EXPERIMENTAL DETERMINATION OF FLAMMABILITY LIMITS OF SOLVENTS

AT ELEVATED TEMPERATURES AND PRESSURES

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There is little published data on the flammability limits
of solvents at elevated conditions in air.  Predictive
models exist for estimating flammable limits based on the
linear dependence of the limits with temperature. The paper
describes the measurement õf flammability limits of ethanol
and 1-propanol and also collates data for other solvents.
The slope of the linear relationship was found to be
different for each of the solvents tested and for the upper
and lower limits. The modified Burgess-Wheeler prediction
model, using average constants, have been found to give
reasonable agreement with measured values.
Flammable Limits  Flammability Limits  Fire and
Explosion Hazards

INTRODUCTION


In order to specify a basis of safe operation for any chemical process it is
necessary to know whether the materials handled are capable of forming
flammable atmospheres and over what range of concentrations and conditions.
The flammable range of concentrations is bounded by the upper and lower
flammable limits and is specific to a particular mixture of gases and/or
vapours.  There are a number of factors which affect the flammable limits but
the most marked of these are temperature, pressure and the oxidant of the
mixture.

Many more processes are operating at elevated temperatures and pressures
in order to increase their efficiency and often for environmental reasons.
Therefore, in order to operate safely it is necessary to know the
flammability limits of a particular mixture at the process operating
conditions.  The measurement of flammable limits at elevated temperatures and
pressures can be complex and time consuming, and the ability to predict them
accurately would be useful particularly for preliminary design studies.  A
few models are available in the literature which predict the flammable
limits, at a particular elevated temperature or pressure, from the measured
limits at ambient conditions.

A flammability rig has been developed and the limits of ethanol and
1-propanol have been measured at elevated temperatures.  This data along with
data available in the literature has been described using the modified
Burgess-Wheeler prediction model with different constants for the upper and
lower limit and for each of the materials.  In addition, general equations
for prediction of the upper and lower limit of all the solvents tested has
been developed based on the modified Burgess-Wheeler model.

EXPERIMENTAL WORK

Flammability Apparatus and Methodology

The flammability vessel used for the tests is a 13 litre sphere which is heated by means of a hot oil jacket. The vessel has two observation windows and a removable lid so that the ignition sources can be changed. High speed data is captured by a computer system and processed to give a pressure profile of the explosion.

The flammability vessel is heated to the appropriate temperature and then evacuated. A specified quantity if solvent is added, by means of either a pump or syringe injection. Cylinder air is then added up to the initial pressure for the particular test and the mixture agitated. A short time was allowed for any turbulence to die away before the mixture was ignited, at the centre of the sphere, by means of a bridge wire (24 Volt supply) which gave a single spark. The propagation of the flame was viewed and the pressure and rate of pressure rise of the explosion were determined.

For a particular solvent the temperature of the test was set and the solvent concentration varied. This was repeated until the 'go/no go' ie. flammable and non-flammable mixtures, were found to at least within 0.7 % v/v. The 'no go' concentration was taken as the flammable limit. The test temperature was then increased and the test procedure repeated. Ignition was determined by both visual observation and an increase in pressure.

Experimental Results

Effect of Temperature

TABLE I - EFFECT OF TEMPERATURE ON THE FLAMMABILITY LIMITS OF ETHANOL AND PROPANOL

| MATERIAL | TEMPERATURE | LOWER FLAMMABLE LIMIT (% V/V) | UPPER FLAMMABLE LIMIT (%V/V) |
|----------|-------------|-------------------------------|------------------------------|
| ETHANOL | 50 | 3.4 +/-0.2%v/v | 15.6 +/-0.7%v/v |
| | 100 | 3.7 +/-0.1%v/v | 16.4 +/-0.3%v/v |
| | 180 | 2.4 +/-0.1%v/v | 19.0 +/-0.5%v/v |
| | 250 | 3.0 +/-0.1%v/v | 22.5 +/-0.5%v/v |
| 1-PROPANOL | 50 | 2.2 +/-0.1%v/v | - |
| | 100 | 2.1 +/-0.1%v/v | 12.9 +/-0.3%v/v |
| | 180 | 1.9 +/-0.1%v/v | 14.2 +/-0.3%v/v |
| | 200 | 1.7 +/-0.1%v/v | 16.2 +/-0.5%v/v |
| | 250 | 1.7 +/-0.1%v/v | 16.8 +/-0.5%v/v |

## Effect of Pressure

TABLE II - EFFECT OF PRESSURE ON THE FLAMMABILITY LIMITS OF ETHANOL AND
          PROPANOL

| MATERIAL | PRESSURE (PSIG) | LOWER FLAMMABLE LIMIT (%V/V) | UPPER FLAMMABLE LIMIT (%V/V) |
|----------|-----------------|------------------------------|------------------------------|
| ETHANOL | 14.7 | 2.4 +/-0.1%v/v | 19.0 +/-0.5%v/v |
| | 50 | 3.1 +/-0.1%v/v | 26.5 +/-0.5%v/v |
| | 100 | 3.5 +/-0.1%v/v | 39.0 +/-1.0%v/v |
| 1-PROPANOL | 14.7 | 1.7 +/-0.1%v/v | 16.2 +/-0.5%v/v |
| | 50 | 1.8 +/-0.1%v/v | 25.5 +/-0.5%v/v |
| | 100 | 1.99 +/-0.1%v/v | - |

Ethanol tests were done at 180 degC and 1-propanol tests were done at 200
degC.

## Existing Literature Data

There are few measured flammability limits at elevated
temperatures available in the literature. In addition, many of the tests
used different sizes and shapes of vessels, ignition sources and directions
of flame propagation. These factors make it very difficult to compare
different sets of results. The limited published data available on the
flammability limits of solvents in air have been collated below.

TABLE III - EFFECT OF TEMPERATURE ON THE FLAMMABILITY LIMITS OF SOLVENTS

| MATERIAL | LOWER FLAMMABLE LIMIT (%V/V) | UPPER FLAMMABLE LIMIT (%V/V) | TEMPERATURE (deg C) | VESSEL TYPE | REFERENCE |
|----------|------------------------------|------------------------------|---------------------|-------------|-----------|
| O-XYLENE | 1.1 | 6.4 | 100 | - | 1 |
| | 1.1 | - | 50 | A | 2 |
| | 1.0 | 5.7 | 100 | A | 2 |
| | 0.9 | 6.2 | 150 | A | 2 |
| | 0.8 | 6.7 | 200 | A | 2 |
| | 0.8 | 7.1 | 250 | A | 2 |
| TOLUENE | 1.20 | 7.20 | 110 | B | 3 |
| | 0.99 | - | 100 | C | 3 |
| | 0.82 | - | 200 | C | 3 |
| | 0.72 | - | 300 | C | 3 |
| | 1.27 | - | 26 | D | 3 |
| | 1.12 | - | 200 | D | 3 |

| MATERIAL | LOWER FLAMMABLE LIMIT (%V/V) | UPPER FLAMMABLE LIMIT (%V/V) | TEMPERATURE (deg C) | VESSEL TYPE | REFERENCE |
|---|---|---|---|---|---|
| | 1.26 | 4.44 | 100 | E | 3 |
| | 1.03 | 4.61 | 200 | E | 3 |
| | 1.20 | 7.10 | 100 | - | 1 |
| | 1.00 | - | 20 | A | 2 |
| | 0.90 | 5.50 | 50 | A | 2 |
| | 0.85 | 5.80 | 100 | A | 2 |
| | 0.80 | 6.00 | 150 | A | 2 |
| | 0.70 | 6.35 | 200 | A | 2 |
| | 0.60 | 6.60 | 250 | A | 2 |
| BENZENE | 1.15 | 5.4 | 20 | A | 2 |
| | 1.10 | 5.6 | 50 | A | 2 |
| | 0.95 | 6.1 | 100 | A | 2 |
| | 0.90 | 6.5 | 150 | A | 2 |
| | 0.80 | 7.0 | 200 | A | 2 |
| | 0.70 | 7.4 | 250 | A | 2 |
| METHANOL | 6.7 | 36.4 | 50 | A | 4 |
| | 5.5 | 44.8 | 200 | A | 4 |
| MEK | 1.92 | - | 16 | F | 12 |
| | 1.98 | - | 30 | F | 12 |
| | 1.77 | - | 125 | F | 12 |
| | 1.61 | - | 200 | F | 12 |
| THF | 1.90 | - | 16 | F | 12 |
| | 1.84 | - | 30 | F | 12 |
| | 1.74 | - | 125 | F | 12 |
| | 1.66 | - | 200 | F | 12 |
| TOLUENE | 1.24 | - | 30 | F | 12 |
| | 1.07 | - | 200 | F | 12 |

VESSEL TYPES:
    Tests were carried out with upward propagation unless otherwise stated.
A  75 mm internal diameter tube, 1500 mm in length.
B  5 cm diameter, 18 inch length tube open at the top.
C  30.6 cm diameter, 39 cm length tube vented at the top.
D  10.2 cm diameter, 96 cm length closed tube.

E  9 cm diameter, 45 cm long tube (downward propagation).
F  Bureau of Mines F-11 apparatus.


## DISCUSSION


There are a number of models available in the literature which have been developed to predict the effect of temperature on the flammability limits of materials in air. Basically these can be categorised as the modified Burgess-Wheeler laws and the equations developed by Bodurtha.


Effect of Temperature


Lower Flammable Limit Burgess and Wheeler showed that the heat liberated by a mole of a lower flammable limit mixture is nearly constant for many fuel/air mixtures at ambient temperature and pressure (ref. 10). However, further work showed that for alkanes the heat liberated is not constant but increases with molecular weight. In addition, since the lower flammable limit is also dependant on temperature and pressure the above law does not hold true for elevated conditions.

Zabetakis and co-workers modified the Burgess-Wheeler law to take account of the effect of temperature on the lower flammable limit.

$$L.\Delta H_c + \Delta Q = k \qquad \text{(1) (ref. 10)}$$

where,

L    = Lower flammable limit,
$\Delta H_c$ = Heat of combustion
$\Delta Q$ = Heat energy added to the limit mixture to raise its temperature from the reference temperature to the test temperature

The equation was further developed by Zabetakis, Cooper and Furno following their tests to determine the effect of temperature on the lower flammable limits of MEK, THF, Toluene and mixtures of these solvents.

They found that their results could be described by the following relationship with a value of 3.14 for the constant $\mu$ (with Heat of Combustion units kJ mol$^{-1}$).

$$L_{t_2} = L_{t_1} - \frac{\mu}{\Delta H_c}(t_2 - t_1), \qquad (t_2 - t_1) \qquad \text{(2) (ref 12)}$$

where,

$L_{t1}$ = Lower flammable limit at temperature $t_1$ (% v/v),
$L_{t2}$ = Lower flammable limit at temperature $t_2$ (% v/v),
t    = Temperature (degC).
$\mu$    = constant

This equation has been used to evaluate previously reported data on the lower flammable limits of solvents and also the results obtained in the current investigation. The data is shown in Table IV.

TABLE IV - VALUES OF CONSTANT μ FOR VARIOUS SOLVENTS

| MATERIAL | $\Delta H_C$ (LIQUID) kJ mol$^{-1}$ | CONSTANT μ |
|----------|------------------|------------|
| BENZENE | 3267.6 | 6.21 |
| TOLUENE | 3910.3 | 6.26 |
| O-XYLENE | 4552.8 | 7.10 |
| METHANOL | 726.1 | 5.81 |
| ETHANOL | 1366.8 | 4.28 |
| PROPANOL | 2021.3 | 5.54 |
| MEK | 2436.3 | 4.56 |
| THF | 2499.0 | 3.02 |
| AVERAGE | | 5.35 |

It can be seen that the constant μ varies between 3.02 and 7.10. Interestingly it is apparent that solvents with a similar chemical nature have a similar constant ie. aromatics 6.21 to 7.1 and alcohols 4.28 to 5.81. However, since the lower flammable limit varies only slightly with increasing temperature an average value for the constant μ of 5.35 for all the data sets has been used. The agreement between predicted values, with the constant μ=5.35 substituted into equation 2, and experimentally determined data is shown in figures 1 and 2.

An alternative method of predicting the lower flammable limit values at elevated temperatures has been proposed by Bodurtha who noted that the lower flammable limits in air decreased by approximately 8% with an increase in temperature of 100 deg C. He proposed the following relationship;

$$L_{t_2} = L_{t_1}(1 - 8x10^{-4}(t_2 - t_1))$$ 
(3)  (ref. 7)

Table V shows the predicted lower flammable limit values for various solvents using both the Bodurtha relationship and the modified Burgess-Wheeler model, with a value of μ equal to 5.35.

TABLE V - MEASURED AND PREDICTED LOWER LIMITS FOR SOLVENTS AT 250 DegC

| MATERIAL | MEASURED LFL (%V/V) | PREDICTED LFL USING MODIFIED B-W (%V/V) | PREDICTED LFL USING BODURTHA (%V/V) |
|----------|------|------|------|
| TOLUENE | 0.6 | 0.63 | 0.76 |
| BENZENE | 0.7 | 0.77 | 0.92 |
| O-XYLENE | 0.8 | 0.86 | 0.92 |
| METHANOL (200 DegC) | 5.5 | 5.59 | 5.90 |
| ETHANOL | 3.0 | 2.62 | 2.86 |
| 1-PROPANOL | 1.7 | 1.67 | 1.85 |

Based on the comparisons above, it can be seen that slightly better prediction values are obtained using the modified Burgess-Wheeler model and that the relationship proposed by Bodurtha tends to predict a higher lower flammable limit for the solvents.

Upper Flammable Limit Zabetakis found that a similar relationship to equation 2 above could be used to describe the behaviour of the upper flammable limits (ref. 1).

$$U_{t_2} = U_{t_1} + \frac{\mu (t_2 - t_1)}{\Delta H_c} , \qquad (t_2 - t_1) \qquad (4) \text{ (ref 1)}$$

where,

$U_{t1}$ = Upper flammable limit at temperature $t_1$ (% v/v),
$U_{t2}$ = Upper flammable limit at temperature $t_2$ (% v/v),

He found that the same value of the constant $\mu$, ie. 3.14 (with Heat of Combustion units kJ $mol^{-1}$), as for the lower flammable limit described the data available for methane and pentane.

Equation 4 has been used to evaluate the upper flammable limit data for solvents and the results can be found in TABLE VI.

TABLE VI - VALUES OF CONSTANT $\mu$ FOR VARIOUS SOLVENTS

| MATERIAL | $\Delta H_C$ (LIQUID) kJ $mol^{-1}$ | CONSTANT $\mu$ |
|---|---|---|
| BENZENE | 3267.6 | 29.41 |
| TOLUENE | 3910.3 | 21.51 |
| O-XYLENE | 4552.8 | 42.80 |
| METHANOL | 726.1 | 40.66 |
| ETHANOL | 1366.8 | 47.43 |
| PROPANOL | 2021.3 | 54.98 |
| | AVERAGE | 39.47 |

It can be seen that the constant varies for the different solvents ranging from 21.51 to 54.98 with an average value of 39.47. The agreement between predicted values, with the constant $\mu$=39.47 substituted into equation 4, and experimentally determined data is shown in figures 3 and 4.

As for the lower flammable limit, Bodurtha noted that the upper flammable limits in air increased by approximately 8% with an increase in temperature of 100 deg C and proposed the following relationship;

$$U_{t_2} = U_{t_1} (1 + 8x10^{-4} (t_2 - t_1)) \qquad (5) \text{ (ref. 7)}$$

Table VII shows the predicted lower flammable limit values for various solvents using both the Bodurtha relationship and the modified Burgess-Wheeler model, with a value of $\mu$ equal to 39.47.

TABLE VII - MEASURED AND PREDICTED UPPER LIMITS FOR SOLVENTS AT 250 DegC

| MATERIAL | MEASURED UFL (%V/V) | PREDICTED UFL USING MODIFIED B-W (%V/V) | PREDICTED UFL USING BODURTHA (%V/V) |
|---|---|---|---|
| TOLUENE | 6.6 | 7.52 | 6.38 |
| BENZENE | 7.4 | 8.02 | 6.50 |
| O-XYLENE | 7.1 | 7.00 | 6.38 |
| METHANOL (200 DegC) | 44.8 | 44.55 | 40.77 |
| ETHANOL | 22.5 | 21.38 | 18.10 |
| 1-PROPANOL | 16.80 | 15.83 | 14.45 |

Based on the comparison above, it can be seen that better prediction values is obtained using the modified Burgess-Wheeler model and that the relationship proposed by Bodurtha tends to predict lower upper flammable limits for the solvents than measured.


Effect of Pressure


Lower Flammable Limits Zabetakis analysed the data obtained by Jones for natural gas in air and developed an empirical method for predicting the effect of pressure;

$$L_{P_2} = L_{P_1} - 0.71 \log \Delta P \qquad\qquad (6) \ (ref.8)$$

Where, $L_{p1}$ = Lower flammable limit at initial pressure p1 (%v/v),
$L_{p2}$ = Lower flammable limit at elevated pressure p2 (%v/v)

The test results so far obtained for ethanol and 1-propanol show a linear dependence of lower flammable limit with increasing pressure. However, unlike the prediction model above the lower limit values appear to increase with increasing pressure.

Upper Flammable Limits Zabetakis developed a similar relationship for the upper flammable limit values,

$$U_{P_2} = U_{P_1} + 20.4 \log \Delta P \qquad\qquad (7) \ (ref \ 7)$$

Bodurtha developed this equation based on data for saturated hydrocarbons up to a pressure of 207 bar,

$$U_{P_2} = U_{P_1} + 20.6 \log \Delta P \qquad\qquad (8) \ (ref.7)$$

Where, $U_{p1}$ = Upper flammable limit at initial pressure P1 (% v/v),
$U_{p2}$ = Upper flammable limit at elevated pressure P2 (% v/v),
$\Delta P$ = Pressure (atm),

Again the test results so far indicate a linear dependence of the upper flammable limits with increasing pressure. As with the models above, the

upper flammable limits increase with increasing pressure.


CONCLUSIONS


## Effect of Temperature


Experimental tests on the flammable limits of ethanol and propanol confirm the linear dependence of both upper and lower flammability limits, for the solvents tested, with temperature.

Lower Flammable Limit  The lower flammable limits of solvents decrease with increases in temperature.

The constants which describe the linear dependence of the limit values with temperature differ for each solvent.  The relationship can be described by the modified Burgess-Wheeler model which also takes account of the heat of combustion of the liquid solvent ($\Delta H_c$).  It is apparent that solvents with a similar chemical nature have a similar value of the constant $\mu$ eg. for aromatics or alcohols.  However, since increases in temperature have very little effect on the lower flammable limits an average value for the constant, $\mu$, can be used.  Graphs of the measured and modified Burgess-Wheeler predicted values against temperature show good agreement and within the same degree of accuracy as different sets of results.

The model developed by Bodurtha for predicting the effect of temperature on the lower flammable limits did not give as good agreement with measured data as the modified Burgess-Wheeler.  In addition the Bodurtha method over predicts the lower flammable limit values such that they actually lie inside the flammable region.

Upper Flammable Limit  The upper flammable limits of solvents increase with increase in temperature.

As for the lower limit values the constants which describe the linear dependence of the limit values with temperature differ for each solvent tested with the relationship being described by the modified Burgess-Wheeler model.  In this case solvents with a similar chemical nature, ie. aromatics and alcohols, do not appear to have similar values of the constant $\mu$ but a reasonable average value can be found.  Graphs of the measured and modified Burgess-Wheeler predicted values against temperature show good agreement and within the same degree of accuracy as different sets of results.

Again, the model developed by Bodurtha for predicting the effect of temperature on the upper flammable limits did not give as good agreement with measured data as the modified Burgess-Wheeler.  The Bodurtha method under predicts the upper flammable limit values by a significant amount with the predicted upper limits lying well inside the flammable region.

## Effect of Pressure

Preliminary experimental results for the solvents ethanol and 1-propanol show an apparent linear relationship between the flammability limits and increasing initial pressure up to 100 psig. The upper limit increases with pressure and unexpectedly the lower limit values also appear to increase with increasing pressure over this range. This is in contrast to the only reported data on the effect of pressure on the flammability limits which was determined for saturated hydrocarbons. In this previous work the limit values showed a logarithmic relationship with pressure up to a pressure of 207 bar with lower limits decreasing and upper limits increasing with increasing pressure. Clearly further work is required to investigate the effect of pressure before simple models can be developed.

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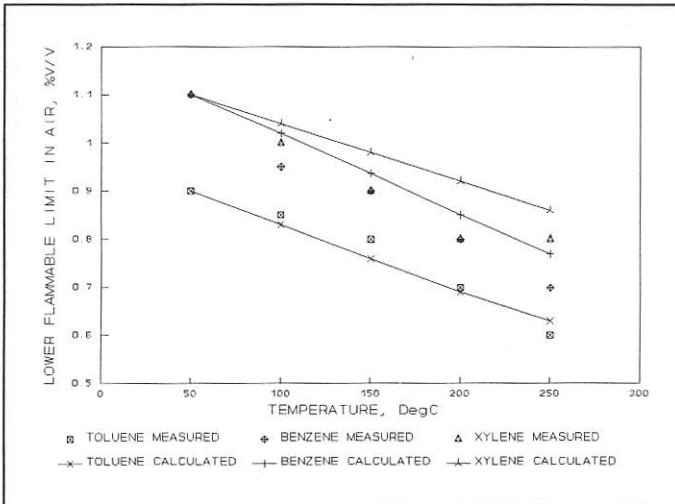
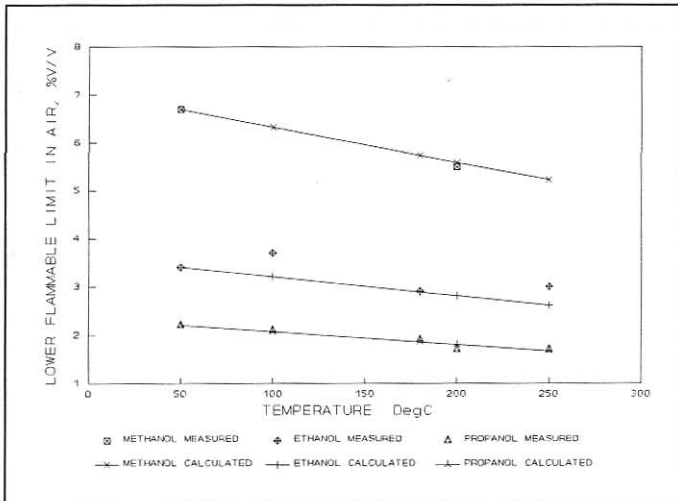**Figure 1** COMPARISON OF MEASURED LFL DATA FOR AROMATICS WITH PREDICTED VALUES



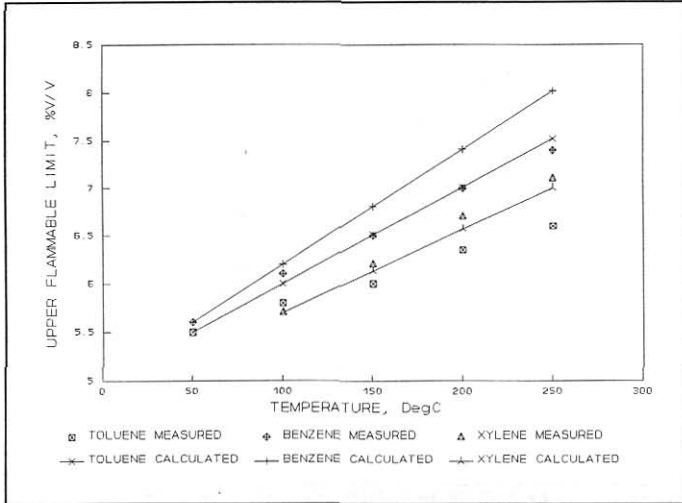**Figure 2** COMPARISON OF EXISTING LFL DATA FOR ALCOHOLS WITH PREDICTED VALUES

**Figure 3** COMPARISON OF EXISTING UFL DATA (REF 2) FOR
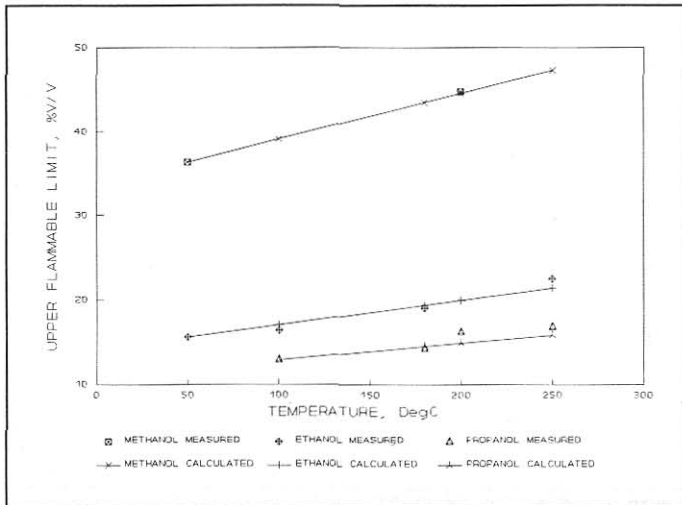AROMATICS WITH PREDICTED VALUES



**Figure 4** COMPARISON OF EXISTING UFL DATA FOR ALCOHOLS WITH
PREDICTED VALUES