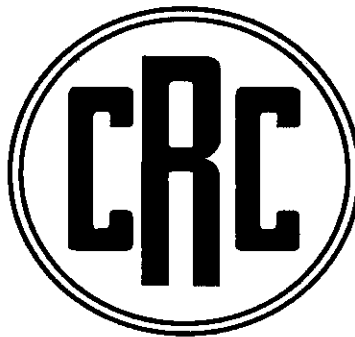


CRC Report No. 640

**2001 CRC HOT-FUEL-HANDLING
PROGRAM FOLLOW-UP STUDY**

April 2004



**COORDINATING RESEARCH COUNCIL, INC.
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American Petroleum Institute
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FOLLOW-UP STUDY**

(CRC Project No. CM-138-03)

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Prepared by the

CRC Volatility Group

April 2004

CRC Performance Committee
of the
Coordinating Research Council

2001 CRC HOT-FUEL-HANDLING PROGRAM FOLLOW-UP STUDY

I. INTRODUCTION

In 2001, the CRC conducted a Hot-Fuel-Handling Program and CRC Report No. 629 summarized the results of this program.¹ The best single gasoline and gasoline-ethanol blend volatility property that correlated with hot fuel handling problems was the temperature at which the vapor-liquid ratio of the fuel equals 1 at 500 kPa (72.5 psi) pressure, which was referred to as TVL1-500 in the report. This test method, developed by General Motors, was set up specifically for this CRC test program and is not a standard ASTM test method. The vapor lock control volatility property currently specified for gasoline and gasoline-ethanol blends in ASTM D 4814 Specification for Automotive Spark-Ignition Engine Fuel is the temperature for a vapor-liquid ratio of 20 (TVL20). It is a standard ASTM test method, D 5188. Other volatility properties specified in D 4814 are vapor pressure (DVPE) and distillation.

Appendix G of CRC Report No 629 presented a study correlating TVL1-500 with TVL20, DVPE, and ethanol content. The correlations with TVL20 and ethanol content and DVPE and ethanol content were developed using gasolines with high vapor pressure (up to 129 kPa or 18.7 psi). The question was raised as to whether the calculation equations were also applicable to gasolines and gasoline-ethanol blends at lower vapor pressures.

II. CONCLUSIONS

The following conclusions resulted from the analysis of the data from the follow-up program to the CRC 2001 Hot-Fuel-Handling Program:

- The equation for calculating TVL1-500 from TVL20 and ethanol content from the CRC Report No. 629 is applicable to fuels with lower vapor pressures.
- A new equation for calculating TVL1-500 from TVL20 and ethanol content developed using combined data from the original and follow-up programs was a slight improvement over the original equation.
- The equation developed using the presence of ethanol (fixed offset) in place of ethanol concentration with TVL20 was not quite as good as the ethanol concentration equation for calculating TVL1-500.

- The original equation for calculating TVL1-500 from DVPE and ethanol content did not work well for fuels with lower vapor pressures.
- A new equation for calculating TVL1-500 from DVPE and ethanol content developed using combined data from the original and follow-up programs was an improvement over the original equation, but the standard error was higher and overall was not as good as the TVL20 based equation.
- The equation developed using the presence of ethanol (fixed offset) in place of ethanol concentration with DVPE was not much different from the ethanol concentration equation for calculating TVL1-500, but was worse than the corresponding TVL20 based equation.
- Overall, the TVL20 based equations are better than the corresponding DVPE based equations.

III. TEST PROGRAM

To determine if the correlations developed to calculate TVL1-500 were applicable to lower vapor pressure gasolines, a program was undertaken using five lower vapor pressure gasolines consisting of two hydrocarbon-only gasolines, two nominally 6 volume percent ethanol blends, and one 10 volume percent ethanol blend. The fuels used in this study were specially blended for the CRC E-67 Evaporative and Exhaust Emissions From Ethanol/Gasoline Blend Fueled Vehicles program. Five of the 12 fuels from the E-67 program were selected for this program to vary the 50% and 90% evaporated distillation points as well as ethanol content. Inspections for the five fuels used in this study are shown in Table 1. Inspections for the fuels used in the 2001 CRC volatility program are shown in Table 2.

The TVL1-500 test apparatus used in the 2001 program had been disassembled after completion of the 2001 program. The components were obtained from General Motors and set up again at Southwest Research Institute (SwRI). The reassembled apparatus was checked out and the thermocouples calibrated. The five fuel samples were sent to SwRI for single TVL1-500 determinations, which are reported in Table 1. Single TVL20 determinations were also obtained for the five test fuels and also are reported in Table 1. Vapor pressure inspections earlier had been obtained by members of the E-67 group as shown in Table 1.

IV. DISCUSSION OF RESULTS

A. Data Set Analysis

The equation for calculating TVL1-500 from TVL20 and ethanol content from the CRC Report No. 629 is:

$$\text{TVL1-500} = 46.63 + 0.540*\text{TVL20} - 0.766*\text{EtOH volume}$$

Using this equation, TVL1-500 was calculated for the five test fuels. These calculations were plotted against the measured TVL1-500 values in Figure 1 along with the original data from CRC Report No. 629. The number adjacent to each data point indicates the volume percent ethanol for that fuel. The original correlation is shown as a dotted line in Figure 1 while the best fit line for all of the data is shown as a solid line. The new data appears to fit the equation quite well, but reduced the correlation slope slightly.

A regression analysis was then run using both the new and old data combined. The resulting equation is as follows:

$$\text{TVL1-500} = 44.38 + 0.565*\text{TVL20} - 0.880*\text{EtOH volume}$$

The addition of the five data points provided a wider range in TVL1-500 with an improvement in the adjusted R^2 (0.986 vs. 0.965), a small increase in the standard error (1.33 vs. 1.20), and a better fit with the 1:1 perfect correlation line as shown in Figure 2.

In addition to a regression analysis of ethanol content and TVL20 as variables for calculating TVL1-500, another regression analysis was conducted using the presence and absence of ethanol as a variable with TVL20. This results in a fixed value offset whenever ethanol at any concentration is present. The resulting equation using the combined data set is as follows:

$$\text{TVL1-500} = 48.17 + 0.541*\text{TVL20} - 7.037*\alpha$$

where $\alpha = 0$ for Hydrocarbon-Only Fuel and $\alpha = 1$ for EtOH Blends

The results of this regression analysis are shown in Figure 3. The adjusted R^2 of this approach was slightly poorer than the ethanol concentration approach (0.978 vs. 0.986) and the standard error was larger (1.68 vs. 1.33).

In addition to developing an equation to calculate TVL1-500 using TVL20 and ethanol content, CRC Report No. 629 also developed an equation for calculating TVL1-500 from DVPE and ethanol content. The resulting equation was as follows:

$$\text{TVL1-500} = 137.07 - 2.279*\text{DVPE} - 0.850*\text{EtOH volume}$$

Using this DVPE equation, TVL1-500 was calculated for the five test fuels. These calculations were plotted against the measured TVL1-500 values in Figure 4 along with the original data from CRC Report No. 629. The original correlation is shown as a dotted line in Figure 4 while the best fit line for all of the data is shown as a solid line. Adding the new data resulted in a significant reduction in the correlation slope and a greater deviation from the 1:1 perfect correlation line.

As was done for the TVL20 study, a regression analysis was then run using the combined data set. The resulting equation is as follows:

$$\text{TVL1-500} = 147.44 - 2.851 \cdot \text{DVPE} - 01.259 \cdot \text{EtOH volume}$$

The addition of the five data points provided a wider range in TVL1-500 with no change in adjusted R^2 (0.941 vs. 0.945) and a significant increase in the standard error (2.73 vs. 1.52) as shown in Figure 5.

A third DVPE regression analysis was conducted using the presence and absence of ethanol as a variable with TVL20 rather than ethanol content. The resulting equation using the combined data set is as follows:

$$\text{TVL1-500} = 146.74 - 2.679 \cdot \text{DVPE} - 10.212 \cdot \alpha$$

where $\alpha = 0$ for Hydrocarbon-Only Fuel and $\alpha = 1$ for EtOH Blends

The results of this regression analysis are shown in Figure 6. The adjusted R^2 of this approach was not much different from the ethanol concentration approach (0.937 vs. 0.941) and the standard error was not much different either (2.83 vs. 2.73).

B. Discussion

The study of extending the calculation of TVL1-500 to lower vapor pressures showed that the current equation using TVL20 and ethanol content as variables worked well. A slightly better equation resulted when a regression analysis was done using both the original and new data. It was judged better because the adjusted R^2 was increased with a slightly poorer standard error and it better fit the 1:1 perfect correlation line. A regression analysis of the combined data base using the presence of ethanol as a variable with TVL20 resulted in an equation that was not as good as the ethanol concentration equation because it had a poorer adjusted R^2 , and a larger standard error.

As a whole, the equations using DVPE instead of TVL20 as a variable with ethanol were not as good as those developed using TVL20. Adding the data for the five lower vapor pressure fuels didn't affect the adjusted R^2 much, but resulted in a significant increase in the standard error. Using the presence of ethanol in place of ethanol concentration didn't have much of an effect, but the standard error of both approaches resulted in a larger standard error than the TVL20 regressions.

V. REFERENCES

- 1) Coordinating Research Council, Inc. 2001 CRC Hot-Fuel-Handling Program, CRC Report No. 629, June 2002.

Appendix A

**Members of the Data Analysis Panel of the
2001 CRC Hot-Fuel-Handling Program Follow-Up Study**

Name

Company

L.M. Gibbs, Leader

Chevron Products Company

Beth Evans

Consultant

B.E. Goodrich

BP

C.H. Jewitt

Renewable Fuels Association

K. L. Perry

General Motors Research

C.E. Richardson

Ford Motor Company

Table 1
CRC 2001 Volatility Program Follow-Up Fuel Inspections
Selected Fuels from the CRC E-67 Emissions Program

Inspection	Units	Fuel A	Fuel B	Fuel C	Fuel H	Fuel I
TVL 1-500	°F	128.4	115.8	113.4	130.2	116.8
TVL 20	°F	147.5	138.0	137.5	148.2	139.9
DVPE	psi	7.76	7.84	7.73	7.89	7.68
Relative Density	60/60°F	0.7310	0.7393	0.7482	0.7366	0.7498
API Gravity	°API	62.08	59.91	57.61	60.61	57.23
Oxygenates--D 4815						
MTBE	vol %	0.03	0.03	0.13	0.04	0.16
ETBE	vol %	0.02	0.02	0.01	0.01	0.01
EtOH	vol %	0.02	5.62	10.37	0.05	5.94
O2	wt %	0.01	1.96	3.63	0.04	2.09
D 86 Distillation						
IBP	°F	94.2	107.6	104.3	94.2	100.7
5% Evaporated	°F	126.3	127.2	124.6	122.7	124.0
10% Evaporated	°F	136.0	133.2	130.5	134.0	130.2
20% Evaporated	°F	148.6	140.8	138.8	151.6	139.0
30% Evaporated	°F	163.6	154.1	146.6	173.3	150.8
40% Evaporated	°F	179.8	176.1	153.7	197.0	191.0
50% Evaporated	°F	194.7	190.9	192.7	216.3	215.9
60% Evaporated	°F	209.0	203.2	223.5	230.4	235.9
70% Evaporated	°F	224.2	219.3	245.7	245.9	260.9
80% Evaporated	°F	243.4	240.9	281.5	273.7	311.3
90% Evaporated	°F	294.3	289.8	329.2	326.9	354.2
95% Evaporated	°F	327.4	325.9	343.4	343.7	366.6
EP	°F	351.2	352.0	374.0	374.4	391.8
Recovery	vol %	97.0	97.9	97.7	98.0	97.9
Residue	vol %	1.8	1.1	1.2	1.0	1.1
Loss	vol %	1.2	1.0	1.1	1.0	1.0
		100.0	100.0	99.9	100.0	100.0
Driveability Index		1082.4	1062.3	1103.1	1176.7	1197.2
E200	vol %	53.6	57.6	52.1	41.7	43.1
E300	vol %	90.9	91.5	84.0	85.2	77.8
Aromatics	vol %	25.9	25.9	25.4	25.6	26.8
Olefins	vol %	5.3	5.5	5.3	5.1	5.2
Saturates	vol %	68.8	68.6	69.3	69.3	67.7
Benzene	vol %	0.90	0.90	1.00	1.00	0.90
Research Octane Number		92.0	91.5	93.2	92.2	93.6
Motor Octane Number		84.0	83.2	84.0	84.8	85.5
(R+M)/2		88.0	87.4	88.6	88.5	89.6

Table 2
Summary of Inspections of CRC 2001 Volatility Program Fuels

Property	Test Method	Units	Fuel Code												
			L0	L3	L6	L10	L0	L3	L6	L10	H0	H3	H6	H10	
TVL1-500	GM		110.8	108.6	105.8	110.5	101.2	101.7	99.7	101.7	96.2	93.2	94.8	92.8	
Temperature for V/L=20	ASTM D 5188	°F	116.7	121.3	119.0	131.7	101.8	105.5	108.9	114.0	88.5	94.2	97.8	99.5	
DVPE	ASTM D 5191	psi	12.4	11.2	11.1	8.2	15.5	14.2	13.1	12.3	18.7	17.3	16.4	16.1	
Distillation	ASTM D 86														
Initial Boiling Point		°F	81.3	86.5	90.7	102.4	78.0	80.4	84.8	85.2	72.9	74.9	76.5	77.8	
5% Evaporated		°F	97.9	105.6	107.9	123.0	85.0	91.8	97.0	101.9	76.9	78.9	82.9	86.5	
10% Evaporated		°F	108.9	115.9	116.9	128.9	94.0	99.4	105.4	110.8	82.4	86.3	92.7	96.4	
20% Evaporated		°F	125.9	131.4	129.9	137.4	108.3	111.0	116.3	123.4	94.7	102.5	106.9	113.0	
30% Evaporated		°F	147.3	156.6	141.0	145.3	125.5	124.4	127.1	135.0	111.2	118.1	122.6	130.5	
40% Evaporated		°F	168.9	182.8	158.0	152.7	147.7	147.4	137.5	145.4	135.8	142.5	138.6	145.6	
50% Evaporated		°F	189.1	200.9	184.5	184.5	173.8	177.4	163.1	154.5	171.3	178.0	165.5	155.3	
60% Evaporated		°F	207.2	216.7	220.2	216.7	201.0	207.4	196.8	200.3	210.1	206.7	214.4	197.5	
70% Evaporated		°F	226.3	233.7	236.8	233.1	225.8	230.7	219.5	227.6	234.3	230.7	236.2	232.4	
80% Evaporated		°F	253.4	258.5	261.0	254.6	251.1	253.6	244.6	254.1	260.1	258.2	262.0	259.2	
90% Evaporated		°F	311.9	314.4	315.4	309.5	303.1	304.9	299.2	312.1	313.7	315.8	321.2	308.0	
95% Evaporated		°F	336.6	340.1	341.6	339.1	333.1	334.2	333.6	337.5	341.1	340.8	343.9	334.3	
End Point		°F	371.0	375.0	382.3	377.3	371.0	370.1	374.7	370.6	379.3	374.9	381.1	371.5	
Recovery		vol %	97.6	97.5	97.4	97.7	96.0	96.4	96.8	97.3	94.6	94.4	95.3	95.6	
Residue		vol %	1.0	0.8	0.8	1.3	1.5	1.4	0.9	0.8	1.2	1.4	1.2	1.3	
Loss		vol %	1.7	1.7	1.8	1.0	2.5	2.2	2.4	1.8	3.9	4.0	3.4	3.1	
Percent Evaporated at 158°F		vol %	35.0	30.5	40.0	42.2	44.0	43.7	48.2	50.9	46.3	44.5	47.8	50.9	
Percent Evaporated at 200°F		vol %	55.7	49.2	50.2	54.7	59.8	57.3	61.1	59.9	57.2	57.5	56.7	60.5	
Percent Evaporated at 300°F		vol %	87.9	87.5	87.2	88.4	89.2	89.0	90.1	87.9	87.6	87.3	86.4	88.3	
Ethanol	ASTM D 4815	vol %	0.0	3.0	6.3	10.0	0.0	2.7	5.9	9.8	0.0	3.0	6.0	10.2	
MTBE	ASTM D 4815	vol %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Gravity	ASTM D 4052	°API	63.0	61.8	61.7	60.8	68.1	66.0	65.2	62.0	69.0	67.4	66.2	62.6	
Corrected Composition															
Aromatics	ASTM D 1319	vol %	23.1	22.8	21.5	20.2	21.1	21.0	19.4	22.3	21.4	18.2	18.2	22.2	
Olefins	ASTM D 1319	vol %	5.3	3.9	3.5	3.5	3.7	6.4	6.4	4.5	6.0	6.0	4.8	3.7	
Saturates	ASTM D 1319	vol %	71.4	70.1	68.5	66.2	74.9	69.6	68.4	63.9	72.2	72.4	71.0	64.1	
Butanes	DHA	vol %	9.7	8.1	5.5	0.5	13.2	7.9	6.1	6.4	20.1	15.8	12.8	13.5	
Pentanes	DHA	vol %	18.6	11.5	16.7	10.7	22.2	24.8	22.6	18.6	21.3	17.1	18.5	14.4	
Benzene	ASTM D 3606	vol %	0.4	0.4	0.3	0.4	0.3	0.5	0.5	0.4	0.4	0.4	0.2	0.9	
Solvent washed gum	ASTM D 381	mg/100ml	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Lead	ASTM D 3237	g/gal	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Research Octane Number	ASTM D 2689	ON	91.1	92.2	94.7	95.4	91.0	93.6	92.0	95.0	94.6	93.4	96.7	94.0	
Motor Octane Number	ASTM D 2700	ON	83.5	84.2	86.0	86.0	84.0	85.0	83.6	85.2	86.2	85.4	87.5	84.0	
(R+M)/2	D 2699/2700	ON	87.3	88.2	90.4	90.7	87.5	89.3	87.8	90.1	90.4	89.4	92.1	89.0	

Figure 1

Original Calculated versus Measured TVL1-500
 $TVL1-500 = 46.63 + 0.540 \cdot TVL20 - 0.766 \cdot EtOH \text{ Vol}$

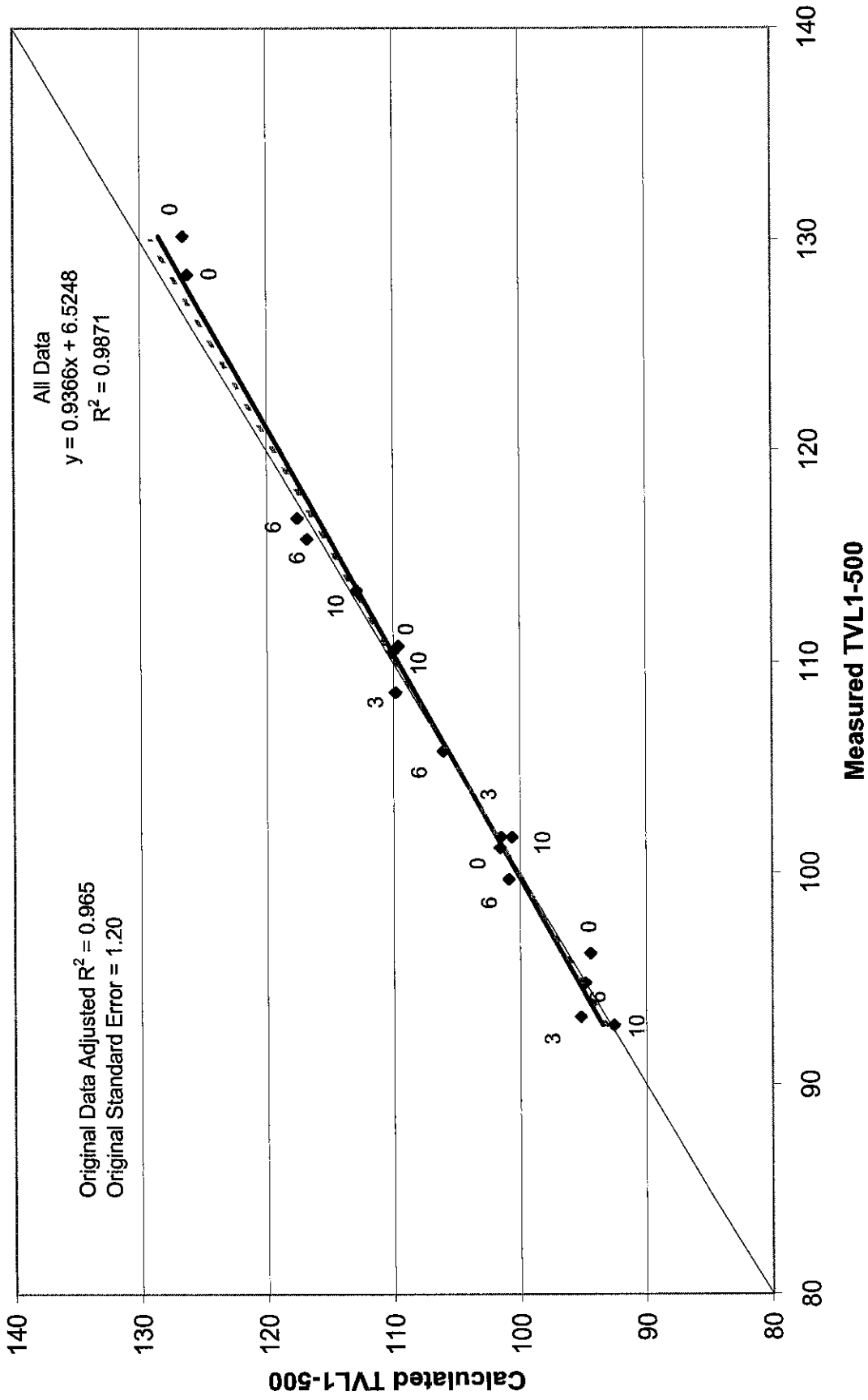


Figure 2

New Calculated versus Measured TVL1-500

$TVL1-500 = 44.38 + 0.565 \cdot TVL20 - 0.880 \cdot EtOH \text{ Vol.}$

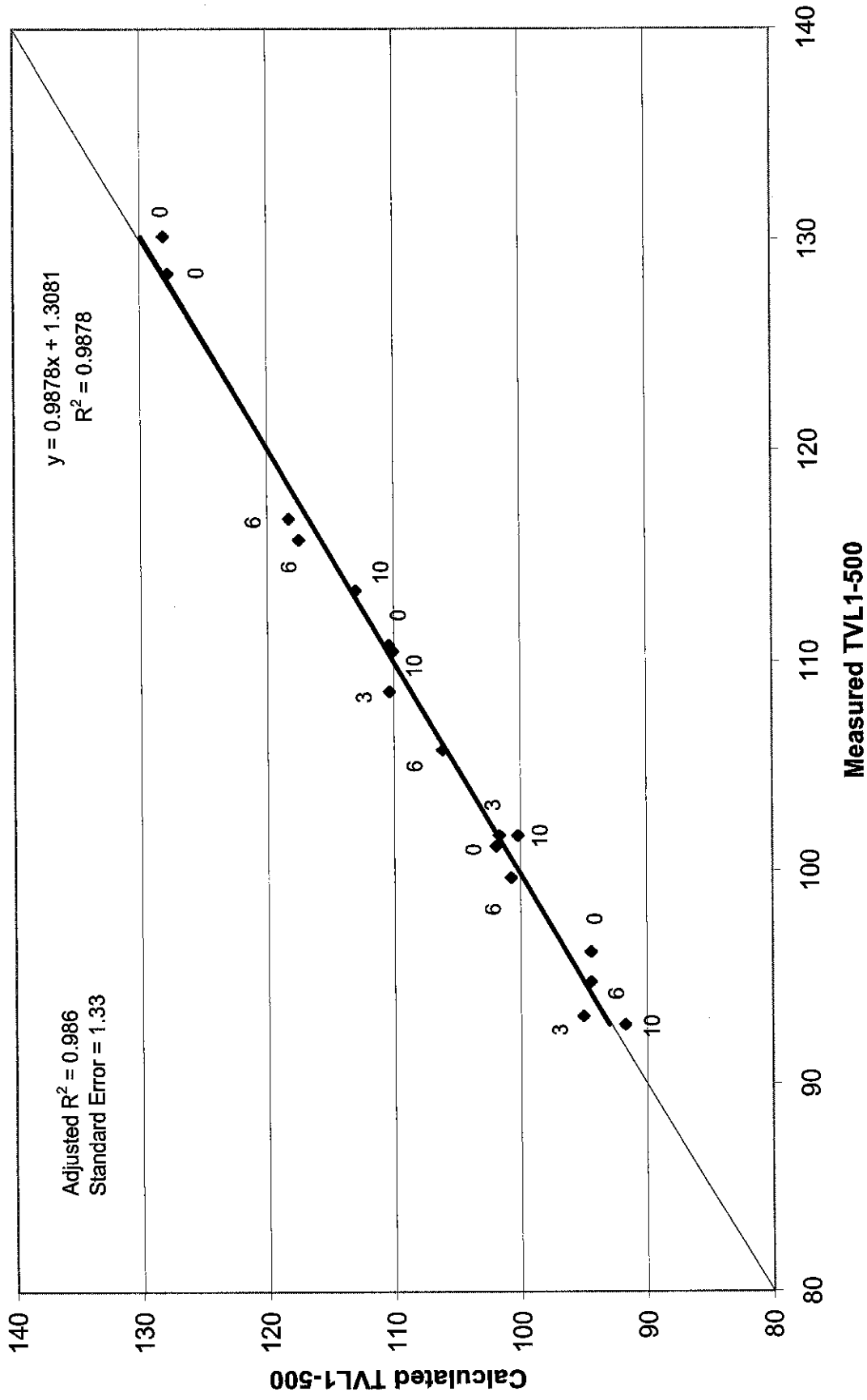


Figure 3

New Fixed Ethanol Calculated versus Measured TVL1-500

$$\text{TVL1-500} = 48.17 + 0.541 \cdot \text{TVL20} - 7.037 \cdot \alpha$$

where $\alpha = 0$ for Hydrocarbon-Only Fuel and $\alpha = 1$ for EtOH Blends

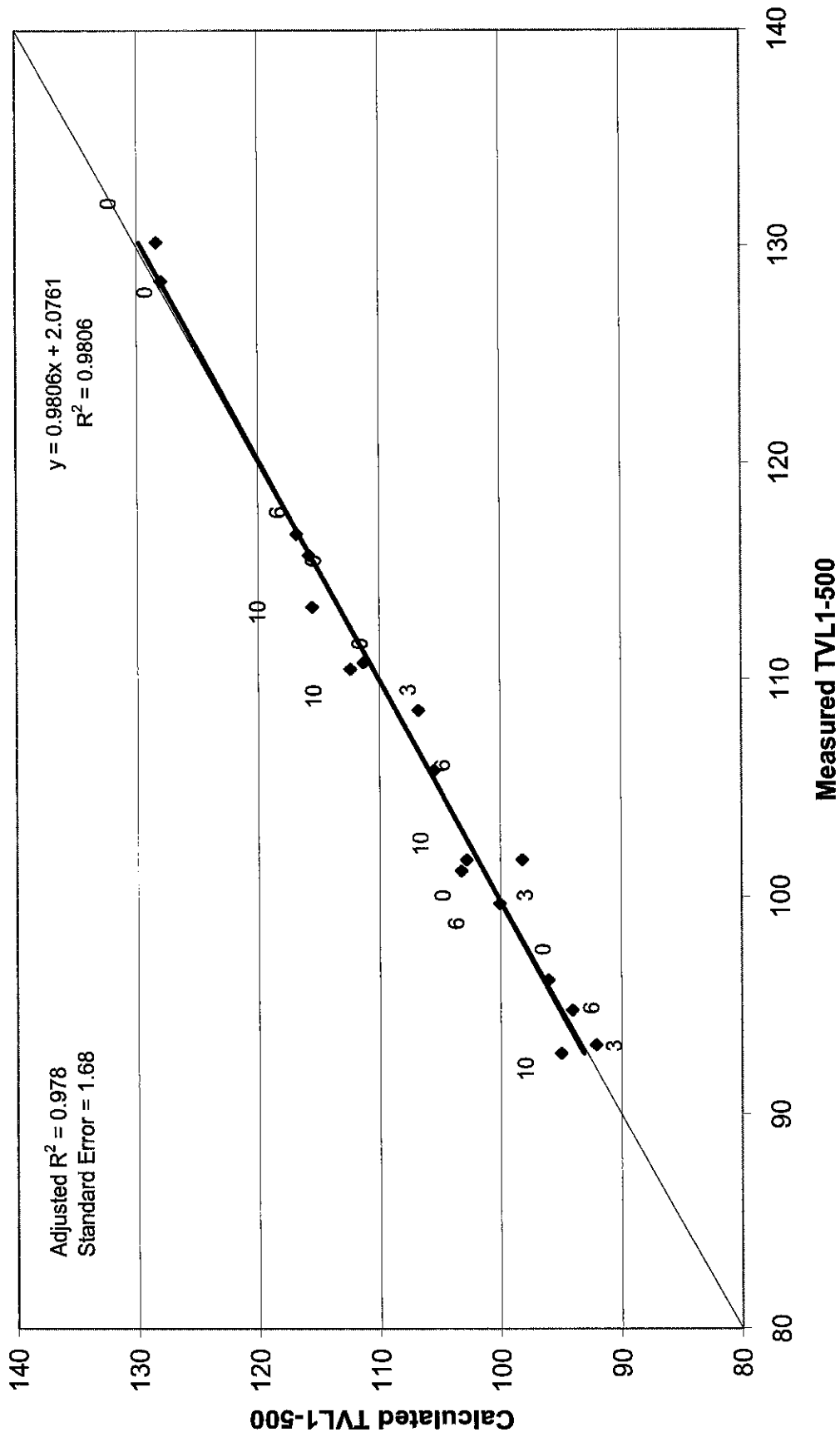


Figure 4

Original Calculated versus Measured TVL1-500
 $TVL1-500 = 137.07 - 2.279 \cdot DVPE - 0.850 \cdot EtOH \text{ Vol}$

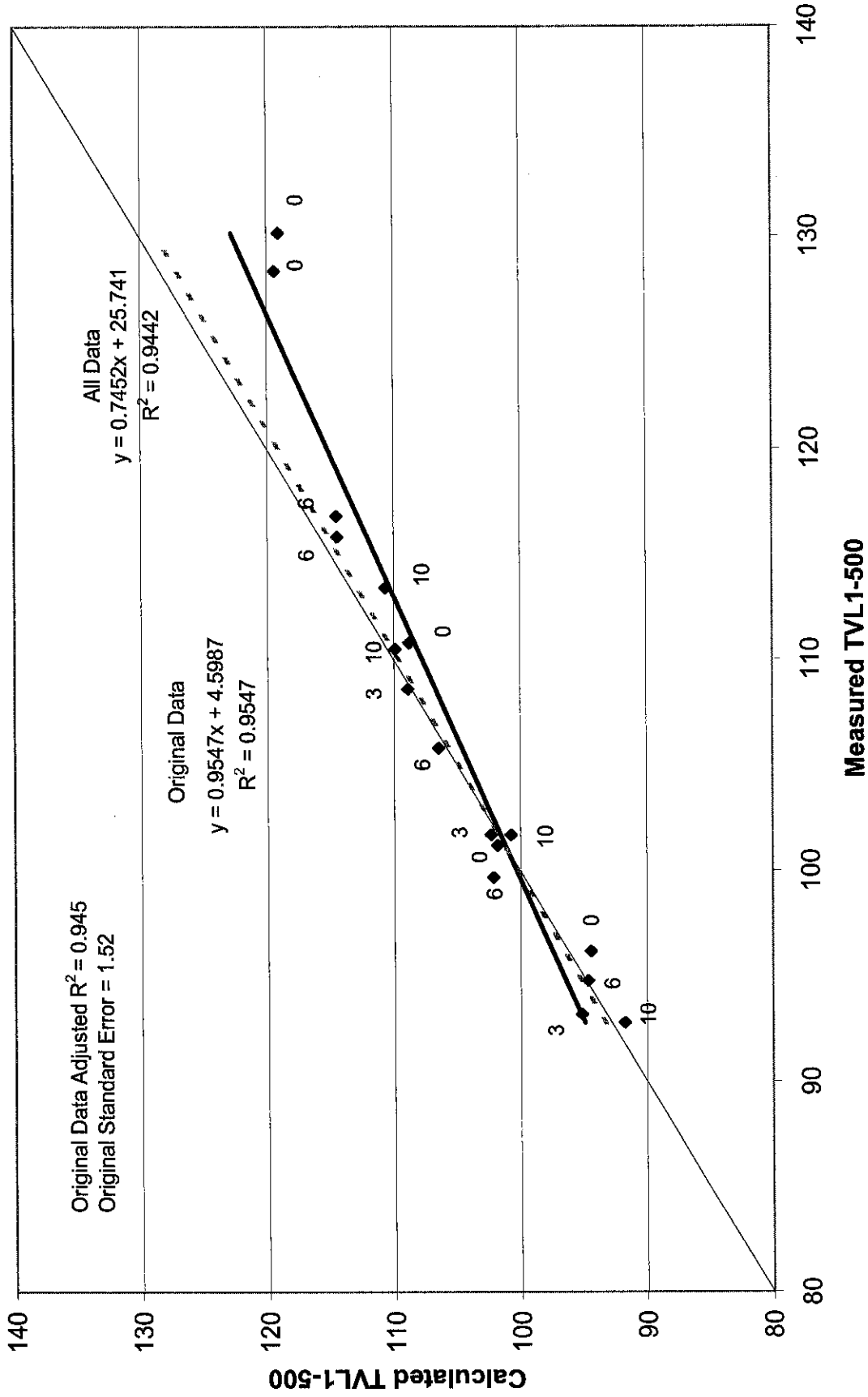


Figure 5
New Calculated versus Measured TVL1-500
TVL1-500 = 147.44 - 2.851*DVPE - 1.259*EtOH Vol.

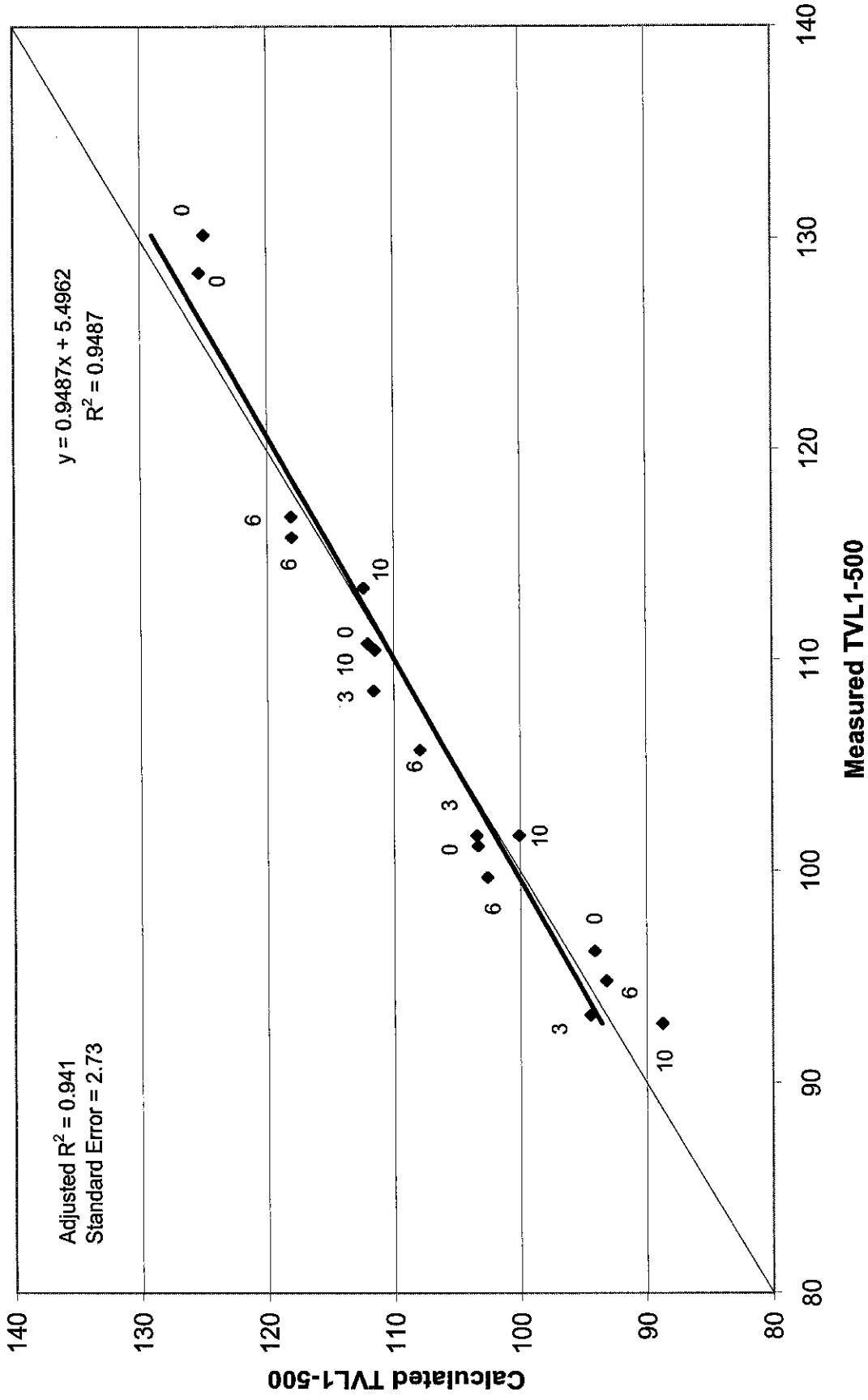


Figure 6

New Fixed Ethanol Calculated versus Measured TVL1-500

$$\text{TVL1-500} = 146.74 - 2.679 \cdot \text{DVPE} - 10.212 \cdot \alpha$$

where $\alpha = 0$ for Hydrocarbon-Only Fuel and $\alpha = 1$ for EtOH Blends

