

**CHAPTER IV**  
**RESULTS & DISCUSSION**

# CHAPTER IV

## RESULTS AND DISCUSSION

In this study, three sets of test fuels were formulated by blending two, three or four refinery streams and one of the employed ether oxygenates . Table 1 lists individual GC analysis of the locally available refinery streams and Table 2 summarizes some information's concerning the employed ether oxygenates . Formulation starts with the all-hydrocarbon gasoline blends as reference samples which are designated RS . These formulated RS gasoline blends are used to facilitate comparison with oxygenated gasolines in which the hydrocarbon portion have the same composition . Oxygenated gasoline blends designated M-, E- and T- consist of number of refinery components and methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), or tertiary amyl methyl ether (TAME), respectively, Table 3 lists the formulated gasoline blends in this study .

At the pre-formulation stage, it was not clear to which extent it would prove possible to simultaneously meet the fuel range of property targets . Consequently, it was considered prudent to define a priority order to assist the formulator to the full adherence to the target property .These properties, were split into two categories; the primary targets are : E70, E150, benzene and aromatics which are essential for the protection of environment through reduction of tailpipe emissions . The remaining secondary targets are also desirable for the required standard specifications of the resultant blends . Various measurements along with the blender own experience, were used as the basis for the criteria as shown in Table 4 .

**Table 1 – GC Analyses and Properties of Refinery Streams Used for Gasoline Formulations**

Composition (wt.%)	Reformat 21 C <sub>1</sub> Bott.	Isomerase 30-SN-5	L. Naphtha* TOP C <sub>7</sub>	H. Naphtha Bott. C <sub>7</sub>
iso-Butane	0.09	0.34	0.00	0.00
n-Butane	0.42	3.78	0.00	0.00
iso-Pentane	2.00	38.15	13.07	0.27
n- Pentane	1.67	11.24	17.33	0.74
2,2-Dimethylbutane	0.35	12.47	0.37	0.04
Cyclopentane	0.12	1.45	1.75	0.22
2,3-Dimethylbutane	0.33	3.88	1.33	0.21
2-Methylpentane	2.28	11.11	8.33	1.53
3-Methylpentane	1.78	6.34	5.46	1.17
n-Hexane	2.45	4.14	13.13	3.53
Methylcyclopentane	0.75	2.33	6.15	2.01
Benzene	3.65	0.01	2.26	0.72
Cyclohexane	0.11	3.10	4.36	2.13
C <sub>7</sub> <sup>+</sup>	84.00	1.66	26.46	87.43
<b>Total</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>

Sp. Gravity 60/60°F	0.7931	0.6471	0.67528	0.74317
Sulphur, wt. %	0.1142	0.0763	0.1185	0.1144
, (ppm)	(114)	(76)	(118)	(114)
RON	93.8	86.2	58.2	69.9
MON	83.5	83.8	56.1	68.1
(RON+MON)/2	88.7	85.0	57.2	69.0

Table 2- Properties of The Employed Oxygenates

Properties	MTBE	ETBE	TAME
Molecular Weight	88.2	102.2	102.2
Boiling point, (°C)	55	72-73	85-86
Density @ 20 °C	0.735	0.740	0.740
Blending RVP, psi	8	4	1
Research octane No. (RON)	118	119	112
Motor octane No. (MON)	103	103	99
Pump octane No. (R+M)/2	110.5	111	105.5
Oxygen Content, mass%	18.15	15.66	15.66
Volume % Oxygenate Required for 2 wt.% O <sub>2</sub>	11.0	12.8	12.8
Volume % Oxygenate Required for 2.7 wt.% O <sub>2</sub>	15.0	17.2	17.2
Water Solubility, g/L			
- Water in organic	14-18	6-8	3-5
- Organic in water	43-54	26	20
Odour & Taste Threshold (ppm)	20-40	50	200

Table 3- The Formulated Gasoline Blends

Formulated Blends	Added Oxygenate	Blended Refinery Streams	Designation of Gasoline Blends	Total Samples
RS-gasoline blends	—	2	1RS, 2RS, 3RS, 4RS	7
	—	3	5RS	
	—	4	6RS, 7RS	
M-gasoline blends	MTBE	2 Reformate Isomerate	1M, 2M, 3M, 4M 5M, 6M, 7M, 8M 9M, 10M, 11M 12M, 13M, 14M	14
E-gasoline blends	ETBE	2 Reformate Isomerate	1E, 2E, 3E, 4E 5E, 6E, 7E, 8E 9E, 10E, 11E 12E, 13E, 14E	14
T-gasoline blends	TAME	2 Reformate Isomerate	1T, 2T, 3T, 4T 5T, 6T, 7T, 8T	8
M-gasoline, E-gasoline, & T-gasoline, blends	MTBE ETBE TAME	3 Reformate Isomerate L.Naphtha	15M, 16M, 17M, 18M	4
			15E, 16E, 17E, 18E	4
			9T, 10T, 11T, 12T	4
M-gasoline blends	MTBE	4 Reformate Isomerate	19M, 20M, 21M, 22M	4
E-gasoline blends	ETBE	L.Naphtha H.Naphtha	19E, 20E, 21E, 22E	4

**Table 4- Property Targets of the Formulated Gasoline Blends**

<b>Property</b>	<b>Target Value</b>	<b>Acceptance Limits.</b>
<b>E100</b>	Variable	± 3.0vol.%
<b>E70</b>	20-35 vol.%	± 3.0vol.%
<b>E150</b>	90 vol. %	± 2.0vol.%
<b>Aromatics</b>	Variable	± 3.0vol.%
<b>Benzene</b>	<2.5 wt.%	
<b>Sulphur</b>	<100ppm	
<b>Oxygen</b>	2.7 wt. % max.	
<b>RON</b>	85-95	

### **1-Two – Refinery Stream Formulations :-**

Reformat and isomereate are the refinery streams employed in these formulations . Four different blends of all-hydrocarbon gasoline, were first formulated using 74, 68, 62 and 56 volume percent of reformate and 26, 32, 38 and 44 volume percent isomereate, respectively . These hydrocarbon blends were designated 1RS, 2RS, 3RS and 4RS . Compositions, specifications and octane numbers are given in Table 5(A), whereas, ASTM distillation, volatility criteria and driveability indices are listed in Table 5(B) . ASTM distillation test was carried out to determine fuel volatility across the entire boiling range of the formulated gasolines.

Full distillation profiles of hydrocarbon gasoline blends 1RS and 4RS are shown in Figure 1 illustrating the effect of blend composition on volatility criteria . In each profile a set of “ T ” points or “ E ” points are located. T10, T50 or T90 is the temperature at which 10%, 50% or 90% of gasoline distilled . E70, E100 or E150 is the volume percentage of gasoline distilled at 70, 100 or 150 °C . The 10% evaporated temperature must be low enough to provide good warm-up and cold weather driveability . The 90% and end point evaporation temperatures must be low enough to minimize crankcase and camber deposits, as well as, spark plug fouling and dilution of engine oil .Volatility criteria, E70, E100 and E150, represent front-end, midrange and tail-end volatilities (**Chevron USA, Inc., 2004, Downstream alternatives, Inc., 1996**) .

Front-end volatility (E70) is adjusted to provide : easy cold and hot starting, freedom from vapour lock, low evaporative emissions, Midrange volatility (E100) is adjusted to provide : rapid warm up, smooth running, protection against carburetor icing and hot stalling, good power and acceleration . Tail-end volatility (E150) is adjusted to provide : minimal hydrocarbon (HC) exhaust

emission, minimal fuel dilution of crankcase oil, freedom from engine deposits and good fuel economy (**Chevron USA, Inc., 2004**) . In the present study, the more tractable E150 value is usually used to fix back end volatility . For this reason T90% = E150 °C was accepted as a design . European Oil Companies have used E150 °C instead of T90 in many formulation design (**EFEFE, 1995**) . The final boiling points of all formulated gasoline blends are in the vicinity of 190 °C to avoid harmful exhaust emissions of heavy gasoline components (**Hochhauser et al, 1991, McArragher et al, 1994; Sado et al.,1995**) .

Careful inspection in Figure 1, which illustrates the distillation profiles of 1RS and 4RS all-hydrocarbon fuels, shows some considerable differences . These differences are mainly due to variation in blend composition as shown in Table 1 . Fuel 4RS is relatively more isomere-enriched than 1RS, which leads to considerable differences in the midrange volatility criteria, E100, of these fuels . The measured E100 values of 1RS and 4RS are 52 and 62 volume percent, respectively . It should be noted that the curves for fuels 1RS to 4RS follow very similar profiles . A gradual increase, in E100 values of these fuels, is evident, this in spite of the fact that the other volatility criteria, E70 and E150 satisfied the acceptance requirements wither the limits outlined in Table 4 .

**Table 5 (A)- Specifications and Octane Numbers of Four Hydrocarbon Gasoline Blends Consisting of Two Refinery Streams as Reference Samples (RS).**

Gasoline No.	1RS	2RS	3RS	4RS
	Blend Composition, vol%			
Reformate, vol. %	74.0	68.0	62.0	56.0
Isomate, vol. %	26.0	32.0	38.0	44.0
Total Gasoline, vol. %	100	100	100	100

<b>Blend Specifications:-</b>				
Sp. Gravity, 60/60 °F	0.7351	0.7325	0.7251	0.7241
Aromatics, vol. %	44.0	41.0	36.0	32.0
RVP, psi	6.08	6.56	7.04	7.52
, K/cm <sup>2</sup>	0.43	0.46	0.50	0.53
Sulphur, ppm	104	98	95	92
Benzene, wt. %	2.4	2.3	2.1	2.0
Oxidation Stability, mint	>480	—	—	>480
Corrosion, Copper Strip Test, 3hrs at 50°C	1	—	—	1

RON	88.2	87.8	87.7	86.4
MON	81.6	81.6	81.5	80.6
(R+M)/2	86.9	84.7	84.6	83.5

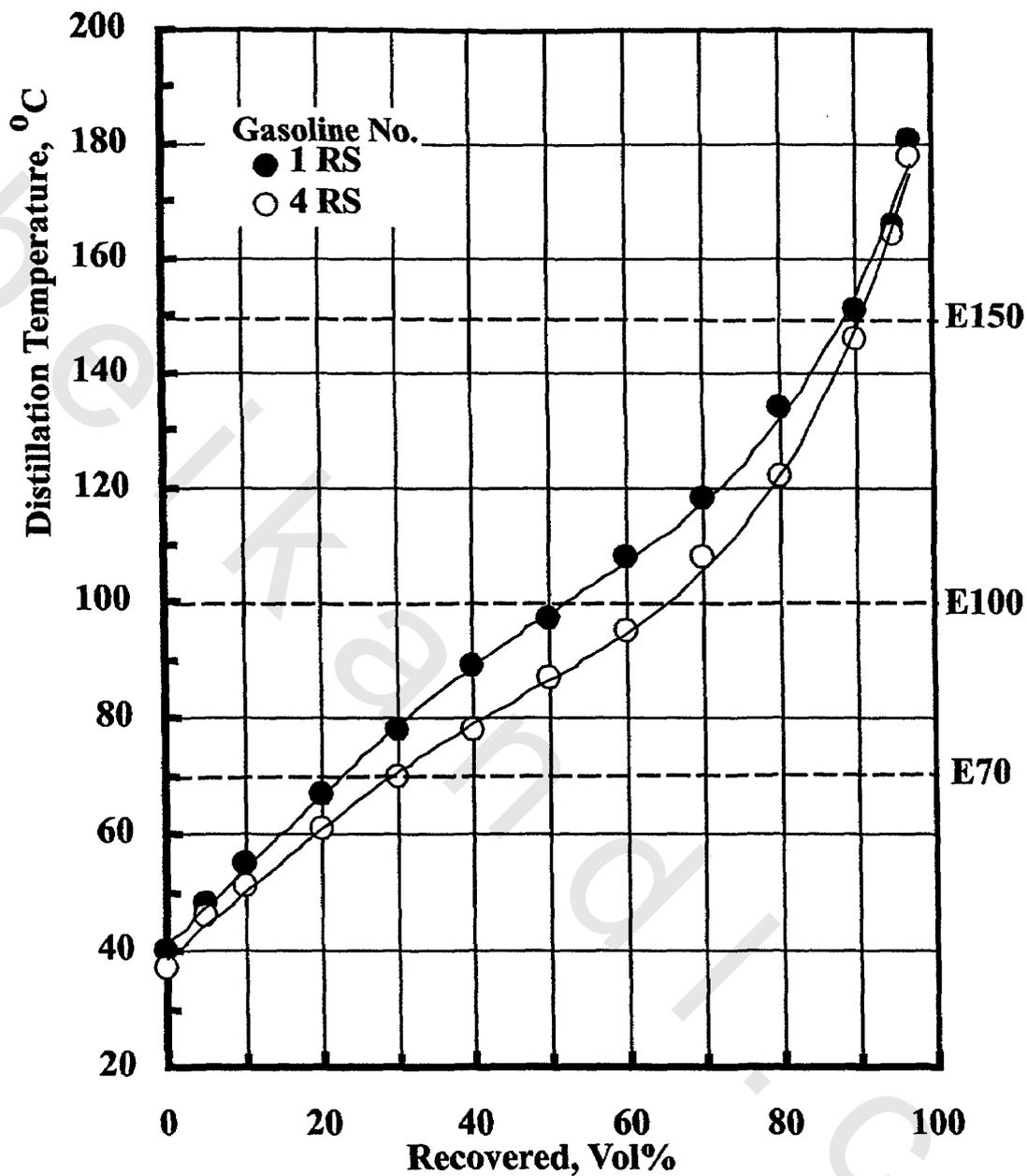
**Table 5 (B)- ASTM Distillation of Four Hydrocarbon Gasoline Blends Consisting of Two Refinery Streams as Reference Samples (RS).**

Gasoline No.	1RS	2RS	3RS	4RS
<b>ASTM Distillation</b>	<b>Temperature, °C</b>			
<b>IBP,</b>	40	40	39	37
<b>5 %</b>	48	48	47	46
<b>10 %</b>	55	55	54	51
<b>20 %</b>	67	66	64	61
<b>30 %</b>	78	75	73	70
<b>40 %</b>	89	84	81	78
<b>50 %</b>	97	93	90	87
<b>60 %</b>	108	104	101	98
<b>70 %</b>	118	114	111	108
<b>80 %</b>	134	128	124	122
<b>90 %</b>	151	150	148	146
<b>95 %</b>	166	165	164	164
<b>FBP,</b>	181	179	179	178

<b>Recovered, vol.%</b>	98.5	98.0	98.0	98.0
<b>Residue, vol.%</b>	0.5	0.8	0.6	0.6
<b>Loss, vol.%</b>	1.0	1.2	1.4	1.4

<b>E 70 vol.%</b>	21	23	25	30
<b>E100 vol.%</b>	52	55	60	62
<b>E150 vol.%</b>	89	89	90	90

<b>Driveability Index (DI) °F</b>	1120	1097	1074	1047
<b>°C</b>	524	512	499	484



**Fig. 1 - Distillation Profiles of 1 RS and 4 RS of All Hydrocarbon Gasolines Showing the Effect of Blend Composition on Volatility Criteria .**

## **2- Oxygenated Two – Refinery Stream Blends :-**

Oxygenated blends consisting of two refinery streams and one of the employed oxygenates, were formulated in three main groups, M, E and T . Each group consists of four oxygenated blends . Gasoline No 1M, 2M, 3M and 4M are oxygenated with MTBE, whereas, gasoline No 1E, to 4E and 1T to 4T, are oxygenated with ETBE and TAME, respectively . Each of the twelve oxygenated blends have 2.0 weight percent oxygen content. At this oxygen requirement, 11.0 volume percent MTBE or 12.8 volume percent ETBE or TAME, are blended with 89 or 87.2 volume percent of all-hydrocarbon fuels . The employed hydrocarbon fuel components, reformate and isomerate, were exchanged in sufficient quantities for the formulation of the twelve oxygenated gasoline blends specified in Table 6(A&B) . It is clear from data in Table 6(A) that MTBE- ETBE- and TAME-blended fuels constitute 42-32 volume percent aromatics and trace amounts of olefins (FIA Method IP 156/65T), 2.0-1.57 weight percent benzene (G.C. analysis), and 96-86 ppm sulphur content (XRF analysis) . Blending any of the employed ether oxygenates does not alter stability standards which control fuel's tendency to contribute to induction system deposits as well as determining the fuel's storage life . A copper corrosivity standard ensures that the resultant oxy-fuels will not create excessive corrosion in the vehicle fuel system . Concerning the anti-knock performance of these formulated test fuels, it can be seen from data in Table 6(A) that Research octane numbers (RON) and Motor octane numbers (MON) are in the range 92-93 and 83-86, respectively .

Gasolines are most commonly rated based on their anti-knock index (AKI), A measure of octane quality . The AKI is a measure of a fuel ability to resist engine knock . The AKI values is the average of the RON and MON or  $(R+M) / 2$  . Data in Table 6(A)

shows that the anti-knock indices values of MTBE-, ETBE- and TAME-blended gasolines are in the vicinity of 88-89 which gives an indication that at this oxygen level (2.0 wt.%), variation in the anti-knock index values is mainly due to changes in blend composition .

To explain how can blend composition affect anti-knock property, gasoline No. 1M and 4M are compared . Gasoline No.1 consists volumetrically of 74 % reformat, 15% isomerate and 11% MTBE, whereas gasoline No.4M consists of 56% reformat, 33% isomerate and the same amount of MTBE, Table 6 (A) . The determined  $(R+M)/2$  values of these gasolines 89.5 and 89.1, respectively . This small differences is mainly attributed to the contribution difference of the employed gasoline components . Similarly, the determined  $(R+M)/2$  values of gasolines No. 1E and 4E are 88.5 and 87.9, whereas, those of gasoline No. 1T and 4T are 89.9 and 89.0, respectively . Reformate, which constitutes relatively higher aromatic content, contributes more efficiently in anti-knock property than isomerate (Furey and Perry, 1990; Piel, 1989) .

It can be seen from data in Table 6(A) that the three formulation group of MTBE-, ETBE- and TAME-blended gasolines have the same oxygen level (2.0 wt.%) . The difference between the aromatic contents of oxygenated gasoline pairs : 1M-4M, 1E-4E and 1T-4T are approximately the same (FIA Method IP 56/65) . This may add an evidence that the difference in  $(R+M)/2$  values is due to difference in combustion characteristics of blends containing different ether oxygenates .

Table 6(A) lists the various specifications of the test oxy-fuels . Sulphur contents are less than 100 ppm . Benzene does not exceed 2.0wt.% copper strip corrosion test ensures that oxygenated gasoline blends will not create excessive corrosion in the vehicle fuel system . Oxidation stability tests give indications

that blending any of the employed ethers, will not alter the fuel's storage life . On the contrary, a noticeable reduction, in Reid vapour pressure (RVP) of the formulated oxy-fuels, is evident .

ASTM distillation, volatility characteristics and driveability indices of gasoline formulations No. 1M to 4M, 1E to 4E and 1T to 4T, are shown in Table 6(B) . At 2.0 wt.% oxygen level, the measured E100 values of these formulations are relatively lower than all-hydrocarbon blends 1RS to 4RS in Table 5(B) . E100 values are better illustrated in Figure 2 and 3 for gasolines No. 1M, 1E and 1T when compared with 1RS and gasoline 4M, 4E and 4T when compared with 4RS . It can be seen from these figures that mid-range volatility (E100) is most affected by TAME. Gasolines No. 1M, 1E and 1T gave E100 values 44, 42 and 38 vol.%, respectively, whereas, 4M, 4E and 4T gave E100 values 55, 53 and 45 vol.%, respectively . One can reach a conclusion that in gasoline formulation consisting of the same components, mid-range volatility (E100) is altered by changing blend composition . Alteration is less severe in front-end or tail-end volatilities (E70 and E150) .

On parallel lines, gasoline formulation No. 5M to 8M, 5E to 8E and 5T to 8T, are shown in Tables 7(A) and 7(B) . These formulations are blended with 15.0 vol.% MTBE or 17.2 vol.% ETBE or TAME, to give the maximum permitted level of oxygen (2.7 wt.%). When oxygen content increases from 2.0 (Table 6) to 2.7 wt.% oxygen (Table 7), a further decrease in Reid vapour pressure (RVP) is noticed, and an increase in anti-knock value is observed .

Distillation profiles, volatility characteristics and driveability indices of gasoline formulations No. 5M to 8M, 5E to 8E and 5T to 8T, are shown in Table 7(B) . The measured E100 values, of these formulations, are lower than all-hydrocarbon blends as illustrated in

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Figures 4 and 5 for gasolines No. 5M, 5E, 5T along with 1RS and 8M, 8E, 8T along with 4RS . In these figures, distillation curves at the bottom represent all-hydrocarbon gasoline blends 1RS and 4RS which have the highest volatilities . Distillation curves at the top represent oxygenated gasoline blends 5T and 8T which have the lowest volatilities .

While octane and volatility are the most important standards relating to driveability, there are other fuel standards covered by ASTM guidelines . Specifications of the test oxy-fuels, listed in Tables 6 and 7, satisfy the widest range of vehicles and operating circumstances possible . Benzene does not exceed 2.0 wt.%, sulphur contents are below 100 ppm, oxidation stability > 480 minutes and oxy-fuels will not create corrosion problems in vehicle fuel system . Concerning the anti-knock indices of the formulated fuels containing 2.0 and 2.7 wt.% oxygen, the (R+M)/2 values are in the range 90-89 and 91-90, respectively . Using gasoline with an anti-knock rating higher than that required to prevent knock will not improve a vehicle's performance, including it's power, unless the vehicle is equipped with a knock sensor **(Khan and Reynolds, 1996; Gibbs,1995; Schuetzle et al., 1994; Schmidt et al., 1993)** .

It is well known that oxygenated gasoline is conventional gasoline to which oxygenates have been added to increase octane and/or, as required by regulation, to reduce emissions . Oxygenated gasoline is required during winter in those metropolitan areas which do not meet air quality standard for carbon monoxide (carbon monoxide nonattainment areas) . Oxygenated gasoline programs require winter grades to have an average of 2.7 wt.% oxygen (15.0 vol.% MTBE, 17.2 vol.% of ETBE or TAME) . Reformulated gasoline (RFG) is always oxygenated during the winter and may be oxygenated year-round . RFG is blended to reduce evaporative and exhaust emissions from

vehicle. RFG requires a minimum of 2,1 wt.% oxygen (11.5 vol.% MTBE, 13.4 vol.% ETBE or TAME) RFG is required in those metropolitan areas which do not meet air quality standard for ozone (ozone nonattainment areas) .

Four gasoline variables are used by refineries in U.S.A to produce Phase I RFG and to judge emissions : Reid vapour pressure, oxygen content, benzene and total aromatics . (Lidderdale and Bohn, 2000; Lidderdale, 1995; U.S.-EPA, 1993). In Phase II RFG refineries were required to introduce four additional variables : sulphur, olefins, and two distillation criteria (T50 & T90) . Data in Table 6(A&B) list the specifications and octane numbers of gasoline formulation consisting of two refinery streams and different oxygenates . It is obvious from data in this table that Reid vapour pressure (RVP) values are between 5.5-7.0, 5.0-6.3, and 4.5-6.0 for MTBE-, ETBE- and TAME-blended gasolines . These RVP values are relatively lower than that for RFG in U.S.A (RVP for California Phase II RFG is in the range 6.7-7.0 psi) . Further addition of oxygenate results in more reduction in RVP values (Table 7) . Changing blend composition is a suitable outlet for increasing RVP values .

In Table 8(A), blend compositions enriched in isomerate are formulated . RVP values of these formulations are found to range between 6.5-7.5 and 6.7-7.6 psi for MTBE-blended gasolines; 6.1-7.0 psi for ETBE-, or TAME-blended gasolines . Other specifications are slightly altered . For example, T50 and T 90 are in the range 92-99 °C and 145-151 °C, respectively . The corresponding values of T50 and T 90 in California Phase II RFG are in the range 93-99 °C and 143-149 °C, respectively . A conclusion could be reached that through reformulation of the available gasoline components in the local market, gasoline properties can be altered to meet seasonal changes .

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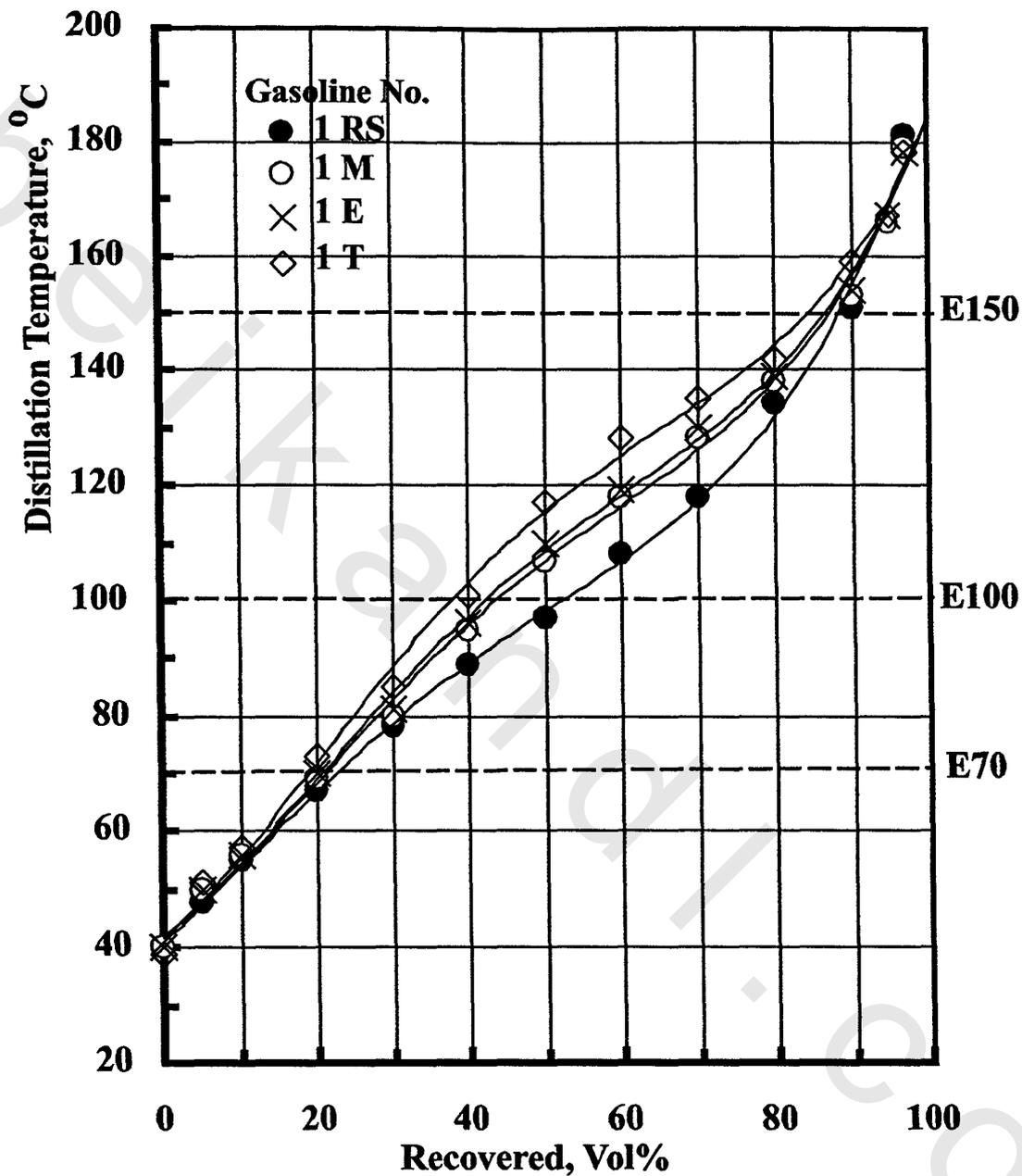
Table 6 (A)-Specifications and Octane Numbers of Gasoline Formulations Consisting of Two Refinery Streams and Different Oxygenates (2.0 wt.% Oxygen Content).

Gasoline No.	1M	2M	3M	4M	1E	2E	3E	4E	1T	2T	3T	4T
Refinery Streams	Blend Composition, vol%				Blend Composition, vol%				Blend Composition, vol%			
Reformate, vol%	74.0	68.0	62.0	56.0	74.0	68.0	62.0	56.0	74.0	68.0	62.0	56.0
Isomate, vol%	15.0	21.0	27.0	33.0	13.2	19.2	25.2	31.2	13.2	19.2	25.2	31.2
Hydrocarbon Gasoline	89.0	89.0	89.0	89.0	87.2	87.2	87.2	87.2	87.2	87.2	87.2	87.2
Added Oxygenate, vol%	11.0	11.0	11.0	11.0	12.8	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Total Blend, vol%	100	100	100	100	100	100	100	100	100	100	100	100
Oxygenate Type	MTBE	MTBE	MTBE	MTBE	ETBE	ETBE	ETBE	ETBE	TAME	TAME	TAME	TAME
Oxygen Content, wt%	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
<b>Blend Specifications:-</b>												
Sp. Gravity, 60/60 °F	0.7503	0.7419	0.7335	0.7251	0.7498	0.7414	0.7270	0.7232	0.7523	0.7439	0.7355	0.7258
Aromatics, vol. %	42.0	39.0	35.0	32.0	42.0	38.0	34.0	32.0	42.0	37.0	33.0	32.0
RVP, psi	5.48	6.00	6.48	7.00	4.91	5.41	5.91	6.31	4.53	5.03	5.53	5.93
, Kg/cm <sup>2</sup>	0.38	0.42	0.45	0.50	0.34	0.38	0.41	0.44	0.32	0.35	0.39	0.42
Sulphur, ppm	96	94	90	88	95	93	91	91	94	94	92	86
Benzene, wt%	2.00	1.90	1.74	1.57	2.00	1.90	1.74	1.57	2.00	1.90	1.74	1.57
Oxidation Stability, mint	>480	—	—	—	>480	—	—	—	>480	—	—	—
Corrosion, Copper Strip Test, 3hrs at 50°C	1	1	1	1	1	1	1	1	1	1	1	1
RON	93.2	93.1	92.8	92.7	92.8	92.4	92.3	92.2	93.7	93.4	93.3	93.1
MON	85.9	85.9	85.4	85.5	84.2	85.0	84.9	83.6	86.2	86.0	85.5	85.0
(R+M)/2	89.5	89.5	89.1	89.1	88.5	88.7	88.6	87.9	89.9	89.2	89.4	89.5

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**Table 6 (B)- ASTM Distillation – Volatility Criteria and Drivability Indices of Gasoline Formulations Consisting of Two Refinery Streams and Different Oxygenates (2.0 wt% Oxygen Content).**

Gasoline No.	1M	2M	3M	4M	1E	2E	3E	4E	1T	2T	3T	4T
ASTM Distillation	Temperature, °C				Temperature, °C				Temperature, °C			
IBP,	40	40	38	38	40	40	39	40	39	38	40	40
5 %	50	50	48	46	50	49	49	47	51	48	48	47
10 %	65	59	57	53	56	55	54	53	57	55	56	57
20 %	69	67	64	63	70	67	66	64	73	71	69	67
30 %	80	77	74	72	81	80	78	74	85	84	82	80
40 %	95	91	85	81	96	93	90	85	101	98	95	90
50 %	107	102	95	92	110	105	101	95	118	112	110	106
60 %	118	112	108	105	119	116	112	109	128	125	121	119
70 %	128	125	121	117	130	128	123	120	135	133	131	130
80 %	138	137	135	134	139	138	136	135	142	141	140	140
90 %	153	151	150	149	154	153	152	150	159	158	155	154
95 %	166	165	165	166	167	167	168	168	167	170	171	173
FBP,	179	178	178	179	178	178	179	179	178	179	178	180
Recovered, vol %	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.5	98.5	98.0	98.0
Residue, vol %	0.8	0.8	0.7	0.7	0.8	0.8	0.8	0.7	0.5	0.5	0.7	0.7
Loss, vol %	1.2	1.2	1.3	1.3	1.2	1.2	1.2	1.3	1.0	1.0	1.3	1.3
E 70 vol %	20	22	25	28	20	22	23	25	18	20	21	22
E100 vol %	44	47	53	55	42	46	49	53	38	41	43	45
E150 vol %	87	90	90	90	86	88	88	89	85	88	88	88
Driveability Index (DI) °F	1224	1181	1134	1106	1221	1189	1164	1123	1274	1137	1223	1213
°C	582	558	532	516	581	563	549	526	610	534	582	576



**Fig. 2 - Distillation Profiles and Volatility Criteria of 1M, 1E and 1T Gasolines Having 2.0 wt% Oxygen Content Compared with 1 RS Blend.**

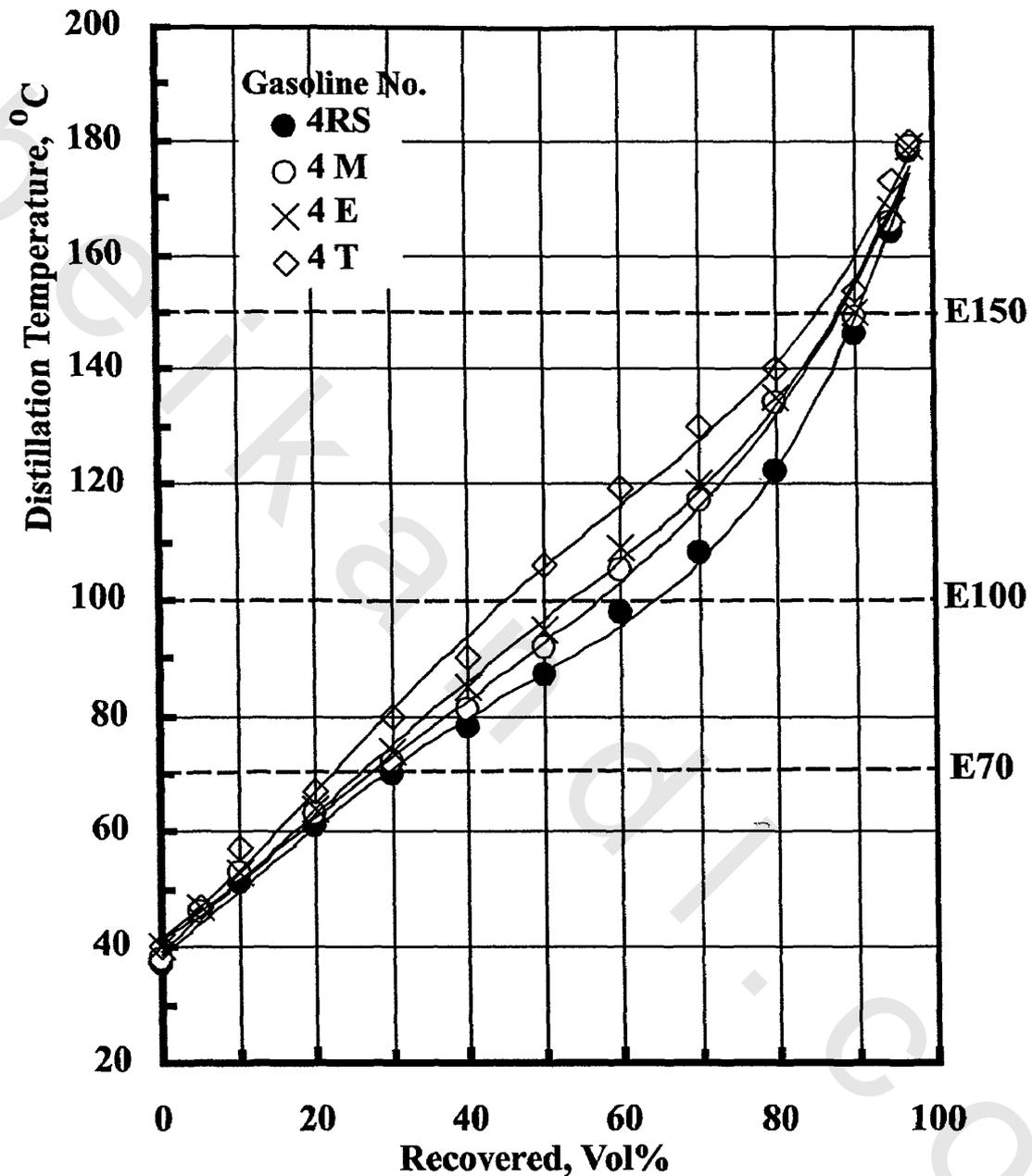


Fig. 3 - Distillation Profiles and Volatility Criteria of 4M, 4E and 4T Gasolines Blends Having 2.0 wt% Oxygen Content Compared with 4 RS Blend.

CHAPTER IV : RESULTS AND DISCUSSION

Table 7 (A)-Specifications and Octane Numbers of Gasoline Formulation Consisting of Two Refinery Streams and Different Oxygenates (2.7 wt% Oxygen Content).

Gasoline No.	5M	6M	7M	8M	5E	6E	7E	8E	5T	6T	7T	8T
Refinery Streams	Blend Composition, vol%				Blend Composition, vol%				Blend Composition, vol%			
Reformate	74.0	68.0	62.0	56.0	74.0	68.0	62.0	56.0	74.0	68.0	62.0	56.0
Isomate	11.0	17.0	23.0	29.0	8.8	14.8	20.8	26.8	8.8	14.8	20.8	26.8
Hydrocarbon Gasoline	85.0	85.0	85.0	85.0	82.8	82.8	82.8	82.8	82.8	82.8	82.8	82.8
Added Oxygenate	15.0	15.0	15.0	15.0	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2
Total Blend, vol%	100	100	100	100	100	100	100	100	100	100	100	100
Oxygenate Type	MTBE	MTBE	MTBE	MTBE	ETBE	ETBE	ETBE	ETBE	TAME	TAME	TAME	TAME
Oxygen Content, wt%	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
<b>Blend Specifications:-</b>												
Sp. Gravity, 60/60 °F	0.7501	0.7418	0.7323	0.7174	0.7484	0.7400	0.7316	0.7232	0.7518	0.7434	0.7350	0.7266
Aromatics, vol. %	41.0	38.0	34.0	32.0	41.0	37.0	34.0	31.0	41.0	36.0	33.0	32.0
RVP, psi	5.32	5.84	6.36	6.78	4.55	5.07	5.59	6.01	4.03	4.55	5.07	5.49
, Kg/cm <sup>2</sup>	0.37	0.41	0.45	0.47	0.32	0.35	0.39	0.42	0.28	0.32	0.35	0.38
Sulphur, ppm	93	91	88	85	90	90	86	82	91	90	85	83
Benzene, wt%	2.00	1.90	1.74	1.57	2.00	1.90	1.74	1.57	2.00	1.90	1.74	1.57
Oxidation Stability, mint	>480	—	—	>480	>480	—	—	>480	>480	—	—	>480
Corrosion, Copper Strip Test, 3hrs at 50°C	1	1	1	1	1	1	1	1	1	1	1	1
RON	95.5	95.1	95.0	94.7	95.1	95.0	94.2	93.7	94.8	94.2	94.1	94.1
MON	88.2	87.7	88.1	87.2	88.1	88.1	86.6	86.1	87.8	87.1	87.1	87.1
(R+M)/2	91.9	91.4	91.5	91.0	91.6	91.6	90.4	89.9	91.3	90.6	90.6	90.6

**Table 7 (B)- ASTM Distillation – Volatility Criteria and Driveability Indices of Gasoline Formulations Consisting of Two Refinery Streams and Different Oxygenates (2.7 wt% Oxygen Content).**

Gasoline No.	5M	6M	7M	8M	5E	6E	7E	8E	5T	6T	7T	8T
ASTM Distillation	Temperature, °C				Temperature, °C				Temperature, °C			
IBP,	38	38	38	38	38	39	40	38	38	40	40	40
5 %	51	50	50	48	53	53	51	49	53	52	50	49
10 %	58	56	55	53	60	59	57	55	61	60	58	57
20 %	71	68	66	65	73	71	68	66	73	71	68	70
30 %	82	78	75	74	86	84	80	77	90	87	84	82
40 %	97	95	91	87	99	97	94	91	107	102	98	94
50 %	109	106	102	99	113	109	105	102	120	116	112	108
60 %	120	116	111	107	123	119	116	112	130	125	124	122
70 %	130	127	123	120	133	130	127	124	138	136	135	134
80 %	139	137	135	134	142	139	135	138	145	144	144	142
90 %	156	155	153	150	157	156	155	153	159	157	157	157
95 %	170	171	170	168	171	170	170	170	176	176	175	174
FBP,	178	179	178	179	179	178	178	179	179	179	179	180
Recovered, vol %	98.5	98.5	98.0	98.0	98.2	98.3	98.0	98.0	98.0	98.0	98.0	98.0
Residue, vol %	0.5	0.5	0.8	0.7	0.5	0.7	0.6	0.5	0.5	0.5	0.5	0.5
Loss, vol %	1.0	1.0	1.2	1.3	1.3	1.0	1.4	1.5	1.5	1.5	1.5	1.5
E 70 , vol %	20	20	23	25	18	19	21	22	17	20	20	20
E10 , vol %	42	43	46	52	40	42	45	48	35	40	43	44
E150 , vol %	87	87	89	91	86	88	89	89	85	85	86	86
Driveability Index (DI) °F	1234	1211	1182	1153	1260	1234	1207	1182	1305	1278	1254	1226
°C	588	575	558	543	602	588	573	559	627	612	599	583

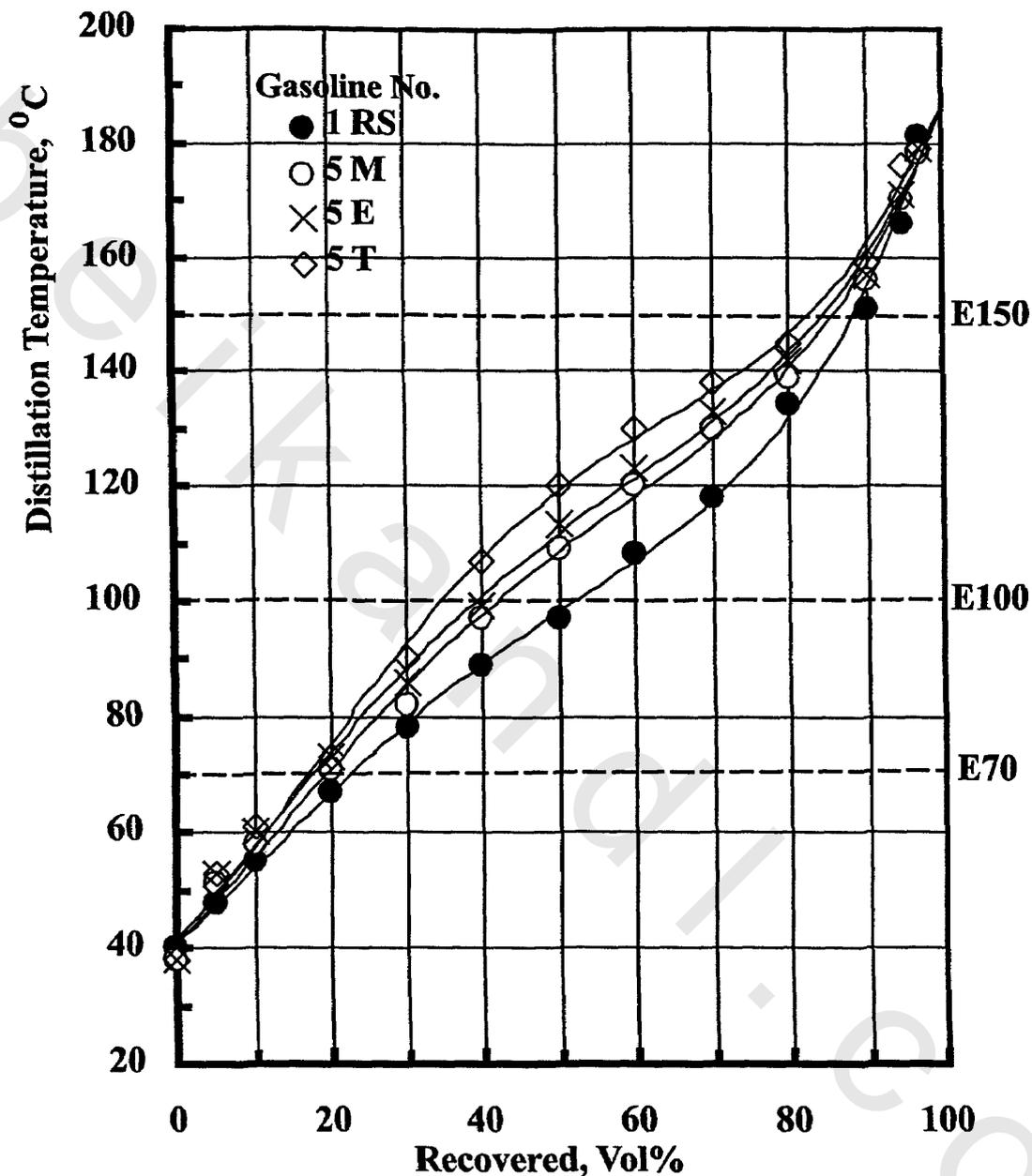
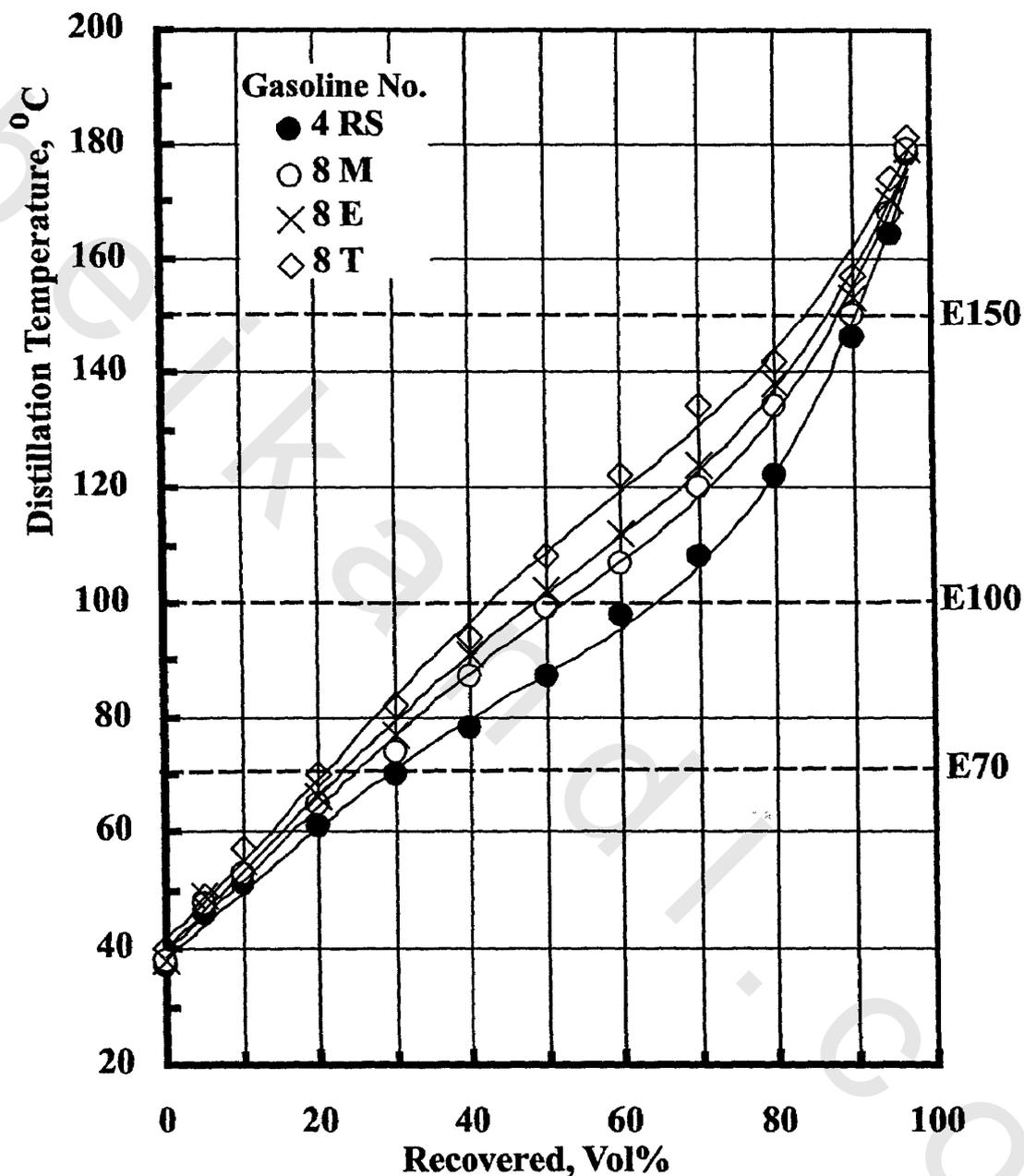


Fig. 4 - Distillation Profiles and Volatility Criteria of 5M, 5E and 5T Gasoline Blends Having 2.7 wt% Oxygen Content Compared with 1 RS Blend.



**Fig. 5- Distillation Profiles and Volatility Criteria of 8M, 8E and 8T Gasoline Blends Having 2.7 wt% Oxygen Content Compared with 4 RS Blend.**

CHAPTER IV : RESULTS AND DISCUSSION

Table 8 (A)- Reid Vapour Pressures and Octane Numbers of MTBE- and ETBE- Blended Gasoline Formulations.

Gasoline No.	9M	10M	11M	12M	13M	14M	9E	10E	11E	12E	13E	14E
	Blend Composition, vol%			Blend Composition, vol%			Blend Composition, vol%			Blend Composition, vol%		
Reformat	63.0	57.0	51.0	59.0	53.0	47.0	61.2	55.2	49.2	56.8	50.8	44.8
Isomerate	26.0	32.0	38.0	26.0	32.0	38.0	26.0	32.0	38.0	26.0	32.0	38.0
Hydrocarbon Gasoline	89.0	89.0	89.0	85.0	85.0	85.0	87.2	87.2	87.2	82.8	82.8	82.8
Added Oxygenate	11.0	11.0	11.0	15.0	15.0	15.0	12.8	12.8	12.8	17.2	17.2	17.2
Total Blend, vol.%	100	100	100	100	100	100	100	100	100	100	100	100
Oxygenate Type	MTBE	MTBE	MTBE	MTBE	MTBE	MTBE	ETBE	ETBE	ETBE	ETBE	ETBE	ETBE
Oxygen Content, wt%	2.0	2.0	2.0	2.7	2.7	2.7	2.0	2.0	2.0	2.7	2.7	2.7
<b>Blend Specifications:-</b>												
Sp. Gravity, 60/60 °F	0.7349	0.7265	0.7181	0.7281	0.7197	0.7113	0.7319	0.7235	0.7151	0.7243	0.7159	0.7069
Aromatics, vol. %	35.0	32.0	28.0	33.0	29.0	25.0	34.0	31.0	27.0	32.0	28.0	23.0
RVP, psi	6.52	7.00	7.48	6.68	7.16	7.64	6.08	6.56	7.04	6.08	6.56	7.04
, Kg/cm <sup>2</sup>	0.46	0.49	0.52	0.48	0.50	0.53	0.43	0.46	0.50	0.43	0.46	0.50
Sulphur, ppm	90	87	85	88	86	82	89	87	84	86	83	80
Benzene, wt%	1.77	1.60	1.43	1.66	1.49	1.32	1.72	1.55	1.38	1.59	1.43	1.26
Oxidation Stability, mint	—	>480	—	—	>480	—	—	>480	—	—	>480	—
Corrosion, Copper Strip Test, 3hrs at 50°C	1	1	1	1	1	1	1	1	1	1	1	1
RON	92.8	92.7	92.6	93.9	93.9	93.8	92.3	92.2	91.9	93.2	93.1	93.0
MON	85.1	85.5	84.3	86.7	86.7	86.6	85.0	85.0	84.8	85.9	85.8	85.5
(R+M)/2	88.9	89.1	88.4	90.3	90.3	90.2	88.7	88.6	88.4	89.6	89.4	89.2

**Table 8 (B)- Volatility Criteria and Drivability Indices of MTBE and ETBE – Blended Gasoline Formulations.**

Gasoline No. ASTM Distillation	9M	10M	11M	12M	13M	14M	9E	10E	11E	12E	13E	14E
	Temperature, °C			Temperature, °C			Temperature, °C			Temperature, °C		
<b>IBP,</b>	38	38	38	38	38	37	39	40	37	38	38	38
<b>10 %</b>	57	53	50	53	51	49	54	52	50	56	54	52
<b>50 %</b>	95	92	89	99	95	92	101	97	93	104	100	97
<b>90 %</b>	151	148	145	150	149	146	152	150	146	153	151	145
<b>FBP,</b>	178	178	179	178	179	178	179	178	177	179	178	178
<b>E 70</b>	25	28	30	25	28	30	23	25	26	20	22	25
<b>E100</b>	52	54	56	52	53	55	49	53	54	45	58	60
<b>E150</b>	90	90	90	89	90	90	88	89	90	88	89	90
<b>Driveability Index (DI) °F</b>	1103	1073	1012	1121	1090	1067	1132	1102	1095	1162	1132	1098
<b>°C</b>	515	498	464	525	507	495	531	514	511	548	531	512

### **3- Oxygenated Three – Refinery Stream Blends :-**

Oxygenated blends consisting of three refinery streams and one of the employed oxygenates, were formulated in three main groups . Each group consists of four oxygenated blends . Gasoline No. 15M to 18M, 15E to 18E, and 9T to 12T, are shown in Tables 9, 10 and 11, respectively. Gasoline No. 5RS is an all-hydrocarbon blend used as a non-oxygenated reference fuel for the sake of comparison . Reformate, isomerate and light naphtha are the employed refinery components used in these formulations. Formulation starts with the all-hydrocarbon blend which is prepared volumetrically from 56% reformate, 34% isomerate and 10% light naphtha . Oxygenated fuel blend which is designated 15M consists of 94.0 volume percent of this hydrocarbon blend and 4.0 volume percent of MTBE . Similarly, formulations No. 16M, 17M and 18M consist of 92, 89 and 85 volume percent of the same hydrocarbon blend and 8.0, 11.0 and 15.0 volume percent MTBE . On parallel lines, gasoline blends No. 15E to 18E and 9T to 12T are formulated using ETBE and TAME, respectively . Blend compositions, specifications and octane numbers of the twelve test oxy-fuels along with the all-hydrocarbon reference sample, are listed in Tables 9(A), 10(A) and 11(A); whereas, ASTM-distillation, volatility criteria and driveability indices are given in Tables 9(B), 10(B) and 11(B), respectively .

#### **3. 1- Volatility and Oxygen Content :-**

Three properties are used to measure gasoline volatility of the formulated test-fuels: vapour pressure, distillation profile and driveability. Oxygenated gasolines No. 15M, 16M, 17M and 18M blended with 4.0, 8.0, 11.0 and 15.0 volume percent MTBE have RVP values 7.2, 7.1, 7.0 and 6.8 psi, respectively . Reduction, in RVP values from 0.2 to 0.5 psi, is achieved by the addition of these

concentrations of MTBE as shown in Table 9(A) . Results shown in Tables 10(A) and 11(A), reveal that ETBE gives more or less the same RVP reduction, whereas, TAME seems to be an attractive blend component in reducing RVP of TAME-blended fuels . RVP, in oxygenated and reformulated gasolines, is required to be lower to reduce evaporative emissions . Pollutants from evaporative emissions can react in sunlight to form ground-level ozone, which is the primary ingredient of smog and should not be confused with stratospheric ozone that is a natural layer some 6 to 20 miles above the earth and provides protection from harmful radiation (Lidderdale and Bohn, 2000, U.S.-EPA, 1999) . Reduction in RVP also reduces the amount of vapourisation during cold start and warm-up (U.S.-EPA, 1994) .

Figures 6 and 7 illustrate the distillation profiles showing volatility criteria (T points or E points) . These figures depict two distillation profiles, the lower for the more volatile all-hydrocarbon gasoline No. 5RS and the upper for the less volatile oxygenated gasoline blends which contain 4.0 and 11.0 vol.% MTBE . Similar distillation profiles were constructed for oxygenated blends containing different concentrations of MTBE, ETBE or TAME . Figures 8 and 9 illustrate the distillation profiles of gasolines No. 15E, 16E, 17E and 18E, whereas, Figures 10 and 11 illustrate the distillation profiles of gasolines No. 9T, 10T, 11T and 12T . In each of these figures, the distillation profile of the reference hydrocarbon blend, 5RS, is constructed with the oxy-fuel blends to facilitate comparison .

**Table 9 (A) – Specifications and Octane Numbers of Gasoline Formulations Consisting of Three Refinery Streams and MTBE**

Gasoline No.	5RS	15M	16M	17M	18M
	Blend Composition, vol%				
Refinery Streams					
Reformate	56.0	53.8	51.5	49.8	47.6
Isomerate	34.0	32.6	31.3	30.3	28.9
Light Naphtha	10.0	9.6	9.2	8.9	8.5
<b>Total</b>	<b>100</b>	<b>96.0</b>	<b>92.0</b>	<b>89.0</b>	<b>85.0</b>
Oxygenate Added, vol.%	0.0	4.0	8.0	11.0	15.0
Oxygenate Type	–	MTBE	MTBE	MTBE	MTBE

<b>Blend Specifications:-</b>					
Sp. Gravity, 60/60 °F	0.7316	0.7247	0.7226	0.7192	0.7149
Oxygen Content, wt.%	0.0	0.73	1.45	2.00	2.70
Aromatics, vol.%	33.0	31.0	30.0	29.0	28.0
Reid Vapour Pressure, psi	7.32	7.16	7.08	6.95	6.82
, kg/cm <sup>2</sup>	0.51	0.50	0.50	0.49	0.48
Sulphur, ppm	102	92	90	87	85
Benzene, wt.%	2.00	1.90	1.86	1.80	1.72
Existent Gum, mg/100 ml	2	2	2	2	2
Oxidation Stability, mint	>480	–	>480	–	>480
Corrosion, Copper Strip Test, 3hrs at 50°C	1	1	1	1	1

RON	86.9	87.1	88.1	88.9	90.1
MON	80.5	80.5	80.1	83.2	83.2
(R+M)/2	83.7	83.8	84.1	86.0	86.7

**Table 9 (B) – ASTM Distillation - Volatility Criteria and Drivability Indices of Gasoline Formulations Consisting of Three Refinery Streams and MTBE.**

Gasoline No.	5RS	15M	16M	17M	18M
	Temperature, °C				
ASTM Distillation					
IBP,	38	37	38	40	40
5 %	46	48	51	52	54
10 %	51	53	56	58	60
20 %	57	60	62	67	69
30 %	65	68	72	75	77
40 %	71	74	80	82	85
50 %	82	85	91	92	95
60 %	92	96	101	104	106
70 %	105	109	111	115	117
80 %	118	121	123	128	130
90 %	147	150	151	156	155
95 %	169	170	172	173	173
FBP,	182	182	183	182	180

Recovered, vol.%	98.5	98.5	98.0	97.8	97.8
Residue, vol.%	0.5	0.5	0.8	1.0	1.0
Loss, vol.%	1.0	1.0	1.2	1.2	1.2

E 70, vol.%	40	33	30	23	21
E100, vol.%	66	63	60	60	57
E150, vol.%	90	90	90	89	89

Driveability Index (DI) °F	1024	1060	1108	1133	1160
°C	471	491	518	532	547

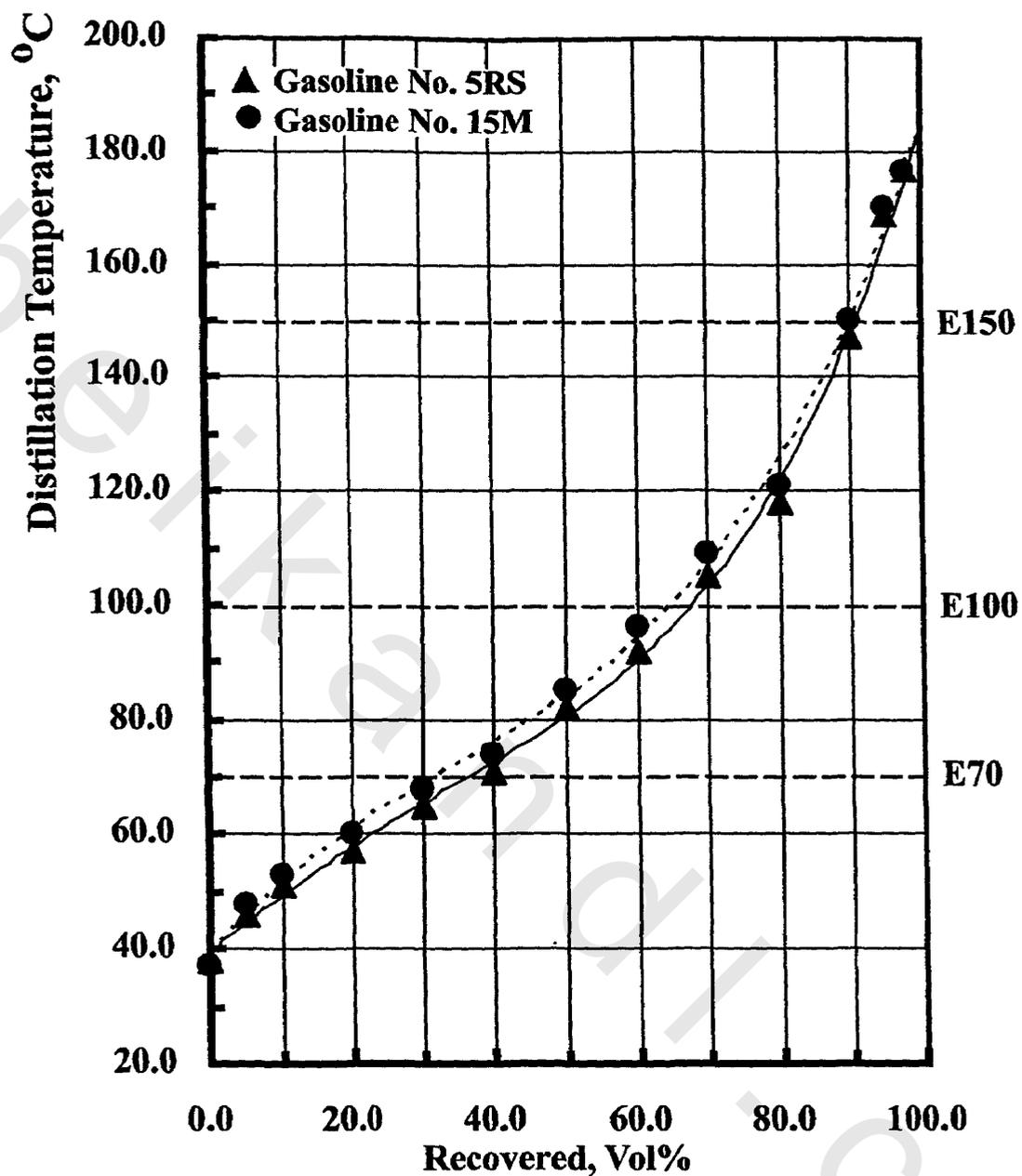


Fig. 6 - Distillation Profiles and Volatility Criteria of MTBE-Blended Gasolines 15M and a Reference Hydrocarbon Gasoline Blend (5RS).

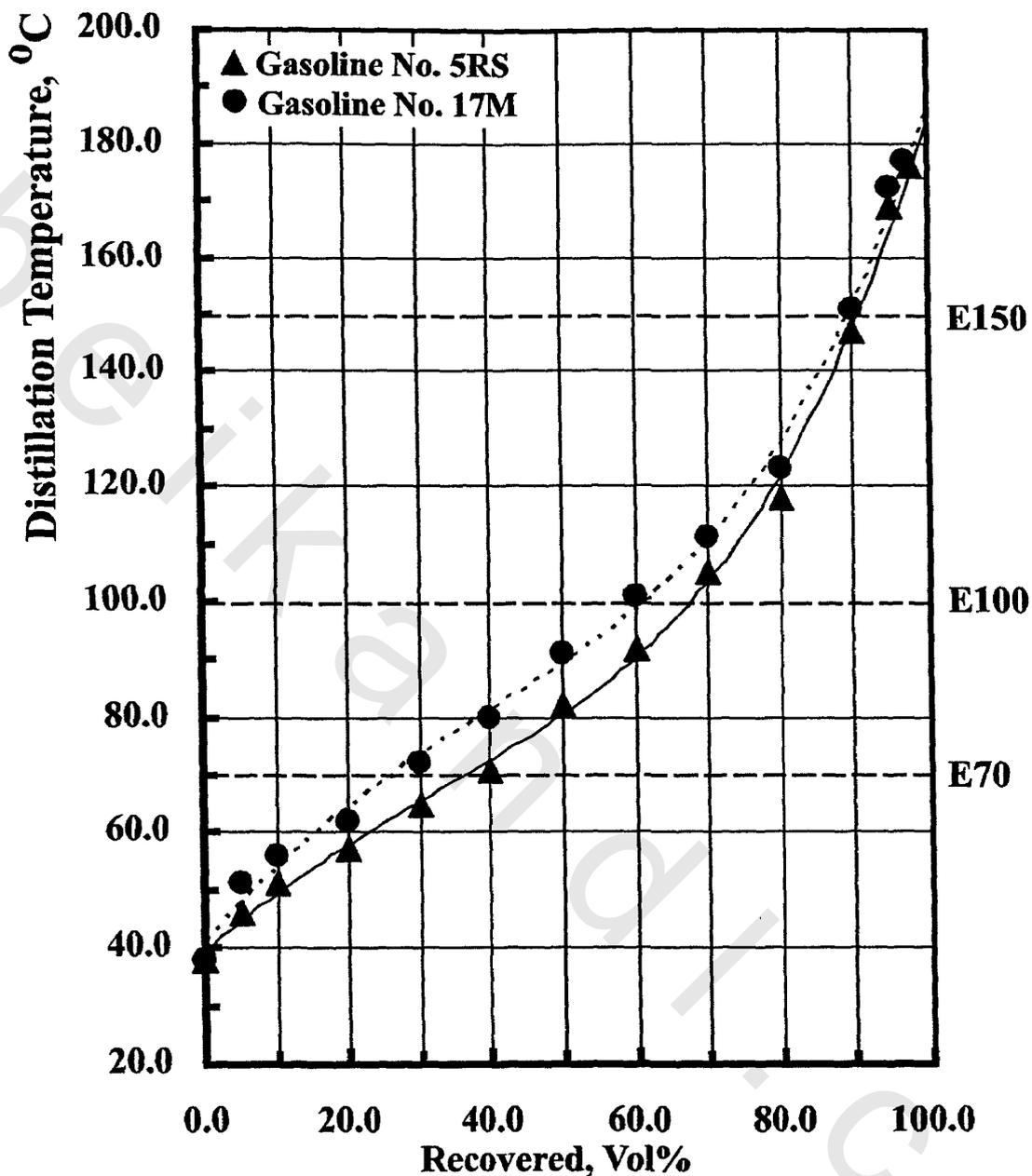


Fig. 7 - Distillation Profiles and Volatility Criteria of MTBE-Blended Gasolines 16M and a Reference Hydrocarbon Gasoline Blend (5RS).

**Table 10 (A) – Specifications and Octane Numbers of Gasoline Formulations Consisting of Three Refinery Streams and ETBE.**

Gasoline No.	5RS	15E	16E	17E	18E
	Blend Composition, vol%				
Reformate	56	53.8	51.5	49.8	46.3
Isomerate	34	32.6	31.3	28.7	28.3
Light Naphtha	10	9.6	9.2	8.7	8.3
<b>Total</b>	<b>100</b>	<b>96.0</b>	<b>92.0</b>	<b>89.0</b>	<b>85.0</b>
Oxygenate Added, vol.%	0.0	4.0	8.0	12.8	17.2
Oxygenate Type	–	ETBE	ETBE	ETBE	ETBE

<b>Blend Specifications:-</b>					
Sp. Gravity, 60/60 °F	0.7316	0.7309	0.7235	0.7193	0.7188
Oxygen Content, wt. %	0.0	0.63	1.25	2.00	2.70
Aromatics, vol. %	33.0	31.0	30.0	29.0	27.0
Reid Vapour Pressure, psi	7.32	7.12	7.06	6.92	6.75
, kg/cm <sup>2</sup>	0.51	0.50	0.49	0.48	0.47
Sulphur, ppm	102	95	93	88	84
Benzene, wt. %	2.00	1.90	1.86	1.75	1.66
Existent Gum, mg/100 ml	2	2	2	2	2
Oxidation Stability, mint	>480	–	>480	–	>480
Corrosion, Cupper Strip Test, 3hrs at 50°C	1	1	1	1	1

RON	86.9	87.2	87.9	88.8	90.0
MON	80.5	82.2	82.4	82.7	83.3
(R+M)/2	83.7	84.7	85.2	85.7	86.7

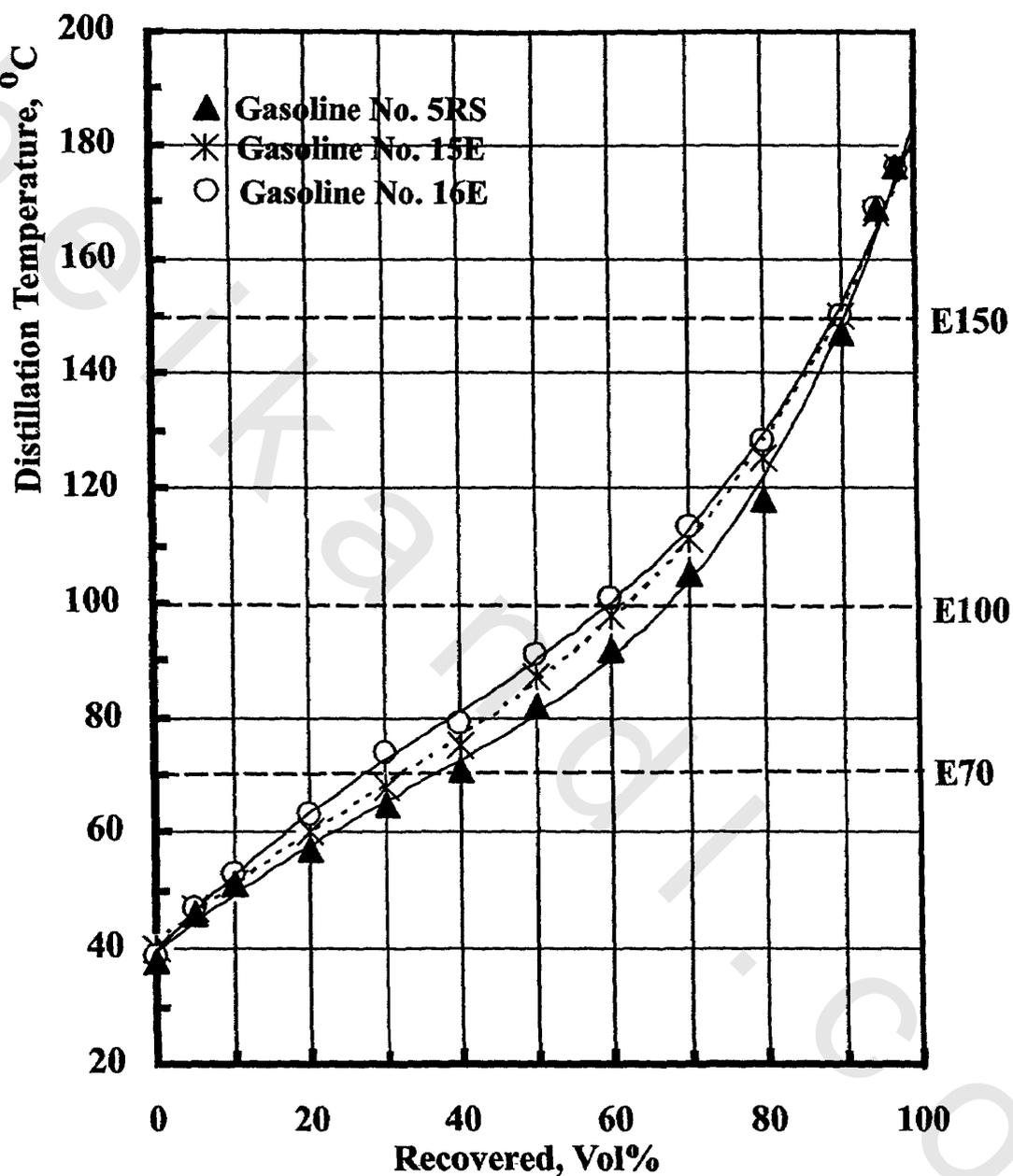
**Table 10 (B) – ASTM Distillation - Volatility Criteria and Drivability Indices of Gasoline Formulations Consisting of Three Refinery Streams and ETBE.**

Gasoline No.	5RS	15E	16E	17E	18E
	Temperature, °C				
<b>ASTM Distillation</b>					
<b>IBP,</b>	38	38	38	40	40
<b>5 %</b>	46	48	50	52	57
<b>10 %</b>	51	53	55	57	62
<b>20 %</b>	57	60	63	68	70
<b>30 %</b>	65	68	72	76	79
<b>40 %</b>	71	75	80	84	89
<b>50 %</b>	82	85	87	90	95
<b>60 %</b>	92	95	98	100	105
<b>70 %</b>	105	107	108	110	114
<b>80 %</b>	118	121	125	127	130
<b>90 %</b>	147	150	152	153	156
<b>95 %</b>	169	172	172	175	179
<b>FBP,</b>	182	179	180	180	181

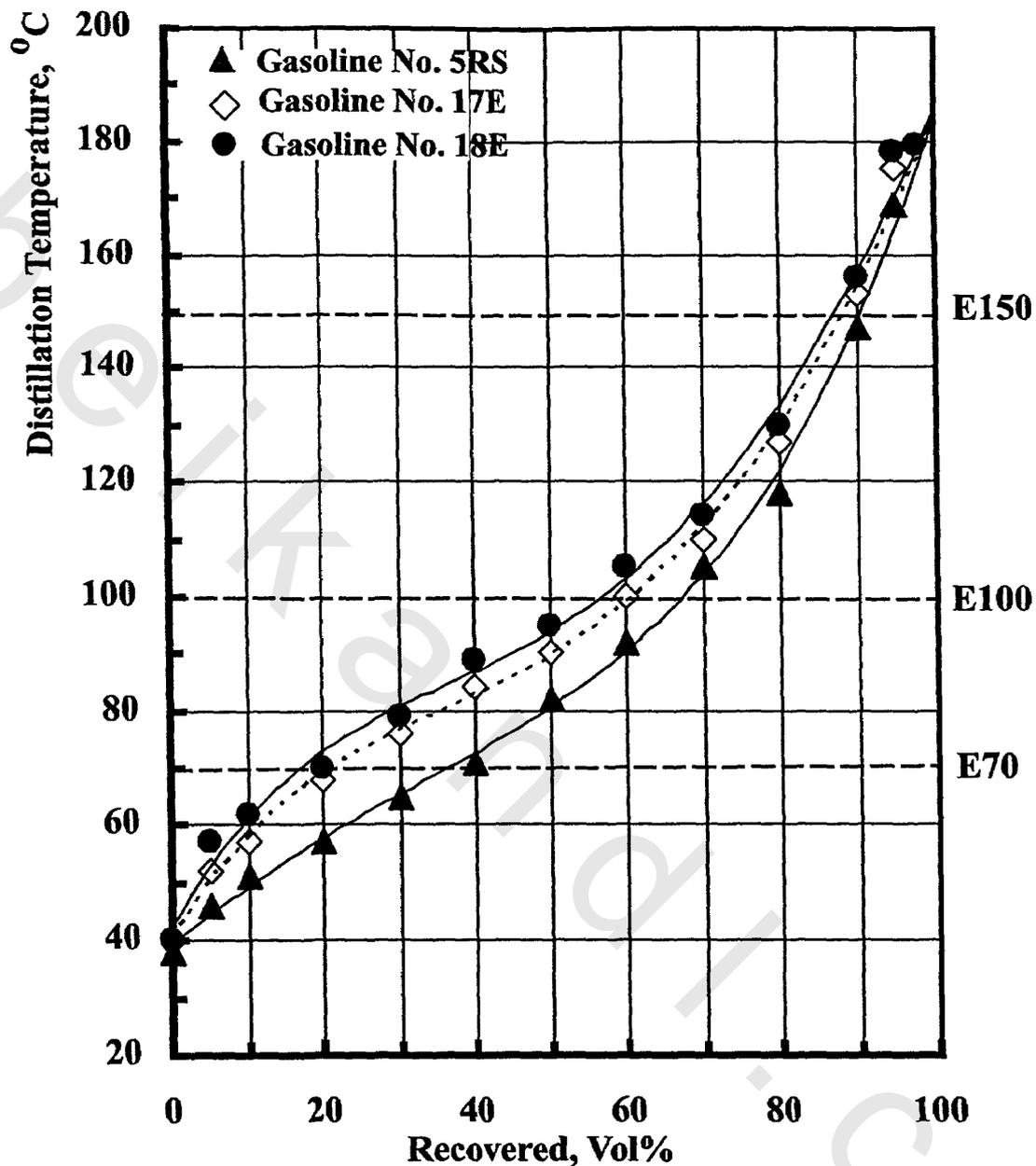
<b>Recovered, vol.%</b>	98.5	98.3	98.0	97.9	97.8
<b>Residue, vol.%</b>	0.5	0.7	0.8	1.0	1.0
<b>Loss, vol.%</b>	1.0	1.0	1.2	1.1	1.2

<b>E 70, vol.%</b>	40	33	28	23	20
<b>E100, vol.%</b>	66	65	62	60	55
<b>E150, vol.%</b>	90	90	89	89	88

<b>Driveability Index (DI) °F</b>	1024	1058	1084	1113	1164
<b>°C</b>	471	490	504	521	549



**Fig. 8 - Distillation Profiles and Volatility Criteria of ETBE - Blended Gasolines (15E & 16E) and a Reference Hydrocarbon Gasoline Blend (5RS).**



**Fig. 9 - Distillation Profiles and Volatility Criteria of ETBE-Blended Gasolines (17 E&18 E) and a Reference Hydrocarbon Gasoline Blend (5RS).**

**Table 11 (A) – Specifications and Octane Numbers of Gasoline Formulations Consisting of Three Refinery Streams and TAME.**

Gasoline No.	5RS	9T	10T	11T	12T
	Blend Composition, vol%				
Reformate	56	53.8	51.5	48.8	46.3
Isomerate	34	32.6	31.3	29.7	28.2
Light Naphtha	10	9.6	9.2	8.7	8.3
<b>Total</b>	<b>100</b>	<b>96.0</b>	<b>92.0</b>	<b>87.2</b>	<b>82.8</b>
Oxygenate Added, vol.%	0.0	4.0	8.0	12.8	17.2
Oxygenate Type	–	TAME	TAME	TAME	TAME

<b>Blend Specifications:-</b>					
Sp. Gravity, 60/60 °F	0.7316	0.7309	0.7242	0.7197	0.7156
Oxygen Content, wt.%	0.0	0.63	1.25	2.0	2.70
Aromatics, vol.%	33.0	31.0	30.0	29.0	27.0
Reid Vapour Pressure, psi	7.32	7.05	6.82	6.56	6.23
, kg/cm <sup>2</sup>	0.51	0.49	0.48	0.46	0.44
Sulphur, ppm	102	93	90	88	84
Benzene, wt.%	2.00	1.90	1.86	1.75	1.66
Existent Gum, mg/100 ml	2	2	2	2	2
Oxidation Stability, mint	>480	–	>480	–	>480
Corrosion, Cupper Strip Test, 3hrs at 50°C	1	1	1	1	1

RON	86.9	87.1	88.0	89.2	89.5
MON	80.5	82.6	80.5	83.3	83.4
(R+M)/2	83.7	84.9	84.3	86.3	86.4

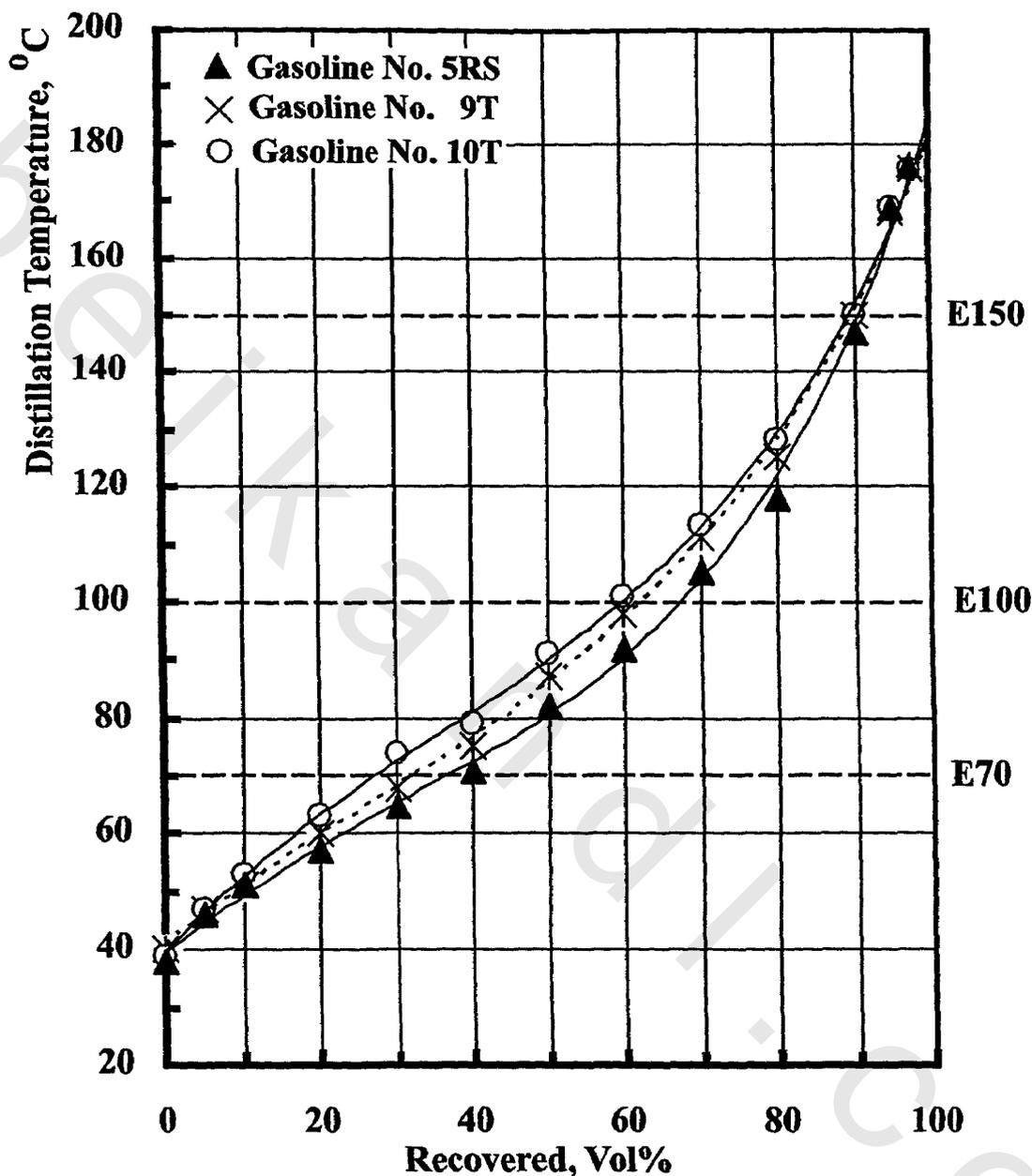
**Table 11 (B) – ASTM Distillation - Volatility Criteria and Drivability Indices of Gasoline Formulations Consisting of Three Refinery Streams and TAME.**

Gasoline No.	5RS	9T	10T	11T	12T
	Temperature, °C				
ASTM Distillation					
IBP,	38	40	39	37	38
5 %	46	47	47	48	48
10 %	51	51	53	55	59
20 %	57	60	63	67	72
30 %	65	68	74	77	83
40 %	71	75	79	85	90
50 %	82	87	91	95	98
60 %	92	98	101	105	112
70 %	105	111	113	117	125
80 %	118	125	128	131	136
90 %	147	150	150	153	162
95 %	169	168	169	172	176
FBP,	182	178	180	179	181

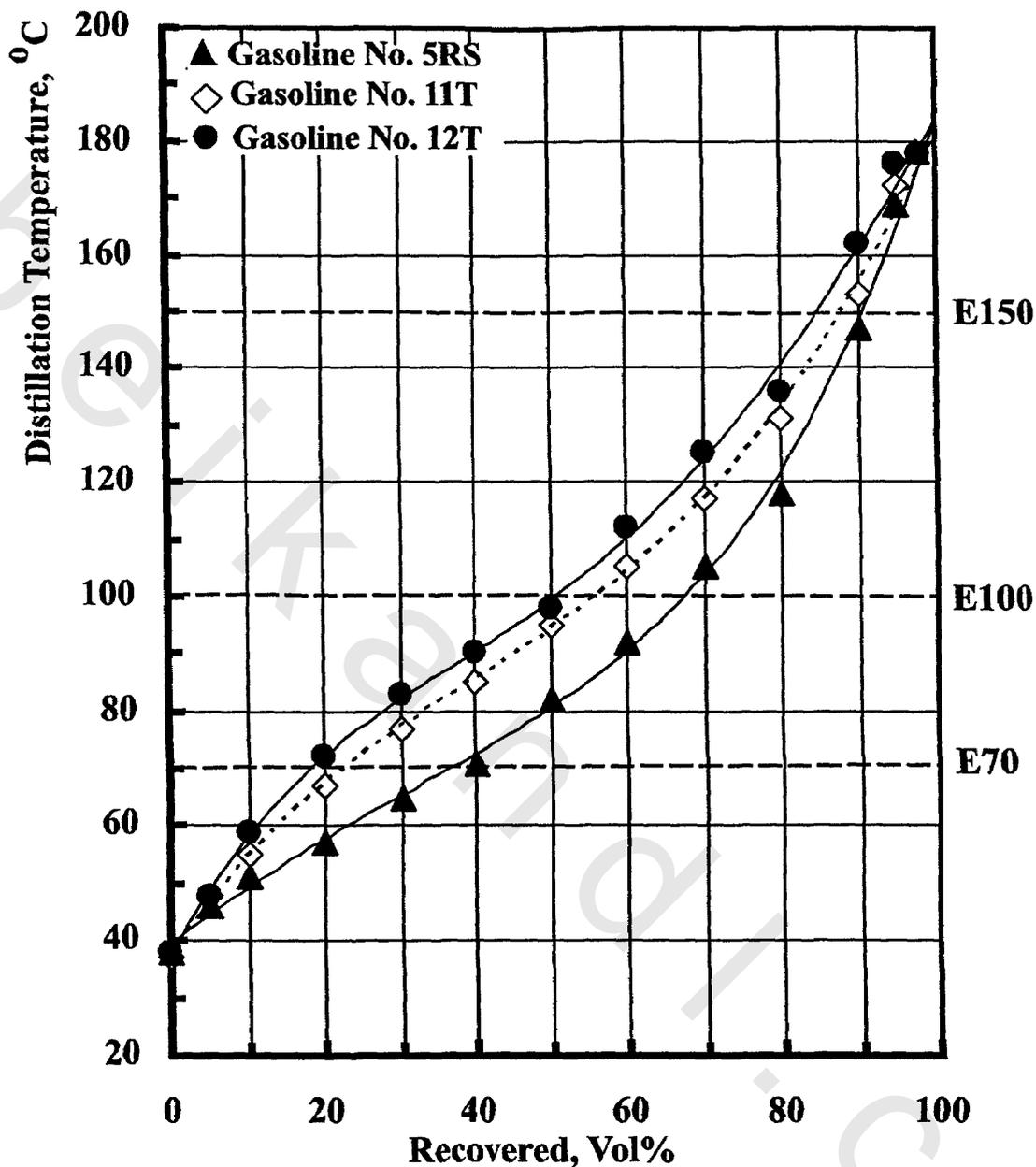
Recovered, vol. %	98.5	98.5	98.0	97.5	97.2
Residue, vol. %	0.5	0.5	1.0	1.0	1.0
Loss, vol. %	1.0	1.0	1.0	1.5	1.8

E 70, vol. %	40	33	29	23	18
E100, vol. %	66	63	60	55	48
E150, vol. %	90	90	90	88	86

Driveability Index (DI) °F	1024	1058	1095	1135	1185
°C	471	490	511	533	561



**Fig.10 - Distillation Profiles and Volatility Criteria of TAME-Blended Gasolines (9 T&10 T) and a Reference Hydrocarbon Gasoline Blend (5RS).**

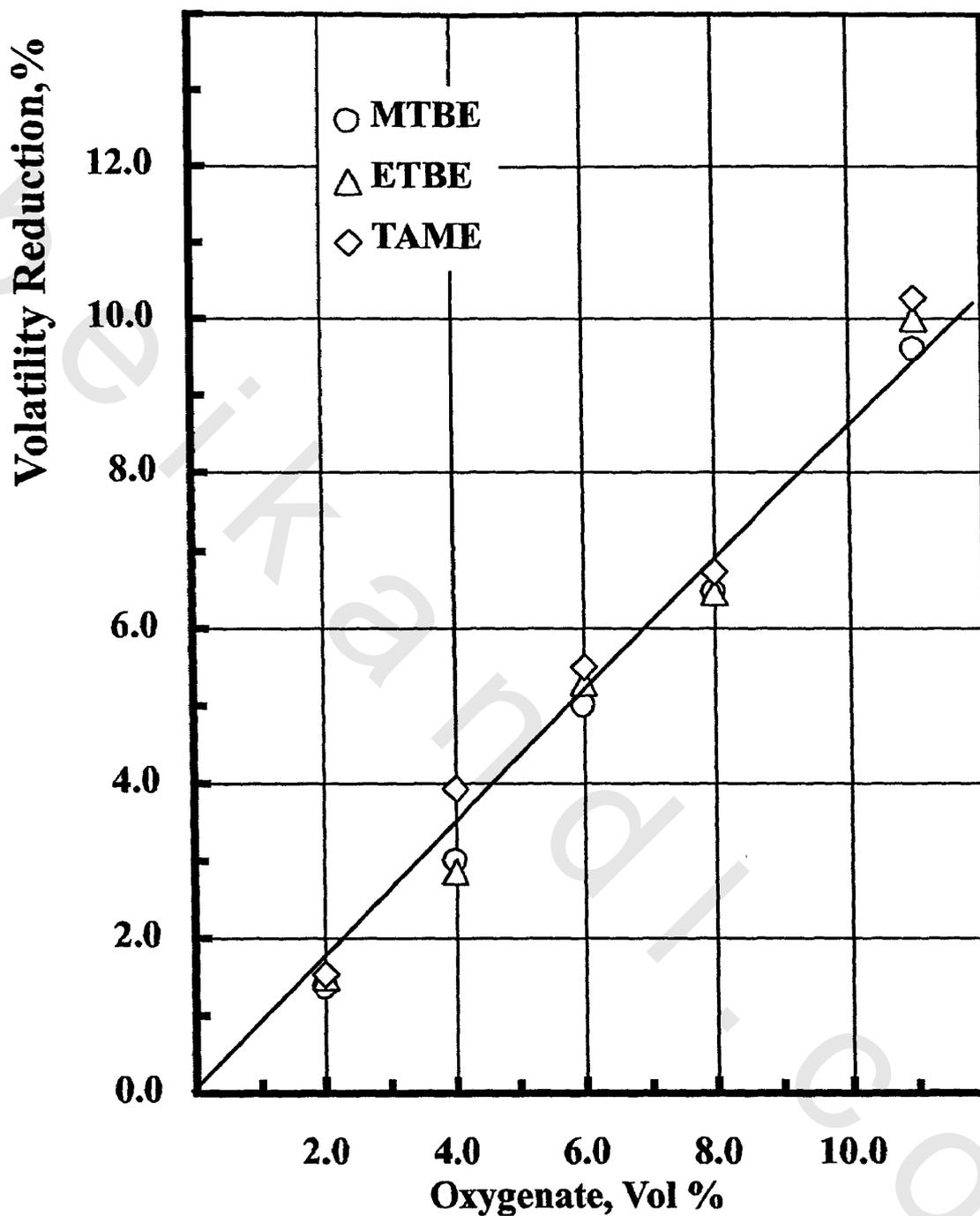


**Fig.11 - Distillation Profiles and Volatility Criteria of TAME-Blended Gasolines (11 T&12 T) and a Reference Hydrocarbon Gasoline Blend (5RS).**

Through computational approach, the area under the more volatile distillation curve i.e. the lower curve of the all-hydrocarbon gasoline, was calculated . Similarly, the area under each of the upper curves for the less volatile oxygenated gasolines, was calculated . The difference between these two areas represents the volatility reduction which resulted in certain level of blended oxygenate . Volatility reduction as a function of added oxygenate is illustrated in Figure 12 . The linear relation obtained shows that the employed ether-oxygenates have more or less the same efficiency in reducing the volatility of the investigated oxy-fuels . The developed equation, relating the percentage of the volatility reduction and the amount (vol.%) of added oxygenate can be written as :

$$\begin{aligned} \text{Volatility Reduction (\%)} \\ = 0.8983 (\text{vol.\% of oxygenate}) - 0.2262 \quad \dots (4) \end{aligned}$$

It is well known that volatility and the other distillation characteristics are frequently altered depending on the availability of gasoline components . This should not alter performance characteristics of the gasoline unless the alteration is severe (**Chevron, 2004, Downstream Alternatives, Inc., 1996**) . Volatility of the test oxy-fuel blends listed in Tables 9-11 (A&B), is only attributed to the amount and physical properties of the employed oxygenate . Thus for a given all-hydrocarbon gasoline formulation, the amount, in vol.%, of blended ether-oxygenate, required for a certain volatility reduction, could be easily deduced through the above-mentioned relation .In order to assure that gasoline has the proper volatility characteristics, refiners adjust gasoline volatility seasonally providing more volatile gasoline in winter and the less volatile in summer .



**Fig. 12 - Volatility Reduction as a Function of Added Oxygenates.**

### **3. 2- Other Fuel Specifications :-**

Gasolines are most commonly rated based on their anti-knock index (AKI), a measure of octane quality . The AKI is a measure of a fuel's ability to resist engine knock . The AKI is the average of the Research Octane Number (RON) and Motor Octane Number (MON) or  $(R+M)/2$  . Data in Tables 9(A)-11(A) show that the performance characteristics of MTBE are similar to ETBE .The maximum permitted levels of these ethers are 15.0 and 17.2 volume percent (2.7 weight percent oxygen) . At this level, any of these ethers contribute up to 3.0 octane numbers to the reference hydrocarbon blend . At the same oxygen level (2.7 weight percent), TAME can contribute up to 2.6 octane numbers only .

While octane and volatility are the most important standards relating to driveability, there are other fuel standards covered by ASTM guidelines . Tables 9(A)-11(A) list the various specifications of the test fuels . Sulphur contents of all oxy-fuel are below 100 ppm . Benzene does not exceed 2.0 weight percent . A copper corrosivity standard ensures that the test fuel will not create excessive corrosion in the vehicle fuel system . Stability standard are controls of a fuel's tendency to contribute to induction system deposits as well as determining the fuel's storage life . Specifications of the test oxy-fuels, satisfy the widest range of vehicles and operating circumstances possible .

### **3. 3- Driveability Index (DI) :-**

While each change of the distillation profile is important, the gasoline represented by the entire profile is what the engine must distribute, vapourise and burn .To predict cold start and warm-up driveability, DI has been developed using the temperatures, in degrees Fahrenheit, for the evaporated percentages of 10% (T10), 50% (T50) and 90% (T90)-(ASTM-D 86 Test Method) .

$$DI_{\text{°F}} = 1.5 (T10) + 3.0 (T50) + (T90) \dots\dots\dots (1)$$

The DI varies with gasoline grade and season; the normal range is 850 to 1300 . Lower values of DI generally result in better cold start and warm-up performance, but once good driveability is achieved, there is no benefit to further lowering the DI . (ASTM-D 4814 Test Method) . Excessively high T50 (low E100) can lead to poor starting and warm-up performance at moderate ambient temperatures .

The Coordinating Research Council (CRC, U.S.) has continued to improve the DI equation (1) and to make it universally applicable (**World Wide Fuel Charter, 2000**) . CRC has tested 29 test fuels: 9 all-hydrocarbon, 11 with 10 volume percent ethanol and 9 with 15 volume percent MTBE. Some important conclusions have been achieved from this CRC study that driveability problems increase for all fuel types as DI increases. At DI levels higher than 550-570 driveability concerns increase dramatically . An oxygen correction factor is required for higher driveability demerits for oxygenated gasoline as compared to all-hydrocarbon gasoline . Equation (2) has been developed (**World-Wide Fuel Charter, 2000**) temperatures are in degrees Celsius and the conversion formula (3) is to be used (ASTM-D 4814) .

$$DI_{\text{°F}} = 1.5 (T10) + 3.0 (T50) + (T90) + (11\text{xwt.\% Oxygen}) \dots\dots(2)$$

$$DI_{\text{°C}} = (DI_{\text{°F}} - 176) / 1.8 \dots\dots\dots (3)$$

Calculated DI values of the examined oxygenated gasolines are listed in Tables 6(B)-11(B) using equation (2) . DI value of all-hydrocarbon reference gasoline (RS) sample is calculated through equation (1) . DI data shown in these tables indicate that gasoline containing 1.0-2.7 weight percent oxygen (4.0-15.0 vol.% MTBE or 4.0-17.2 vol.% ETBE or TAME) have  $DI_{\text{°F}}$  values within those specified above, i.e. in the range 850-1300 ( $DI_{\text{°C}}$  does not exceed

550-570 range when oxygen content is considered) . Limited data on LEV/ULEV vehicles suggest that a similar oxygenate correction may be needed for ether oxygenates (**Pfalzgraf et al., 1996 & Otto et al., 1998**) . The magnitude of oxygen correction will be determined as more data are needed (**World-Wide Fuel Charter, 2000**) .

### **3. 4- Tailpipe Exhaust Emissions :-**

It is well Known that a key strategy to reducing exhaust emissions from gasoline fueled engine, is to modify the gasoline properties (**Piel & Thomas, 1990**). For example, less aromatics in gasoline's contribute to less tailpipe emissions because aromatics due to their high carbon content compared to other gasoline hydrocarbon-types posses unfavorable properties to good vapourisation and combustion (**Piel, 1989, Colucci, 1989; Deherty, 2001; HEI-Health Effect Institute, 2004**) Mid-range and tail-end volatilities of the test fuel, can also contribute to reduce HC emissions in the engine exhaust . (**Stump, 1990; Newkirk, 1997; Reuter et al, 1992; Furey, 1990**) . Also, studying the effects of oxygenates on tailpipe emissions without adjusting the oxygenate-gasoline blend back to its original octane level, will underestimate the benefits from high octane oxygenates that are blended into gasoline (**Piel & Thomas, 1990**) .

Twelve oxygenated test fuels along with one hydrocarbon reference gasoline blend, were tested for their tailpipe exhaust emissions using the same test vehicle . Volatility criteria E70, E100 and E150 were determined from distillation profiles . E70 for front-end volatility, E100 for mid-range volatility and E150 for tail-end volatility. In all formulations, E150 value is used to fix back-end volatility and accepted T90=E150 as a design basis (T90 is difficult to predict and E150 is more practical which is usually used by the

European Oil Companies). In this study emission analyses consider the effect of mid-range volatility (E100) over a narrow range of fuel aromatics level . Though this narrow aromatics level (33-28 vol.%) seems to have a significant impact on emissions, the scatter in the data also suggests that other gasoline properties have influence as well (**World-Wide Fuel Charter, 2000**) .

### **3.5- Net Effect of Oxygenates :**

The examined test fuels have various gasoline properties as shown from the data in Tables 9-11(A) and (B) . gasoline properties as aromatic content, Octane number, Reid vapour pressure, Volatility criteria, may influence gasoline related vehicle emissions .

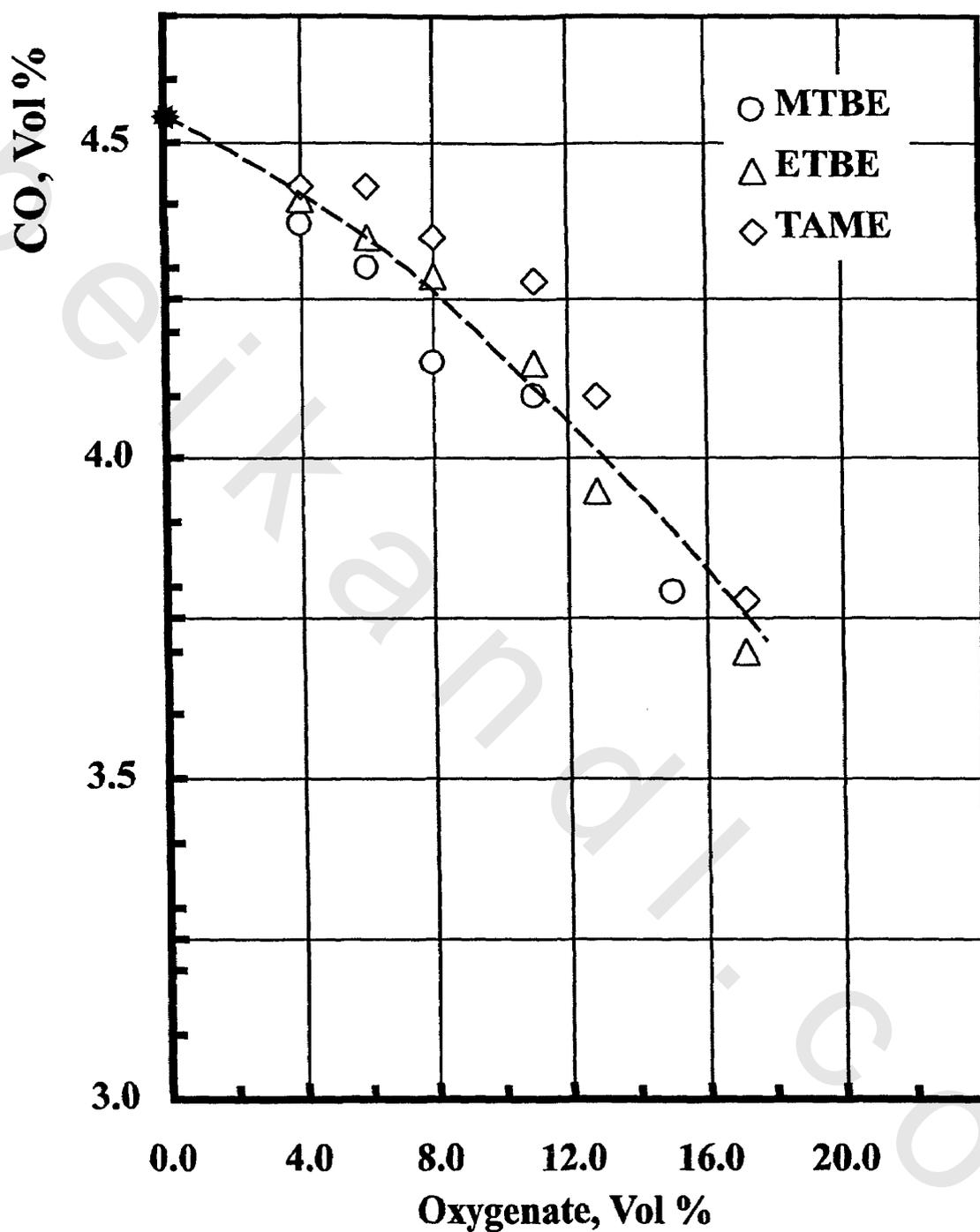
Blending of high octane oxygenates such as ethers are expected to have a much greater overall emission reduction benefit because blending of these oxygenates (4.0-17.2 vol.%) leads to alterations in blend composition. Subsequently, aromatic contents, volatility criteria (E70&E100) are decreased, whereas, octane numbers are increased . Reduction in aromatic levels and volatility will also contribute to lower CO and HC emissions (**Doherty, 2001**).

The net reduction in tailpipe CO and HC emissions from ether blending would be expected to reach maximum values at 2.7wt.% oxygen (Fig 13&14) : More reduction can be achieved by making more reformulation changes beyond that realized from just blending ethers .

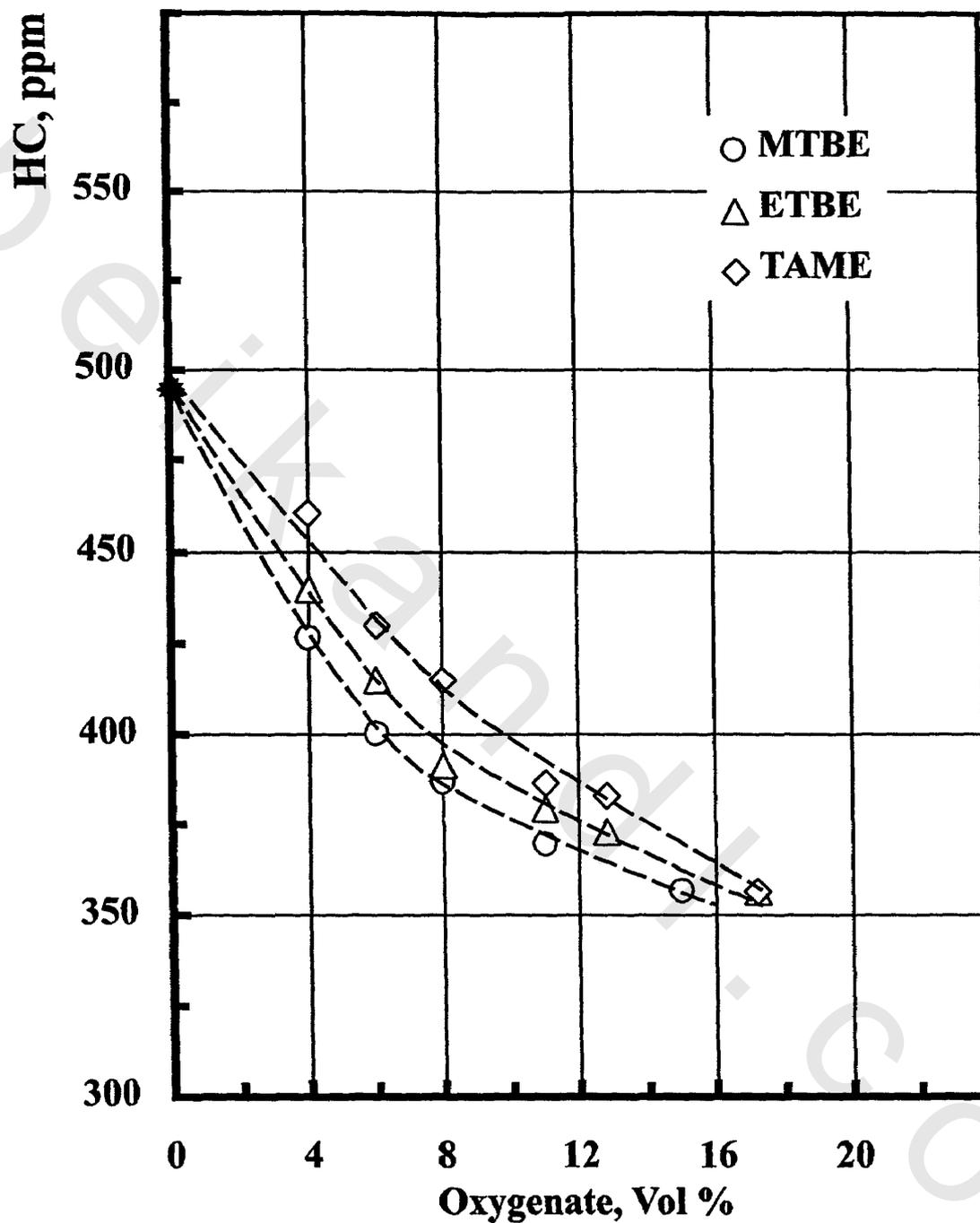
Oxygenates are mostly known for their ability to reduce CO emissions by enleaning the Fuel-to-Air mixture. Though enleanment generally has the most pronounced effect on CO emissions, the sensitivity to aromatic level indicates other fuel properties that have additional influence. At lower oxygen content,

it appears that enleanment effect plays a smaller role . At higher oxygen levels, i.e. 2.0 wt.% or higher, more lowering NO<sub>x</sub> emissions are observed in each employed ethers as shown in Fig.15 .

Since ether oxygenates are originally blended as octane enhancers or octane substitute for the higher flame temperature aromatics in gasoline blending (Piel & Thomas, 1990), the observed NO<sub>x</sub> emission reduction due to oxygenate blending at all concentrations is expected to be lower than a hydrocarbon fuel having equal octane number .



**Fig. 13 - CO Reduction with Blending of Different Oxygenates.**



**Fig. 14 - HC Emission Reduction with Blending of Different Oxygenates.**

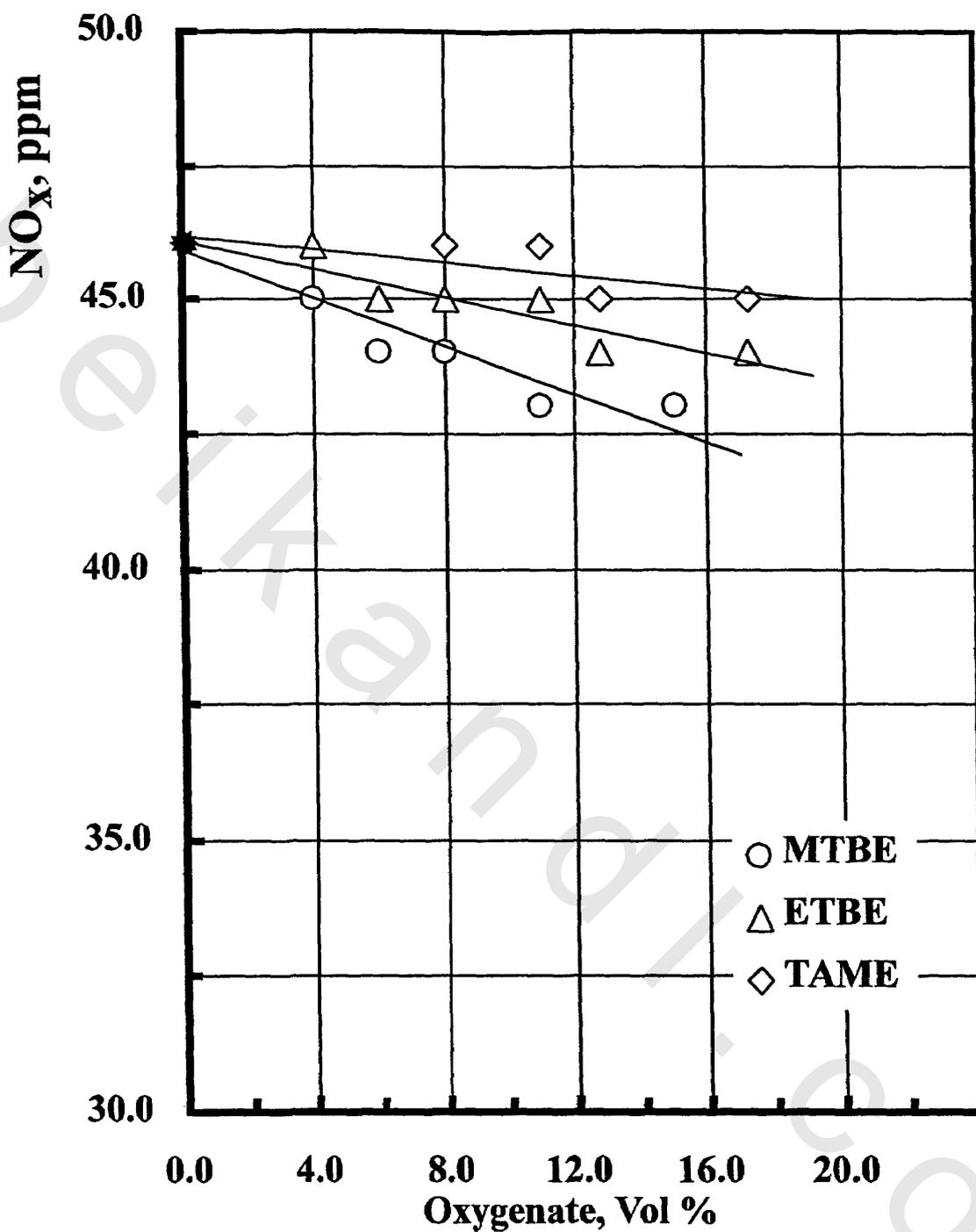


Fig. 15 - NO<sub>x</sub> Emission with Blending of Different Oxygenates

#### **4- Four – Refinery Stream Oxygenated Blends :**

Oxygenated gasoline blends, consisting of four refinery streams, were formulated in two main groups. The first group is MTBE-gasoline blends and the second is ETBE-gasoline blends . Refinery components employed in these formulations were : reformate, isomerate, light naphtha and a fraction of heavy naphtha having a boiling range 43-180 ° c . Formulation starts with the all-hydrocarbon reference gasoline samples 6RS and 7RS .

It can be seen from data in Table 12(A) that gasoline blends No. 19M and 19E are oxygenated with 11.0 vol.% MTBE and 12.8 vol.% ETBE, respectively, each has 2.0 wt.% oxygen content . Also, gasoline blends no. 20M and 20E are oxygenated with 15.0 vol.% MTBE and 17.2 vol.% ETBE, respectively, each has 2.7 wt.% oxygen content . Each of the formulated gasoline blends No. 19M, 20M, 19E and 20E along with the hydrocarbon reference 6RS, consists of 50 vol.% reformate, 20 vol.% isomerate, and 30 vol.% of naphthas plus oxygenate . Also, each of the formulated gasoline blends No. 21M, 22M, 21E and 22E along with the hydrocarbon reference 7RS, consists of 44 vol.% reformate, 33 vol.% isomerate, and 23 vol.% of naphthas and oxygenate .

Specifications, octane numbers and blend compositions of gasoline formulations, are shown in Table 12(A) . It is clear from data in this table that the introduction of a fraction of heavy naphtha does not severely alter the specifications of the formulated oxy-fuels . Subsequently, performance characteristics of these oxygenated fuels is expected to be slightly altered . For instance, the anti-knock index, AKI or R+M/2 values of oxygenated gasoline's No. 20M and 20E are 82.8 and 82.6, respectively . This means that the maximum permitted levels of MTBE or ETBE (15.0 and 17.2 vol.%) Contribute 2.0-1.8 octane number to the reference all-hydrocarbon blends 6RS . Similarly, the anti-knock index values

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of oxygenated gasoline blends No.22M and 22 E, which contain the same oxygen level, are 83.8 and 83.3, giving contributions of 2.1 and 1.6 octane number to the reference all -hydrocarbon blends 7RS respectively.

Volatility characteristics , E70 and E100 values which represent front-end, and mid-range volatilities of oxygenated gasoline blends presented in Table 12(B) illustrated in Figures 16-19, show a distinct difference between the formulated groups . Tail-end volatility, E150 values , adhere to the target property shown in Table 4 . In the first group, which includes gasoline's No. 19M , 20M, 19E and 20E, the determined Volatility criterion E70 values are 20, 19, 19, and 17 volume percent distilled, respectively . Gasolines No. 21M, 22M, 21E and 22E of the second group, gave E70 values 23, 20, 23, and 20 volume percent distilled, respectively. On light of these findings, one can expect that formulations of oxygenated gasoline in the second group will not cause cold-start and warm-up driveability problems which is not anticipated in the second group .

It is clear from data in Table 12(B) that higher values of E70 and E100 were obtained in case of formulations containing 2.0 wt.% oxygen . Lower values of these volatility criteria were achieved through further oxygenate addition, i.e. oxygenated blends became less volatile . At this point, one can reach a conclusion that when the hydrocarbon portion of gasoline is kept unaltered, increased oxygen content will lead to noticeable volatility reduction in the produced oxy-fuels . Thus, oxygenate should be carefully blended with the hydrocarbon gasoline components to achieve the desirable seasonal volatility which permits minimum evaporative emissions .

Driveability index (DI) derived from T10, T50 and T90 for all-hydrocarbon gasoline blends were calculated using Equation (1), whereas, DI values of oxygenated gasoline blends were calculated

from T10, T50, T90 and oxygen content through Equation (2). DI values of oxygenated gasoline of the two formulated groups are given in Table 12(B) . World-Wide Fuel Charter in 2000 proposed driveability index range between 550-570 . At DI levels higher than these values, driveability problems increase dramatically . It can be seen from data in Table 12( B) that the first group of these formulations , which include gasolines No. 19M , 20M ,19E and 20E, have DI levels higher than those specified above . On the contrary, the second group, which includes 21M, 22M,21E and 22E, have DI levels within the specified range . It has been reported ( **World- Wide Fuel Charter in 2000** ) that control of DI can also be used to assure good cold-start and warm-up performance . This means that the second group of oxy-fuel formulations, is not anticipated to cause driveability problems .

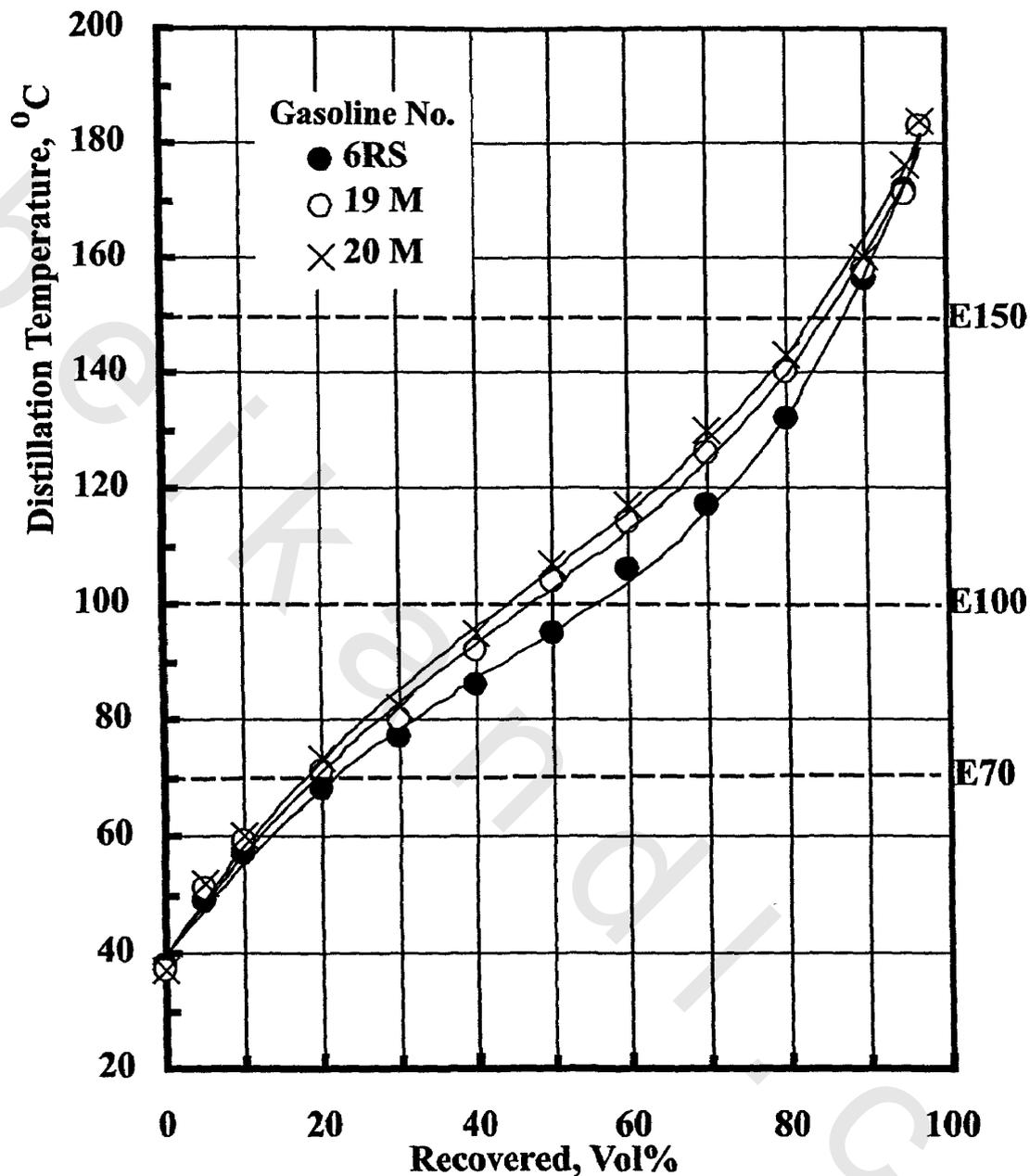
CHAPTER IV : RESULTS AND DISCUSSION

Table 12 (A)-Specifications and Octane Numbers of Gasoline Formulations Consisting of Four Refinery Streams and Two Different Oxygenates.

Gasoline No.	6RS	19M	20M	19E	20E	7RS	21M	22M	21E	22E
<b>Refinery Streams</b>	<b>Blend Composition, vol%</b>					<b>Blend Composition, vol%</b>				
Reformate, vol %	50.0	50.0	50.0	50.0	50.0	44.0	44.0	44.0	44.0	44.0
Isomerase, vol %	20.0	20.0	20.0	20.0	20.0	33.0	33.0	33.0	33.0	33.0
Light Naphtha, vol%	15.0	9.5	7.5	8.6	6.4	11.5	6.0	4.0	5.1	2.9
Heavy Naphtha, vol%	15.0	9.5	7.5	8.6	6.4	11.5	6.0	4.0	5.1	2.9
Hydrocarbon Gasoline, vol%	100	89.0	85.0	87.2	82.8	100	89.0	85.0	87.2	82.8
Oxygenate Added, wt%	0.0	11.0	15.0	12.8	17.2	0.0	11.0	15.0	12.8	17.2
Oxygenate Type	—	MTBE	MTBE	ETBE	ETBE	—	MTBE	MTBE	ETBE	ETBE
<b>Blend Specifications:-</b>										
Sp. Gravity, 60/60 °F	0.7321	0.7315	0.73951	0.7354	0.7285	0.7261	0.7292	0.7298	0.7302	0.7312
Oxygen content, wt%	0.0	2.0	2.7	2.0	2.7	0.0	2.0	2.7	2.0	2.7
Aromatics, vol%	32.0	31.0	30.0	31.0	30.0	28.0	27.0	26.0	27.0	26.0
RVP, psi	6.55	5.73	5.43	5.59	5.26	6.96	6.13	5.83	5.99	5.67
, kg/cm <sup>2</sup>	0.46	0.40	0.38	0.39	0.37	0.49	0.43	0.41	0.42	0.40
Benzene, wt%	2.3	2.2	2.0	2.1	2.0	1.8	1.6	1.4	1.5	1.3
RON	83.3	86.1	86.4	85.9	86.2	84.3	86.7	87.3	87.2	87.5
MON	78.2	79.3	79.2	78.8	79.0	79.1	79.6	80.3	80.0	79.1
(R+M)/2	80.8	82.8	82.8	82.3	82.6	81.7	83.1	83.8	83.6	83.3

**Table 12 (B)- ASTM Distillation – Volatility Criteria of Gasoline Formulations Consisting of Four Refinery Streams and Two Different Oxygenates.**

Gasoline No.	6RS	19M	20M	19E	20E	7RS	21M	22M	21E	22E
	Temperature, °C					Temperature, °C				
<b>IBP,</b>	38	37	37	38	38	37	38	37	37	37
<b>5 %</b>	49	51	52	52	53	49	48	50	49	51
<b>10 %</b>	57	59	60	60	61	54	55	56	56	57
<b>20 %</b>	68	71	73	72	76	65	66	70	67	71
<b>30 %</b>	77	80	82	81	83	73	75	79	76	80
<b>40 %</b>	86	92	95	93	96	82	85	89	86	90
<b>50 %</b>	95	104	107	104	108	91	94	98	95	99
<b>60 %</b>	106	114	117	115	119	102	104	108	105	109
<b>70 %</b>	117	126	130	127	132	112	115	121	116	122
<b>80 %</b>	132	140	143	142	145	128	133	134	134	135
<b>90 %</b>	156	158	160	160	162	151	154	157	155	158
<b>95 %</b>	172	171	176	172	178	168	170	174	171	175
<b>FBP,</b>	183	183	184	183	182	184	184	184	183	183
<b>Recovered, vol %</b>	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0
<b>Residue, vol %</b>	0.8	0.8	0.7	0.7	0.8	0.8	0.8	0.7	0.7	0.6
<b>Loss, vol %</b>	1.2	1.2	1.3	1.3	1.2	1.2	1.2	1.3	1.3	1.4
<b>E 70</b>	23	20	19	19	17	26	23	20	23	20
<b>E100</b>	53	47	43	47	43	59	55	53	54	50
<b>E150</b>	88	87	87	87	85	90	89	88	88	87
<b>Driveability Index (DI) °F</b>	1123	1204	1234	1210	1245	1085	1131	1169	1141	1179
<b>°C</b>	526	571	588	574	594	505	531	552	536	557



**Fig.16 - Distillation Profiles and Volatility Criteria of 19 M and 20M Gasolines Having 2.0 and 2.7 wt% Oxygen Content Compared with 6RS Blend.**

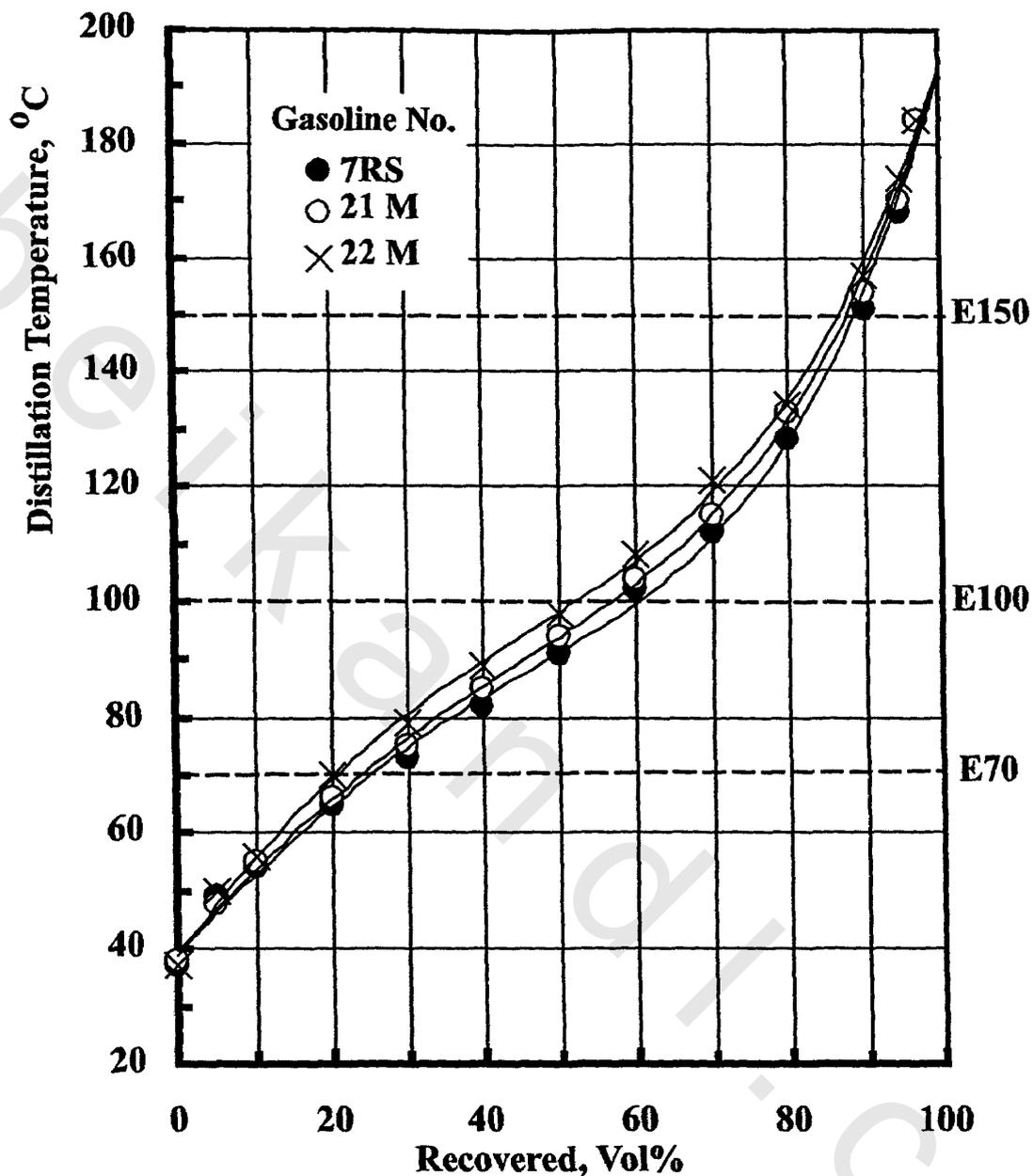


Fig. 17- Distillation Profiles and Volatility Criteria of 21 M and 22M Gasolines Having 2.0 and 2.7 wt% Oxygen Content Compared with 7RS Blend.

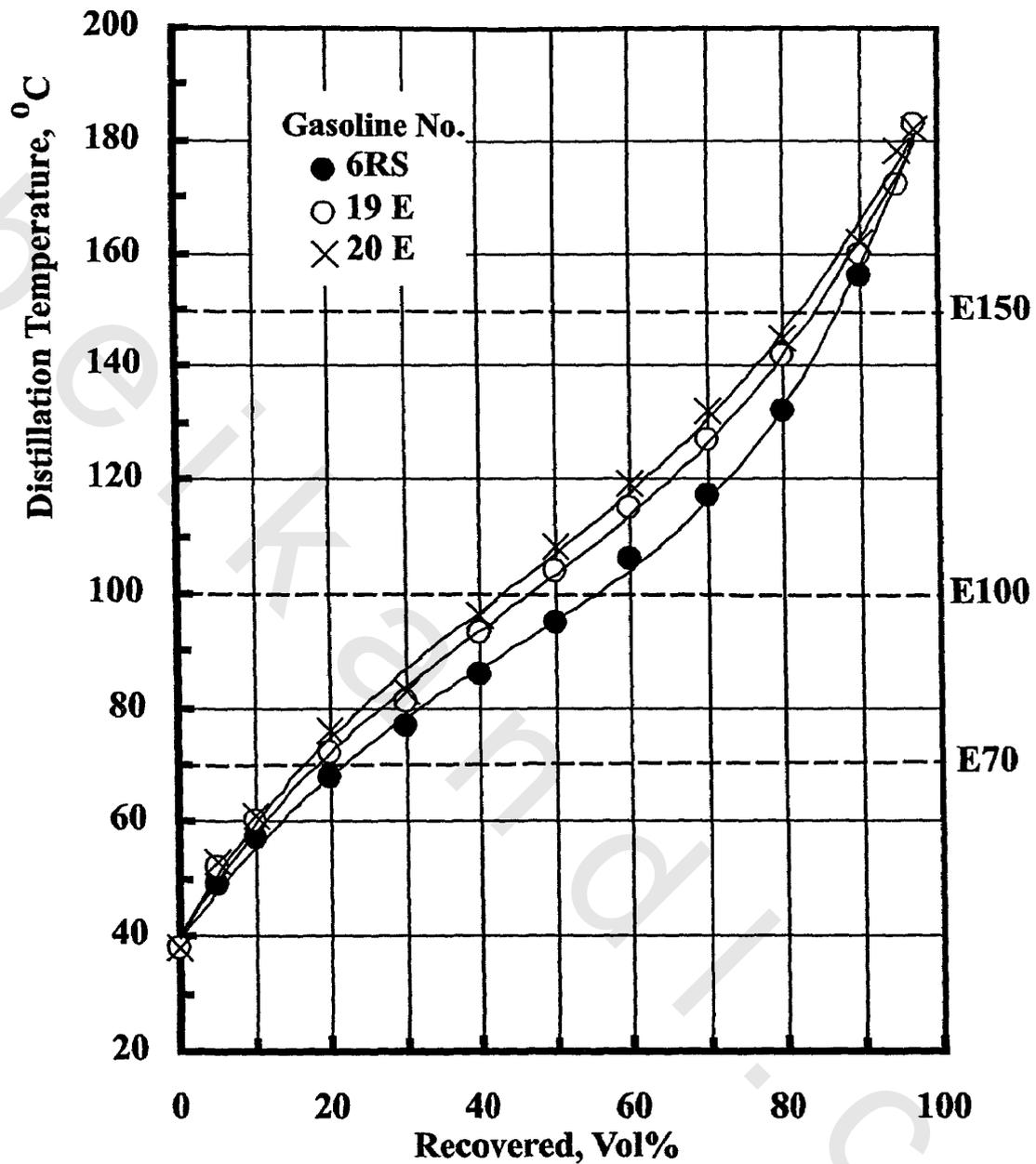
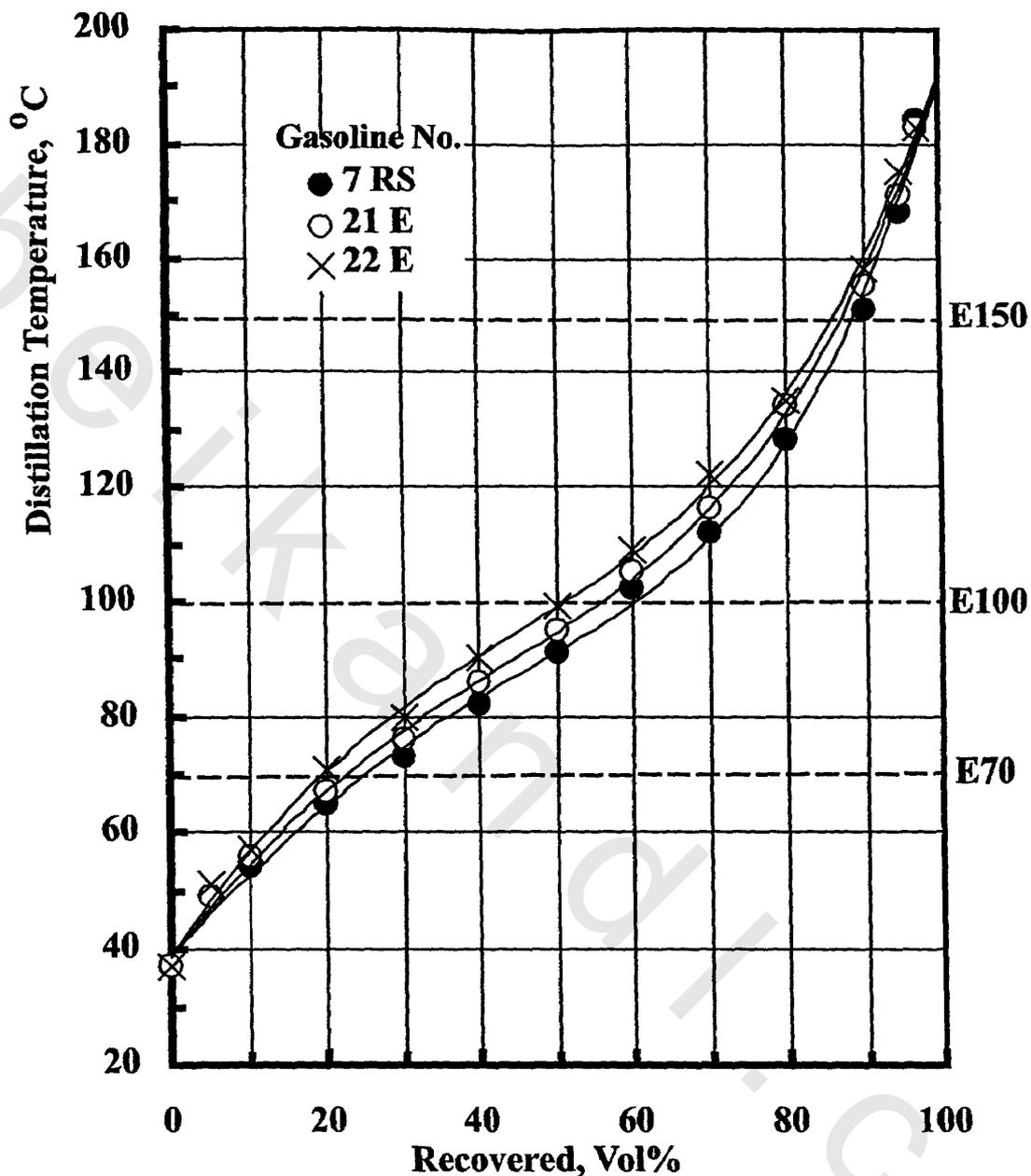


Fig. 18- Distillation Profiles and Volatility Criteria of 19 E and 20E Gasolines Having 2.0 and 2.7 wt% Oxygen Content Compared with 6RS Blend.



**Fig.19 - Distillation Profiles and Volatility Criteria of 21 E and 22E Gasolines Having 2.0 and 2.7 wt% Oxygen Content Compared with 7RS Blend.**

### **5- Driveability Index and Tailpipe Exhaust Emissions :-**

The effect of driveability index on hydrocarbon (HC) and carbon monoxide (CO) exhaust emission, was studied using the same test vehicle following the same vehicle / engine preparations and emission test precautions as previously mentioned in the experimental section of this study .

Six test-fuels, ten liters each, were selected from the oxygenated blends shown in Table 12 . Test fuel blends were kept refrigerated (below 5 °c) in well-stoppered labeled containers . The selected test fuels have a wide range of driveability index (DI) but very narrow ranges of E70(17-20 vol.%), AKI (82-84), and aromatics (26-32 vol.%) . Through this selection, the influence of front-end volatility, anti-knock index and aromatics on tailpipe emissions , is almost equal . It is well known that excessively high T50 or very low E100 can lead to poor starting and warm-up performances at moderate ambient temperatures (**World-Wide Fuel Charter, 2000**). The ratios of T10/T50 and E70/E100 are used to show that the selected test-fuels have almost the same volatility features as shown in Table 13 . The obtained analytical data presented in this table show that driveability index is directly related to HC and CO emissions. HC emissions increase significantly at DI levels higher than 570 .

**Table 13- Driveability Index (DI) and Tailpipe Exhaust Emissions.**

Gasoline No.	T10/T50	E70/E100	DI*	Tailpipe Emissions	
				HC PPM	CO vol. %
22M	0.57	0.40	531	350	3.5
22E	0.57	0.40	536	355	3.5
19M	0.57	0.43	571	360	3.7
19E	0.57	0.40	574	360	3.7
20M	0.56	0.44	588	375	3.8
20E	0.57	0.40	594	380	4.1

\* DI in degrees Celsius