TABLE 5-9
 'EFFECTIVE' HEAT OF VAPORIZATION AND SURFACE RERADIATION LOSS FOR
 DIMETHYL-SILOXANE ASKAREL AND HYDROCARBON-ASKAREL MIXTURES

Wt % of Askarel in the Mixture	'Effective' Heat of Vaporization _c (kJ/g) ^a		Surface Reradiation Loss (kW/m ²) ^b	
	Dimethyl- Siloxane	Hydrocarbon High Temp Fluid-2	Dimethyl- Siloxane	Hydrocarbon High Temp Fluid-2
0	0.214	0.610	0.730	22
0.5	0.301	-	46	-
1.0	0.390	0.556	46	32
2.0	0.438	-	45	-
3.0	0.529	0.550	45	31
4.0	0.595	0.550	44	31
6.0	0.585	-	42	-
7.0	0.595	0.613	40	29
8.0	0.582	-	39	-
9.0	0.578	-	38	-

^a Defined as the ratio of 'actual' heat of vaporization to surface absorptivity (L_g/ϵ).

^b q''_0 in eq (5-1).

^c High temperature hydrocarbon fluid was used in this study. Hydrocarbon fluid-2 which is different than the high temperature hydrocarbon fluid was used only for comparison.

5.5.1.2 Vaporization Rate in the Pyrolysis of Dimethyl-Siloxane/Askarel and Hydrocarbon/Askarel Mixtures - Figure 5-7 is a plot of vaporization sensitivity of the fuel to external heat flux, S , in pyrolysis as a function of amount of askarel in the mixtures at different heat flux values. The smaller the value of S , the lower is the degree of fire hazard expected. The data in Figure 5-7 show that the value of S for dimethyl-siloxane fluid is reduced drastically as the amount of askarel is increased. Askarel, however, shows no significant effect on the S values for the hydrocarbon fluid. The value of S for pure dimethyl-siloxane fluid is about twice the value for pure hydrocarbon fluid; however, in the presence of askarel, the value for dimethyl-siloxane is reduced substantially below the values for the hydrocarbon fluid. In this respect the askarel contamination of dimethyl-siloxane fluid is beneficial.

The data in Table 5-9 show that for dimethyl-siloxane/askarel mixtures, the decrease in the value of S by increasing the amount of askarel is correlated with an increase in the 'effective' heat of vaporization. The 'effective' heat of vaporization and surface reradiation loss for hydrocarbon/askarel mixtures show insignificant variations with changes in the amount of askarel.

5.5.2 Vaporization Rate of the Fuel in Combustion

The vaporization sensitivity of the fuel to external heat flux, S , in combustion is considerably higher than the sensitivity in pyrolysis, because of additional energy supplied to the fuel by the flame; i.e., χ_a becomes positive in eq (3-3). As the fire size increases, flame radiation increases; the energy supplied to the fuel by the flame thus increases, resulting in an increase in the sensitivity. The degree of fire hazard from a fuel with highly radiating flame is, therefore, higher than the degree of fire hazard from a fuel with flame having negligible radiation.

Equation (3-3) can be rewritten as follows for combustion:

$$\dot{m}''_b = \frac{\epsilon}{L_g} (\dot{q}''_e + \dot{q}''_{fr} + \dot{q}''_{fc} - \dot{q}''_o) \quad , \quad (5-2)$$

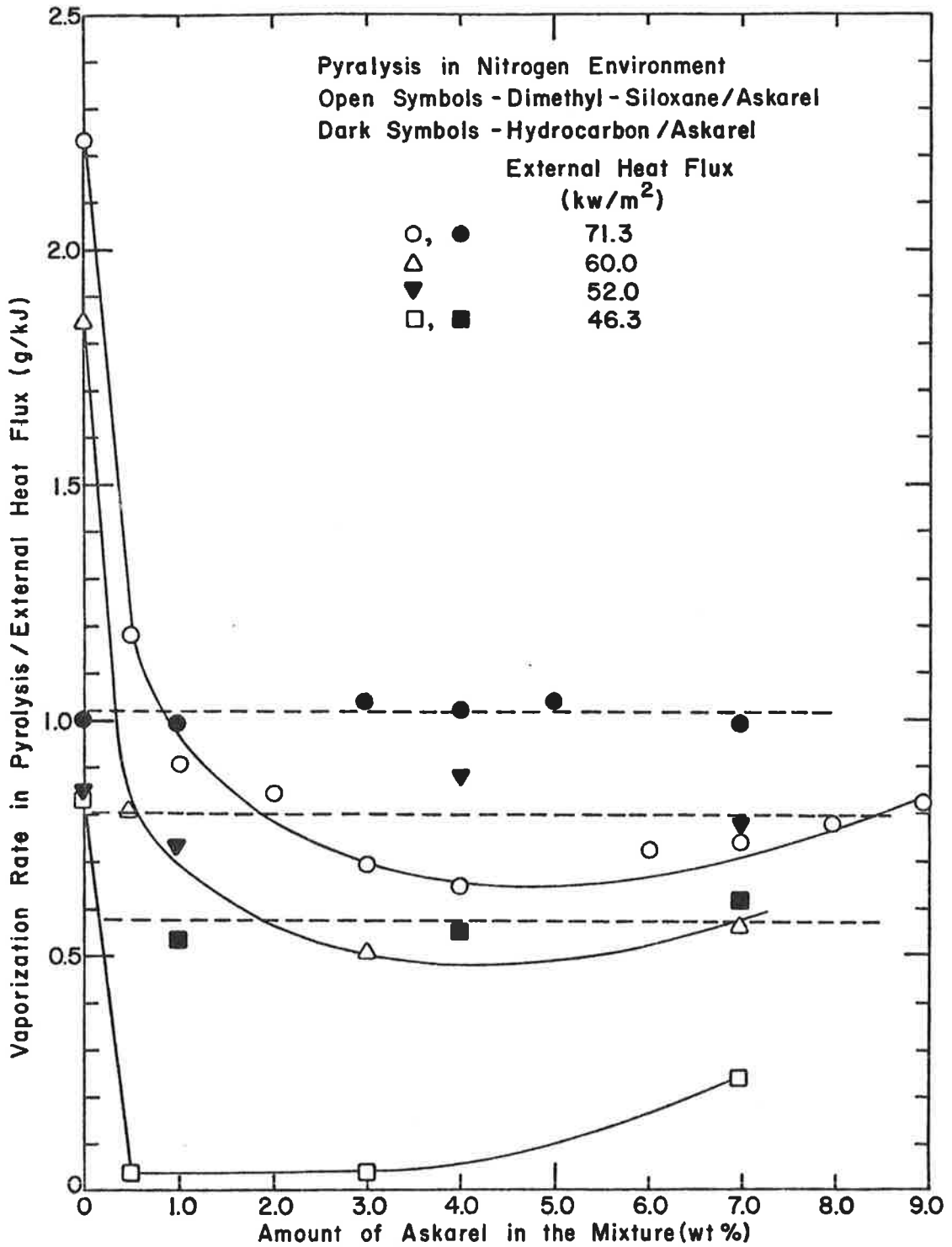


Figure 5-7. Vaporization Sensitivity of the Fuel to External Heat Flux in Pyrolysis for Dimethyl-Siloxane/Askarel and Hydrocarbon/Askarel Mixtures as a Function of Amount of Askarel in the Mixture

where, \dot{m}''_b = vaporization rate of the fuel in combustion per unit fuel surface area ($\text{g}/\text{m}^2\text{s}$); ϵ = surface absorptivity; L_g = 'actual' heat of vaporization of the fuel (kJ/g); \dot{q}''_e = external heat flux applied to the fuel (kW/m^2); \dot{q}''_{fr} = radiative heat flux from the flame supplied to the fuel (kW/m^2); \dot{q}''_{fc} = convective heat flux from the flame supplied to the fuel (kW/m^2); \dot{q}''_o = surface reradiation loss (kW/m^2). In the absence of the external heat flux,

$$\dot{m}''_b = \frac{\epsilon}{L_g} (\dot{q}''_{fr} + \dot{q}''_{fc} - \dot{q}''_o) \quad (5-3)$$

5.5.2.1 Vaporization Rate in the Combustion of Pure Fluids - Table 5-10

lists some data for the combustion of fluids at various fuel surface areas taken from Refs (2), (6), and (7). The data indicate three regions:

1) For very low fuel surface areas, the vaporization rate is very high. This region is dominated by heat transfer by conduction; the flow is laminar. This region, however, is not important in fires.

2) For intermediate values of fuel surface areas, the vaporization rate is low; is dominated by heat transfer by convection; i.e., \dot{q}''_{fc} with $\dot{q}''_{fr} \ll \dot{q}''_{fc}$ in eq (5-3) and is a transition region.

3) For higher values of fuel surface areas, the vaporization rate in combustion increases with increase in the fuel surface area and finally reaches an asymptotic value. The vaporization rate at its asymptotic value is independent of the fuel surface area. The increase in the vaporization rate and achievement of the asymptotic value with increase in the fuel surface area is due to increase in flame radiation; i.e., \dot{q}''_{fr} with $\dot{q}''_{fc} \ll \dot{q}''_{fr}$ in eq (5-3). This region where flow is turbulent is important in larger-scale fires.

Data in Table 5-10 indicate that "gasoline," tractor kerosine, kerosine and diesel oil have asymptotic vaporization rates of approximately $48 \text{ g}/\text{m}^2\text{s}$, and methanol and heptane have rates of approximately 20 and $71 \text{ g}/\text{m}^2\text{s}$ respectively. Transformer oil, solar oil and hydrocarbon fluid-2 do not appear to have reached their asymptotic vaporization rates because fuel surface areas are not large enough.

In the FM Flammability Apparatus used in this study, the fuel surface area is equal to about 0.007 m^2 , which corresponds to the transition region in Table 5-10, where convection is the dominant heat transfer process. Parameters

TABLE 5-10
 VAPORIZATION RATE IN THE COMBUSTION OF FUELS PER UNIT FUEL SURFACE AREA
 UNDER NATURAL AIR FLOW CONDITION IN SMALL AND LARGER-SCALE FIRES^d

Fuel Surface Area (m ²)	Vaporization Rate Per Unit Fuel Surface Area (g/m ² s)								
	"Gasoline" ^a	Tractor Kerosine ^a	Kerosine ^a	Diesel Oil ^a	Transformer Oil ^a	"Solar Oil" ^a	Methanol ^b	Heptane ^c	Hydrocarbon ^c
0.000011	-	144	144	96.6	72.7	137.9	-	-	-
0.000020	214	90	84.8	70	54.9	75.6	-	-	-
0.000028	126.5	76.8	82.0	58.0	48.9	60.8	-	-	-
0.000040	-	57.6	45.1	49.0	40.0	48.9	-	-	-
0.000075	73	-	-	-	-	-	-	-	-
0.000095	-	38.4	26.0	35.0	26.7	35.6	-	-	-
0.00011	58.4	-	-	-	-	-	-	-	-
0.00021	46.2	-	-	-	-	-	-	-	-
0.00031	36.5	22.8	17.8	23.8	16.3	16.3	-	-	-
0.00047	28.0	-	-	-	-	-	-	-	-
0.00053	-	-	-	-	-	-	17.2	-	-
0.00071	-	16.8	13.7	18.2	10.4	8.9	-	-	-
0.00093	25.6	25.6	-	-	-	-	-	-	-
0.0017	21.9	16.8	13.7	15.4	10.4	8.9	-	-	-
0.0030	24.3	-	-	-	-	-	-	-	-
0.0045	-	-	-	-	-	-	11.9	-	-
0.0050	23.1	10.8	12.3	8.4	-	8.9	-	-	-
0.0088	24.3	-	-	-	-	-	-	-	-
0.017	19.5	14.4	12.3	9.8	7.4	8.9	10.8	-	-
0.071	29.2	22.8	21.9	-	11.9	11.9	12.5	-	-
0.196	46.2	33.6	-	25.2	26.7	25.2	-	-	-
0.292	-	-	-	-	-	-	14.5	-	-
0.503	-	40.8	31.4	37.8	-	-	-	-	-
1.17	-	-	-	-	-	-	17.2, 20.5 ^c	70.0	21.9
1.33	49.9	48.0	-	46.2	-	-	-	-	-
1.52	-	-	35.5	-	-	-	-	-	-
2.37	-	-	-	-	-	-	19.5 ^c	72.6	26.3
4.67	-	-	-	-	-	-	20.8 ^c	-	-
5.31	-	50.4	36.9	49.0	-	-	-	-	-
58.0	46.2	-	-	-	-	-	-	-	-
412.0	45.0	-	49.2	-	-	-	-	-	-

^a Data calculated from liquid burning velocities and densities for ambient conditions given in Ref (6).

^b Data from Ref (7).

^c Data from Ref (2); hydrocarbon fluid-2 was used.

^d Data taken from literature.

obtained from the apparatus under this condition are not expected to represent the fuel behavior in large-scale fires. However, fuel combustion in the FM Flammability Apparatus can be changed from a convective heat transfer to a radiative heat transfer dominated process by manipulating the external heat flux and oxygen concentration in the air supplied to the fuel. This is shown in Figure 5-8 for some selected fuels taken from Ref (4). Vaporization rates measured by Kung⁽²⁾ in larger-scale fires are also included in Figure 5-8. Vaporization rate increases with increase in the oxygen concentration and approaches its asymptotic value for high oxygen concentration where flame is highly luminous.

In the region where vaporization rate reaches its asymptotic value, all parameters become almost independent of oxygen concentration with flame radiation dominating the region. In this fashion the fire behavior of the fuel in laboratory-scale experiments is similar to the fire behavior of the fuel in larger-scale fires. Parameters obtained under these conditions in the laboratory-scale experiments are, thus, expected to describe the fire behavior of the fuels in larger-scale fires. This is one of the most important principles of operation of the FM Flammability Apparatus. The asymptotic vaporization rates of fuels are achieved by increasing the oxygen concentration. Once the asymptotic values for fuels have been established, the parameters are obtained for the combustion of fuels in normal air where external heat flux is applied to set the vaporization rates at their respective asymptotic values.

The asymptotic vaporization rate for heptane is about $70 \text{ g/m}^2\text{s}$ for oxygen concentration greater than about 30 percent in the laboratory-scale experiments. The asymptotic vaporization rate for heptane measured in larger-scale fires in air by Kung⁽²⁾ is $71 \text{ g/m}^2\text{s}$. For methanol there are two distinct combustion regions: 1) the luminous flame region for oxygen concentration between about 32 to 38 percent; and 2) the highly luminous flame region for oxygen concentration greater than about 48 percent. For the luminous flame region the asymptotic vaporization rate for methanol is about $24 \text{ g/m}^2\text{s}$. Kung⁽²⁾ reports values of $20.3 \text{ g/m}^2\text{s}$ respectively for the combustion of methanol in larger-scale fires. For the highly luminous flame region, the asymptotic vaporization rate for methanol is about $37 \text{ g/m}^2\text{s}$. For hydrocarbon fluid-2, the asymptotic vaporization rate is $40 \text{ g/m}^2\text{s}$ which is within the range of the asymptotic vaporization rates for "gasoline," tractor kerosine, kerosine, and diesel oil in Table 5-10 for large fuel surface areas (larger-scale fires).

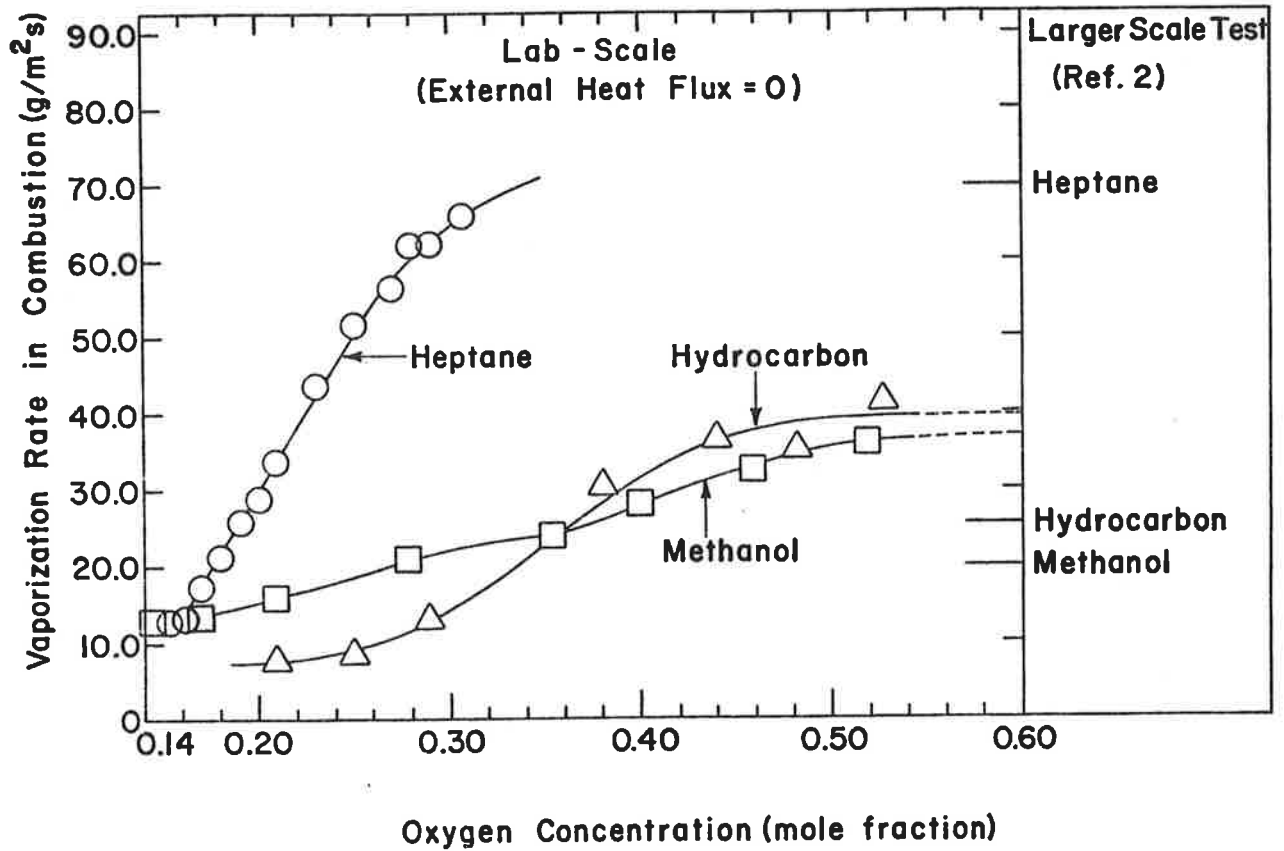


Figure 5-8. Variation of Vaporization Rate in the Combustion of Fuels with Oxygen Concentration in the Absence of External Heat Flux and Larger-Scale Fuel Vaporization Rate-Data from Ref (2)

The increase in vaporization rate with oxygen concentration is due to increase in flame radiative heat flux, \dot{q}''_{fr} , in eq (5-3). This is shown in Figure 5-9 for the hydrocarbon fluid-2 taken from Ref (4). The parameters in Figure 5-9 show three types of dependency on the oxygen concentration:

1) Parameters slightly dependent on the oxygen concentration - actual heat of combustion per unit mass of the fuel (H_A) and yield of CO_2 (Y_{CO_2}).

2) Parameters decreasing with increase in the oxygen concentration - convective heat of combustion per unit mass of the fuel (H_c), convective heat flux from the flame supplied to the fuel (\dot{q}''_{fc}), yield of CO (Y_{CO}), and the ratio of optical density per unit path length to fuel vapor concentration (OC).

3) Parameters increasing with increase in the oxygen concentration - radiative heat of combustion per unit mass of the fuel (H_R), vaporization rate of the fuel (\dot{m}''_b), and radiative heat flux from the flame supplied to the fuel (\dot{q}''_{fr}).

An accurate comparison of asymptotic vaporization rates for dimethyl-siloxane fluid obtained from laboratory-scale combustion experiments and larger-scale fires could not be made in this study, because the vaporization rate could not be measured accurately due to the formation of a solid crust at the surface of dimethyl-siloxane fluid. The vaporization rate during combustion for dimethyl-siloxane fluid measured under high oxygen concentrations and high external heat flux values is only approximately equal to about one tenth the asymptotic vaporization rate for hydrocarbon fluid (see Table 5-11). Note that vaporization rate in the pyrolysis of dimethyl-siloxane fluid is about twice the value for the hydrocarbon fluid.

The formation of solid crust at the surface in the combustion of dimethyl-siloxane fluid is, thus, one of the most important processes in reducing the vaporization rate and hence the expected degree of fire hazard involving stagnant pools. If the combustion process involves flowing dimethyl-siloxane fluid or if the formation of solid crust at the surface is disturbed, for example, by applying jets of extinguishing agents to the surface, or in very early stages of fire if solid crust formation is small, the vaporization rate or expected degree of fire hazard of dimethyl-siloxane fluid could increase significantly.

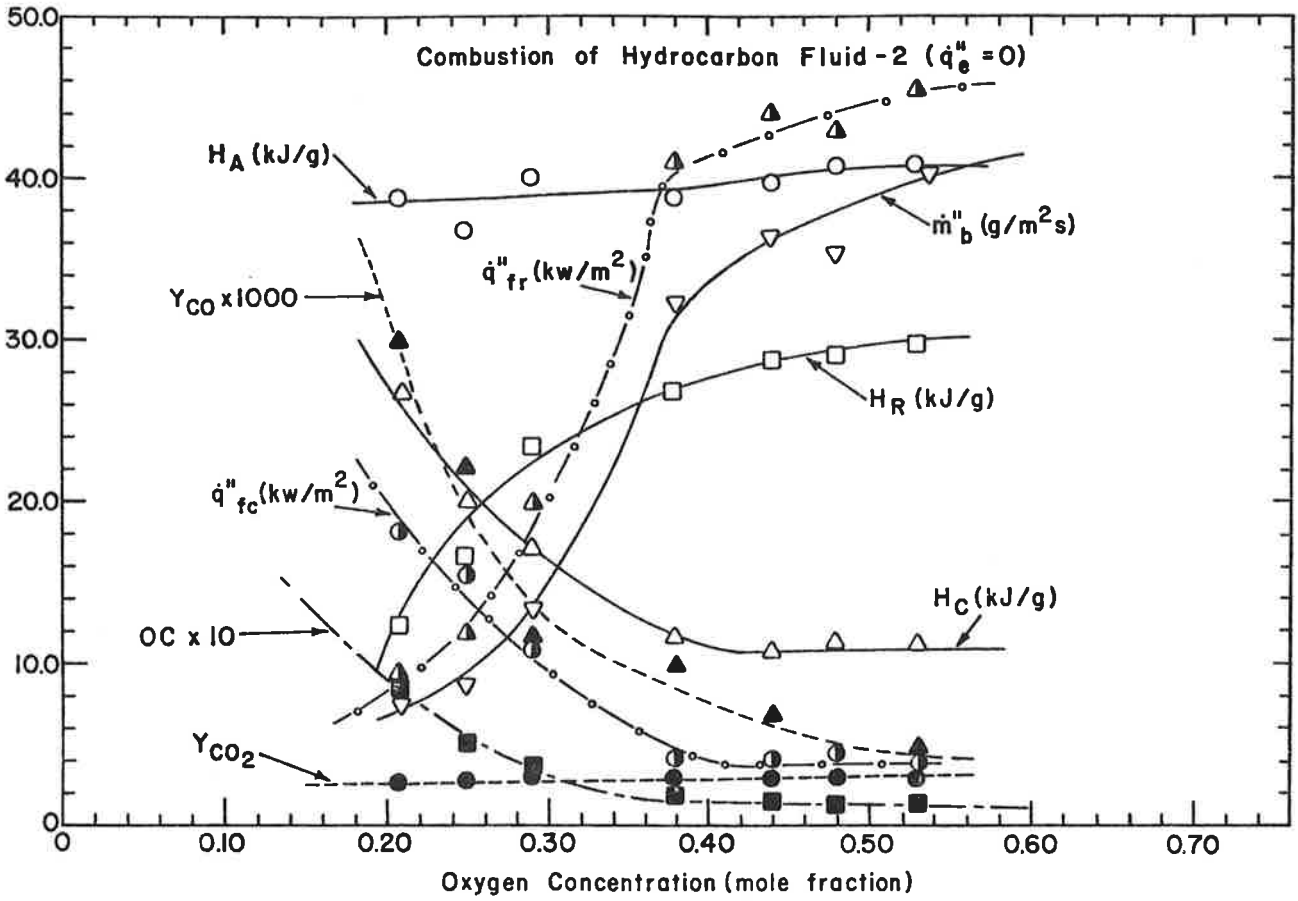


Figure 5-9. Variations of Flame Convective and Radiative Dominated Quantities with Oxygen Concentration for Hydrocarbon Fluid-2 in the Absence of External Heat Flux (see Nomenclature for the Definition of the Quantities)*

*p. viii, ix.

In terms of asymptotic vaporization rate in combustion, heptane is expected to vaporize at about twice the rate of hydrocarbon fluid-2 and methanol and about twenty times the rate of dimethyl-siloxane fluid. The vaporization rate of hydrocarbon fluid-2 is about ten times the rate of dimethyl-siloxane fluid. Our data indicate that the hydrocarbon fluid-2 and the high temperature hydrocarbon fluid do not show significant differences in the combustion parameters, and the conclusion derived for hydrocarbon fluid-2 is expected to be applicable to the high temperature hydrocarbon fluid.

5.5.2.2 Vaporization Rate in the Combustion of Askarel Contaminated Fluids -

Figure 5-10 shows a plot of vaporization rate in the combustion of hydrocarbon/askarel mixtures at 37 kW/m^2 in normal air under natural air flow as a function of time. The vaporization rate at 37 kW/m^2 in normal air is higher than the asymptotic vaporization rate of $40 \text{ g/m}^2\text{s}$ for hydrocarbon fluid and was selected intentionally. The peak values of the vaporization rate for the mixtures are somewhat higher than the rate for pure hydrocarbon fluid. The peak occurs earlier for 1 percent by weight of askarel and later for 4 and 7 percent by weight of askarel than the peak for pure hydrocarbon fluid. The ignition of pure hydrocarbon fluid vapor/air mixture as well as the mixtures occurs when the vaporization rate reaches a value of about $3 \text{ g/m}^2\text{s}$, which is within the range found for a variety of solid and foamed materials including wood⁽⁴⁾.

The data in Figure 5-10 show that askarel contamination of hydrocarbon fluid does not alter the vaporization rate significantly.

From the data for vaporization rate in pyrolysis and combustion, the following conclusions can be derived:

- 1) Dimethyl-siloxane fluid is expected to vaporize about twice as fast as hydrocarbon fluid in pyrolysis if heat flux applied to the fluids is high. Dimethyl-siloxane is thus expected to present a higher degree of fire hazard than the hydrocarbon fluid in pyrolysis. Hydrocarbon fluid, however, is expected to vaporize about ten times as fast as the dimethyl-siloxane fluid in combustion. The degree of fire hazard expected for hydrocarbon fluid is, thus, considerably higher than dimethyl-siloxane. This difference is predominantly due to the formation of a solid crust at the surface of dimethyl-siloxane fluid under stagnant pool fire conditions.

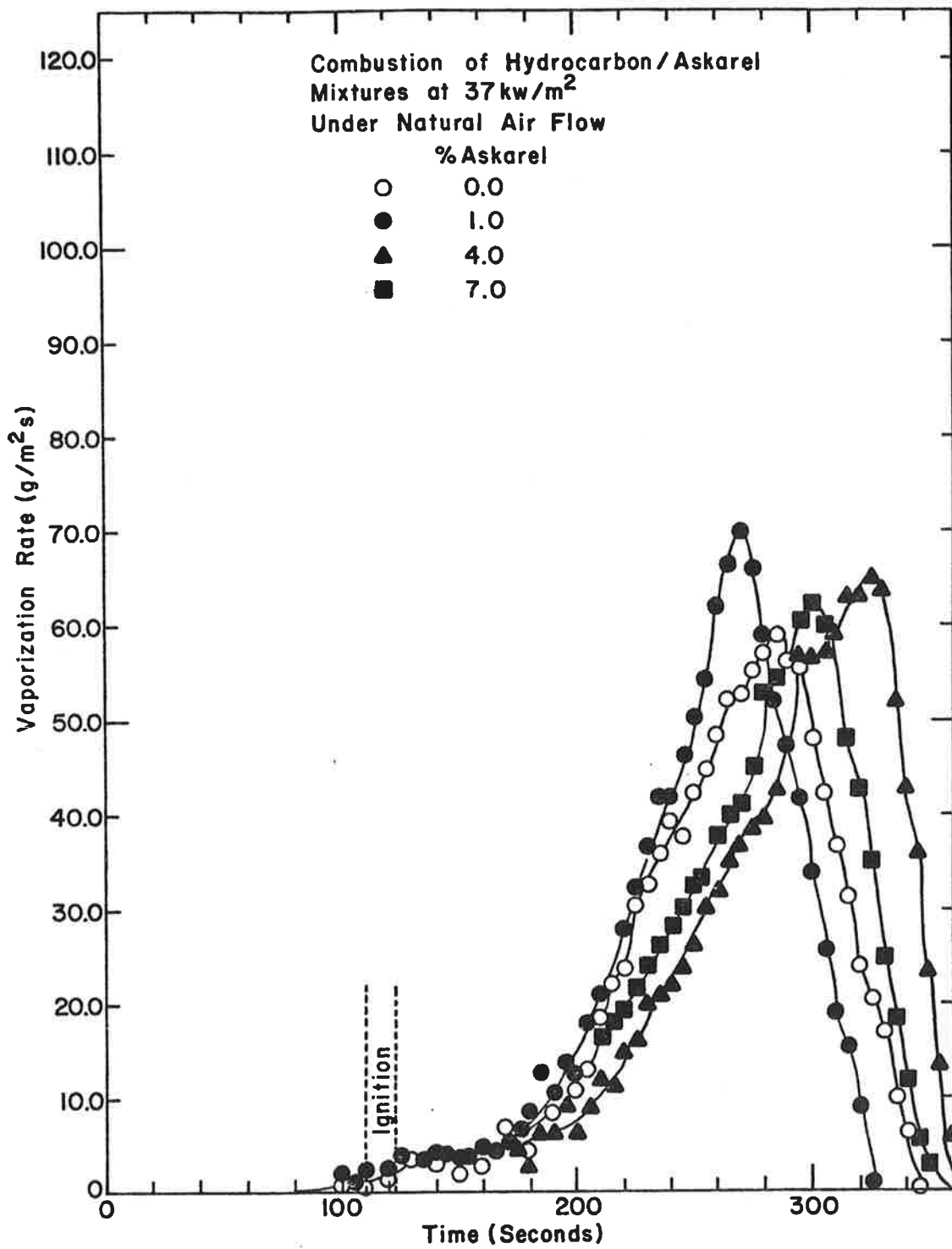


Figure 5-10. Vaporization Rate as a Function of Time for the Combustion of Hydrocarbon/Askarel Mixtures at 37 kW/m^2 Under Natural Air Flow

2) The vaporization rate of hydrocarbon fluid is not expected to be affected to any significant extent by askarel contamination. The askarel contamination of pure dimethyl-siloxane fluid, however, is expected to be beneficial in reducing the vaporization rate. The vaporization rates of pure and askarel-contaminated hydrocarbon fluid are expected to be similar. The expected vaporization rate of askarel-contaminated dimethyl-siloxane fluid is expected to be lower than that of pure dimethyl-siloxane fluid.

3) The vaporization rate for hydrocarbon fluid is about half the rate expected for heptane. The vaporization rate expected for dimethyl-siloxane fluid is about one-twentieth the rate expected for heptane.

5.6 HEAT RELEASE RATE

Heat release rate is defined as a quantity equal to vaporization rate times the heat of combustion, where the heat of combustion can be actual, convective, and radiative as defined in Section 3.3. The heat release rate will vary with variations in the vaporization rate and heat of combustion. The variations of vaporization rate with fuel surface area have been discussed in Section 5.5.

Figure 5-11 shows some data for the effect of fuel-lean and fuel-rich combustion conditions on actual and convective heat of combustion (H_A and H_C respectively). ϕ in Figure 5-11 is equal to the ratio of the flow rate of oxygen to vaporization rate of the fuel divided by the stoichiometric mass oxygen-to-fuel ratio. When $\phi < 1.0$, combustion is fuel rich and when $\phi > 1.0$, combustion is fuel lean. In Figure 5-11, $\phi = \infty$ represents combustion under natural air flow condition.

For fuel-rich combustion, the actual and convective heat of combustion (H_A and H_C respectively) decrease as ϕ decreases. For fuel-lean conditions, H_C and H_A become almost independent of ϕ .

In this study, no attempt was made to examine H_A and H_C as functions of ϕ and all the data were obtained under natural air flow condition ($\phi = \infty$).

5.6.1 Heat Release Rates Obtained in the Laboratory-Scale Experiments and Larger-Scale Fires

Table 5-11 lists heat release data for methanol, heptane, hydrocarbon fluid-2 and dimethyl-siloxane fluid obtained in the laboratory-scale experiments and larger-scale fires. The larger-scale data are taken from Ref (2).

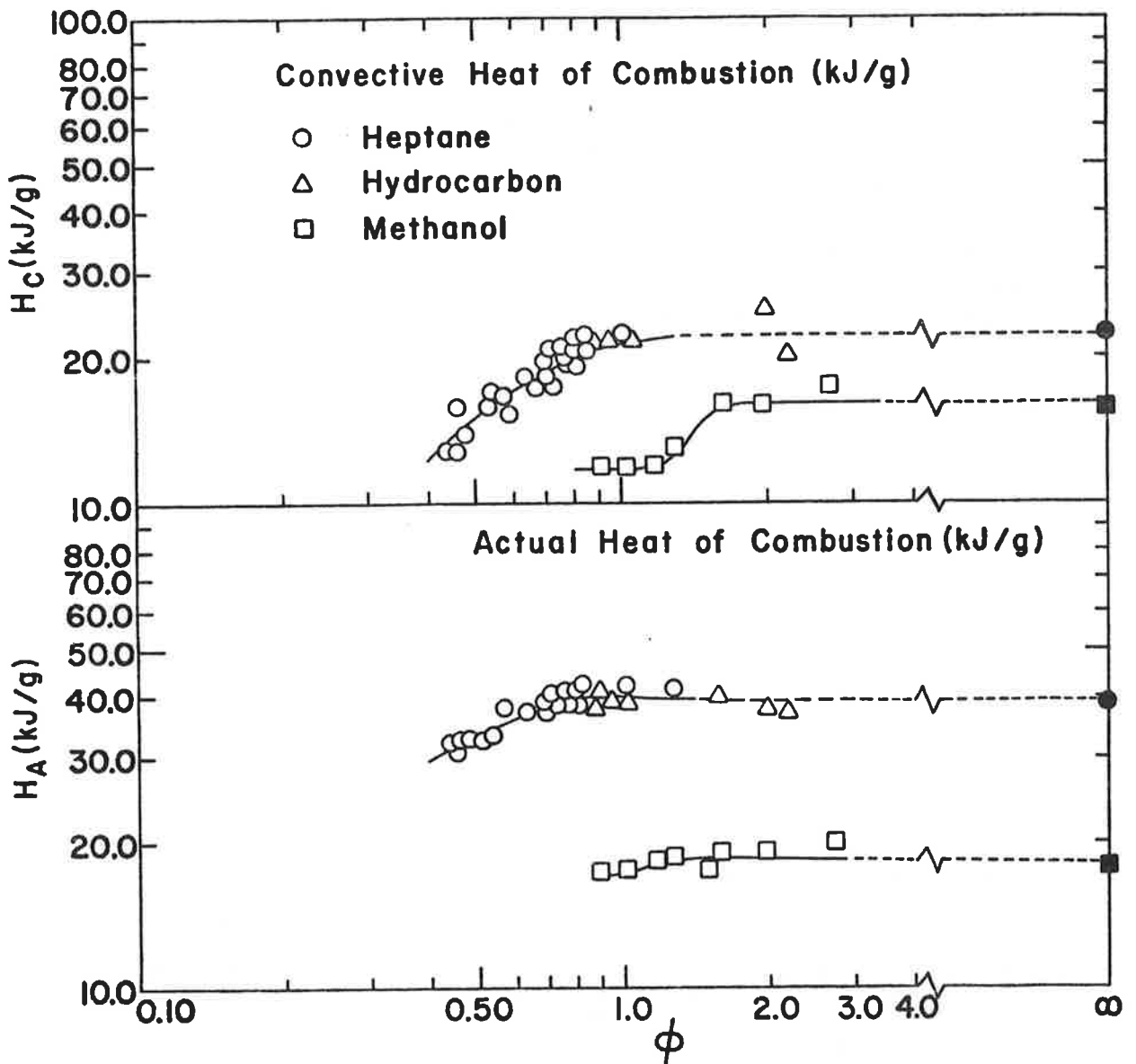


Figure 5-11. Variations of Actual and Convective Heat of Combustion with Fuel-Lean and Fuel-Rich Combustion Conditions in the Absence of External Heat Flux

TABLE 5-11
LABORATORY-SCALE AND LARGE-SCALE DATA FOR HEAT RELEASE RATES^a

	Methanol		Heptane		High-Temperature Hydrocarbon ^d		Dimethyl-Siloxane	
	Lab-Scale	Large-Scale ^c	Lab-Scale	Large-Scale ^c	Lab-Scale	Large-Scale ^c	Lab-Scale	Large-Scale ^b
Heat of Combustion ^b (kJ/g)								
Convective	15.5	-	21.6	-	18.2	-		
Radiative	2.1	3.4	17.4	14.4	20.4	16.3		
Actual	17.6	-	39.0	-	38.6	-		
Complete Combustion	20.0	-	44.6	-	46.3	-	26.9	-
Vaporization Rate (g/m ² s)								
Luminous Flame Region	~24.0	20.3	-	-			~2 ^{e,g}	2 ^e
Highly Luminous Flame Region	37.0	-	~70	70.1	40.0	26.8 ^h	-	
Heat Release Rate (kW/m ²)								
a) Luminous Flame Region								
Convective	~372	315 ^f	-	-			84 ^g	58
Radiative	~50	69	-	-			48 ^g	24
Actual	~422	384 ^f	-	-			132 ^g	
b) Highly Luminous Flame Region								
Convective	574	-	1512	1514 ^f	728	534 ^h		
Radiative	78	-	1218	1009	816	415 ^h		
Actual	651	-	2730	2523 ^f	1544	-		

^a Average steady state (maximum) values under natural air flow condition.

^b Heat of combustion = heat release rate/vaporization rate.

^c Data from Ref (2); fuel surface areas: 1.17, 2.37, and 4.67 m².

^d Hydrocarbon fluid-2.

^e Very approximate because vaporization rate cannot be measured accurately due to solid crust formation at the surface.

^f Estimated from laboratory-scale data; larger-scale data are not available as yet.

^g Average for external heat flux values 60 to 71.3 kW/m² under forced air flow condition.

^h The high-temperature hydrocarbon does not appear to have reached its asymptotic vaporization rate in large-scale fire tests performed by Kung², based on a comparison with data in Table 5-10 for the hydrocarbon type fuels.

- Data not measured.

A good agreement can be noted in the laboratory-scale and larger-scale data for the radiative heat release rate for methanol and heptane, considering that laboratory-scale data are based on predicted asymptotic vaporization rate values. The laboratory-scale data indicate that, for the highly luminous flame region, the heat release rates for methanol and hydrocarbon fluid-2 are much higher than for the luminous flame region and could be achieved for large fuel surface areas ($>5 \text{ m}^2$). The radiative heat release rate for dimethyl-siloxane fluid, obtained for external heat flux values in the range of 60 to 71.3 kW/m^2 , in the laboratory-scale experiments, is higher than the rate measured in the larger-scale fires (fuel surface area up to 2.4 m^2). This suggests that actual vaporization rate for dimethyl-siloxane fluid for external heat flux values in the range of 60 to 71.3 kW/m^2 is higher than the actual rate in the larger-scale fire.

Using the heat release rate data for the highly luminous flame region from Table 5-11, the degree of fire hazard expected for heptane is about two times the hazard expected for hydrocarbon fluid-2, about four times the hazard expected for methanol, and about twenty times the hazard expected for dimethyl-siloxane fluid. The fire hazard expected for hydrocarbon fluid is about ten times the hazard expected for dimethyl-siloxane fluid under stagnant pool fire conditions. The lower degree fire hazard of dimethyl-siloxane fluid is due to its ability to form a solid crust at the surface in combustion reducing the vaporization rate considerably. Note that if the solid crust did not form at the surface, the vaporization rate of dimethyl-siloxane could be about twice the rate of the hydrocarbon fluid (see Section 5.5.1.1); thus, the degree of fire hazard could be equal to that of the hydrocarbon fluid (the heat of complete combustion of dimethyl-siloxane fluid is about half the value for the hydrocarbon fluid). This situation could occur in flow systems or if forced jets of extinguishing agents are applied to the surface of burning dimethyl-siloxane fluid or in the early fire stages if solid crust formation is negligible.

The data in Table 5-11 also indicate that heat release rates for asymptotic mass loss obtained in the FM Flammability Apparatus are realistic and predict the expected degree of fire hazard of fluids in larger-scale fires.

5.6.2 Heat Release Rates, Product Generation Rates, and Optical Transmission Through the Products of Dimethyl-Siloxane/Askarel and Hydrocarbon/Askarel Mixtures

The data for heat release rates, product generation rates and optical transmission through the products of hydrocarbon/askarel and dimethyl-siloxane/askarel mixtures are given in Tables 5-12 and 5-13 respectively. The data are for natural air flow conditions. Vaporization rates in combustion are equal to or greater than the asymptotic values achieved by applying external heat flux to the fluids.

5.6.2.1 Pure Hydrocarbon and Dimethyl-Siloxane Fluids - The data in Table 5-12 indicate that, for an external heat flux of 31 kW/m^2 , the vaporization rate of the hydrocarbon fluid is close to the asymptotic value. For dimethyl-siloxane fluid an external heat flux value of 52 kW/m^2 was used as indicated in Table 5-13. The data indicate that the expected degree of fire hazard (measured by heat release rate) in stagnant pools of hydrocarbon fluid is about ten times the hazard expected for dimethyl-siloxane fluid. The mass generation rates of CO and CO₂ from hydrocarbon fluid are 40 and 17 times the rates from dimethyl-siloxane fluid. The reason for such a drastic difference between these two fluids is the formation of a solid crust at the surface of dimethyl-siloxane fluid as discussed previously. In the absence of the solid crust at the surface, the degree of fire hazard expected for dimethyl-siloxane fluid could be equal to the hazard expected for the hydrocarbon fluid.

5.6.2.2 Hydrocarbon/Askarel Mixtures - The data in Table 5-12 show that there are some variations in the vaporization rate, heats of combustion, yields of products, heat release rates, and product generation rates as the amount of askarel in the mixture is varied. The data, however, indicate that the fire hazard expected for hydrocarbon fluid is not modified to any significant extent by the presence of askarel.

TABLE 5-12

DATA FOR HEAT RELEASE RATE AND PRODUCT GENERATION RATE
IN THE COMBUSTION OF HYDROCARBON/ASKAREL MIXTURES UNDER NATURAL AIR FLOW^a

Wt % of Askarel in the Mixture	1.0				4.0				7.0			
	31	37	31	37	31	37	31	37	31	37	31	37
External Heat Flux (kW/m ²)	48.1	56.3	48.4	60.9	43.6	58.6	55.4	56.4				
Vaporization Rate (g/m ² s)	11.7	11.0	11.9	10.2	11.7	12.5	10.2	10.4				
Heat of Combustion (kJ/g) ^b	18.5	19.0	21.4	19.8	20.7	24.0	21.0	21.6				
Actual	30.2	30.0	33.3	30.0	32.4	36.7	31.2	32.0				
Yield of Product ^c												
CO ₂	2.02	2.01	2.23	2.00	2.16	2.42	2.08	2.10				
CO	0.033	0.039	0.035	0.033	0.043	0.045	0.041	0.043				
Heat Release Rate (kW/m ²)												
Convective	563	619	576	621	510	733	565	587				
Radiative	890	1070	1036	1206	903	1407	1163	1218				
Actual	1453	1689	1612	1827	1413	2151	1728	1805				
Product Generation Rate (g/m ² s)												
CO ₂	97.2	113.0	1079	122.0	94.2	141.8	115.2	118.4				
CO	1.6	2.2	1.7	2.0	1.9	2.6	2.3	2.4				

^a Average steady state (maximum values).

^b Heat of combustion = heat release rate/vaporization rate of the fuel.

^c Yield of product = generation rate of the product/vaporization rate of the fuel (g/g).

TABLE 5-13

DATA FOR HEAT RELEASE RATE, PRODUCT GENERATION RATE, AND OPTICAL TRANSMISSION THROUGH THE PRODUCTS
IN THE COMBUSTION OF DIMETHYL-SILOXANE/ASKAREL MIXTURES UNDER NATURAL AIR FLOW^a

Wt % of Askarel in the Mixture	0	1.0	4.0	7.0
External Heat Flux (kW/m^2)	52.0	52.0	60.0	60.0
Heat Release Rate (kW/m^2)				
Convective	87.8	36.2	42.6	55.9
Radiative	46.2	22.6	10.0	11.7
Actual	134.0	58.8	52.6	70.9
Product Generation Rate ($\text{g/m}^2 \text{ s}$)				
CO_2	5.66	3.30	3.60	3.18
CO	0.039	0.032	0.035	0.044
Optical density per unit path length (m^{-1}) ^b	0.918	0.287	0.215	0.265
			0.284	0.356
			4.36	0.055
			0.043	0.967

^a Average steady state (maximum) values.

^b $\frac{1}{\ell} \ln I_0/I$, where ℓ = optical path length (m); I and I_0 = optical transmission in the presence and absence of the products.

5.6.2.3 Dimethyl-Siloxane/Askarel Mixtures - The data in Table 5-13 show that the presence of askarel in otherwise pure dimethyl-siloxane is beneficial in reducing somewhat the heat release rate of pure dimethyl-siloxane fluid. There is some increase in the heat release rate, product generation rate and optical density per unit path length as the amount of askarel is increased from 4 to 7 percent; however, the heat release rates are less than the rates for pure dimethyl-siloxane fluid. A similar conclusion had been derived in Section 5.5.1.2, where vaporization sensitivity was reduced by increasing the amount of askarel.

From the heat release rate data, the following conclusions can be derived:

1) The heat release rate in larger-scale fires of high temperature hydrocarbon fluid and hydrocarbon fluid-2 is expected to be about ten times the rate for dimethyl-siloxane fluid. The low heat release rate for dimethyl-siloxane fluid is predominantly due to the formation of a solid crust at the surface under stagnant pool fire conditions.

2) The heat release rates in larger-scale fires of hydrocarbon are expected to show insignificant variations due to askarel contamination up to about 7 percent by weight. For dimethyl-siloxane the effect of askarel contaminate appears to be beneficial with regard to heat release rate.

3) The heat release rate in larger-scale fires of hydrocarbon fluid is expected to be about half the rate for heptane. The heat release rate in larger-scale fires of dimethyl-siloxane fluid is expected to be about one-twentieth the rate for heptane. The heat release rate in larger-scale fires of heptane is expected to be about 2700 kW/m^2 .

4) The FM Flammability Apparatus is useful in evaluating the heat release rates of fluids expected in larger-scale fires.

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APPENDIX A

THE TECHNIQUE OF OXYGEN DEPLETION FOR ACTUAL HEAT RELEASE RATE OF FUELS

The net heat of complete combustion for a fuel per unit mass of oxygen consumed is equal to H_T/k_{O_2} , where H_T is net complete heat of combustion per unit mass of the fuel and k_{O_2} is the stoichiometric mass oxygen to fuel ratio. The actual heat release rate then can be expressed as:

$$\dot{Q}_A'' = \frac{H_T}{k_{O_2}} \cdot \dot{M}_{O_2}'' \quad , \quad (A-1)$$

where \dot{Q}_A'' = actual heat release rate from the combustion of the fuel per unit fuel surface area (kW/m²); \dot{M}_{O_2}'' = mass depletion rate of oxygen per unit fuel surface area (g/m²s); H_T/k_{O_2} is given in kJ/g.

The actual heat of combustion, which is defined as the ratio of actual heat release rate to vaporization rate, then can be expressed as:

$$H_A = \frac{\dot{Q}_A''}{\dot{m}_b''} = \frac{H_T}{k_{O_2}} \cdot \frac{\dot{M}_{O_2}''}{\dot{m}_b''} \quad , \quad (A-2)$$

where H_A = actual heat of combustion per unit mass of the fuel (kJ/g); \dot{m}_b'' = vaporization rate of the fuel in combustion per unit fuel surface area (g/m²s).

The only unknown quantity in eqs. A-1 and A-2 is H_T/k_{O_2} .

Data available in the literature for H_T and k_{O_2} show that H_T/k_{O_2} is approximately constant for gases, liquids, solids, foams, etc., irrespective of their generic nature as shown in Table A-1.

For silicone type fuels, eqs A-1 and A-2 can be expressed as:

$$\dot{Q}_A'' \approx 14.9 \cdot \dot{M}_{O_2}'' \quad , \quad (A-3)$$

$$H_A \approx 14.9 \cdot \frac{\dot{M}_{O_2}''}{\dot{m}_b''} \quad . \quad (A-4)$$

Table A-1
 H_T/k_{O_2} (kJ/g) Values For Common Materials^a

Granular		Foamed		Liquids		Silicones ^c	
Polymethylmethacrylate	13.2	Polyurethanes ^b		Pentane	12.5	Linear	
Polystyrene	12.7	GM-21	11.6	Hexane	12.7	MM	16.2
Polypropylene	12.6	GM-23/FR	13.0	Heptane	12.7	MDM	15.5
Polyethylene (PE)	12.7	GM-25	11.3	Benzene	13.0	MD ₂ M	13.7
PE/25%Cl	12.7	GM-27/FR	10.4	Toluene	12.9	MD ₃ M	15.4
PE/36%Cl	12.8	GM-29	11.5	Benzaldehyde	13.2	Cyclics	
PE/42%Cl	12.8	GM-31	11.0	Aniline	11.6	D ₃	14.2
PE/48%Cl	12.8	GM-37	11.8	Styrene	13.1	D ₄	14.7
Polyvinyl chloride	12.8	Polyisocyanurates ^b		Methyl alcohol	13.3	D ₅	14.6
Nylon 6/6	11.8	GM-41	11.3	Ethyl alcohol	12.8	D ₆	14.6
Styrene/Butadiene	13.3	GM-43	9.8	Propyl alcohol	12.7		
Polyoxymethylene	14.5	Polystyrenes ^b		Acetone	12.9		
		GM-47	12.3	Acetaldehyde	13.6		
		GM-49	12.4	Formaldehyde	14.5		
		GM-51	11.6				
		GM-53	12.3				
		Phenolic Foam ^b					
		GM-57	(16.8)				
		Polyethylenes					
		1	12.1				
		2	11.8				
		3	12.0				
		4	12.0				
Mean	12.9		11.7		13.0		14.9
Standard Deviation	0.65		0.77		0.64		0.80

^a Taken from Ref. (1)

^b GM numbers identified in Ref. (1)

^c M = (CH₃)₃SiO_{0.5}; D = (CH₃)₂SiO

For other types of fuels, eqs A-1 and A-2 can be expressed as:

$$\dot{Q}_A'' \approx 12.5 \cdot \dot{M}_{O_2}'' \quad (A-5)$$

$$H_A \approx 12.5 \cdot \frac{\dot{M}_{O_2}''}{\dot{m}_b''} \quad (A-6)$$

The usefulness of the method is that by measuring \dot{M}_{O_2}'' alone, \dot{Q}_A'' can be obtained irrespective of the size of fire, presence or absence of extinguishing agents, shape, size, configuration, or arrangements of the fuels etc. If \dot{m}_b'' is also measured, H_A can be obtained as function of time to describe various fire stages and differences in the fire behavior of the fuels including the effect of additives and contaminants. Note that for the measurement of \dot{Q}_A'' , no information is required except \dot{M}_{O_2}'' .

APPENDIX B

REPORT OF NEW TECHNOLOGY

A review of the work performed under this contract discloses no invention or discovery. However, a great deal of new data were generated concerning the flammability of transformer coolant fluids using the Factory Mutual calorimeter.

