

Antiknock Properties and Volatility Criteria of Some Gasoline-Butanol Blends

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Abstract
Antinock properties and volatility criteria were studied for all-hydrocarbon gasoline before and after blending with 8 and 12 volume percent n-and iso-butanol. Composition and specifications of the hydrocarbon- base gasoline and the formulated gasoline- oxygenate blends, were determined through gas chromatographic analysis and the standard test methods. The effects of n-and iso-butanol addition on driveability performance and volatility criteria, were studied.
Keywords: oxygenated gasoline, gasoline-butanol blend volatility criteria, antiknock properties.

INTRODUCTION

Oxygenates that are added to unleaded hydrocarbon gasoline function in two ways. Firstly, they have high blending octane, and so can replace the high octane aromatics in fuel. Oxygenates also cause significant reduction in carbon monoxide (CO) emission. It has been reported that 2.0 wt% oxygen can reduce CO by 16 % and HC by 10 %[1-4]. Oxygen in the fuel canot contribute energy, consequently the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in combustion efficiency that oxygenate provide on some engines usually do not completely compensate for the oxygen. Although both alkyl lead and oxygenates are effective at suppressing knock, the chemical modes through which they act are entirely different[5,6].

After phasing out MTBE in some areas due to the issue of ground water contamination[6,9], ethanol was widely considered to be the primary replacement option for MTBE due to its low toxicity compared to many other gasoline constituent. Moreover, ethanol biodegrades readily and does not present taste and odour issue when blended at low concentration[10-13]. Ethanol is approximate 3.5 wt% oxygen so10vol% blend would contain approximately 3.5 wt% oxygen. Blends exceeding 10 vol.% ethanol are not permitted because ethanol costs much more than gasoline[14,15].

Butanol can be used as a fuel in internal combustion engine. It is in more several ways more similar to gasoline then ethanol. It has been reported that butanol can reduce HC and CO showing some superior properties as an alternative fuel additive when compared to ethanol[16]. These include higher energy content; butanol gives about 110,000 Btu per gallon vs 84,000 Btu per gallon of ethanol. Gasoline gives about 115,000 Btu per gallon. Also butanol is six times less evaporative than ethanol, and 13.5 times less evaporative than gasoline[17,18]. Butanol can be shipped through existing fuel pipelines where ethanol must be transported via rail barge or truck[19].

In the present study, gasoline-n-butanol and gasoline-iso-butanol blends were studied and volatility criteria were evaluated using standard test methods.

EXPRIMENTAL

MATERIALS AND METHODS

1-Refinery Streams

Three petroleum distillates, namely reformate, isomerate and light naphtha, were kindly supplied by Cairo Petroleum Company- Mostorod Refinery, Cairo, Egypt. Tables 1 and 2list the main specifications and GC analysis for these distillates as received from the producer.

2- Gasoline Formulation

Hydrocarbon- base fuel (HBF) was formulated volumetrically from neat refinery streams: reformate (56%), isomerate (34%) and light naphtha (10%). HBF was blended with 8 and 12 volume % of iso-butanol and n-butanol. The obtained blends were designated HBF-8 nB and HBF-8 iB for gasoline blends having 8 vol.% and iso-butanol. Similarly, HBF-12 nB and HBF 12 iB for gasoline blends having 12 vol.% butanol.

The formulated HBF and the four fuel blends, were kept refrigerated in well- stoppered labeled containers. An ice-box was used to keep these blends refrigerated when sent for emission analysis and octane number tests, to avoid any change in blend composition. Also, precautions need to be taken to prevent contamination with water absorbed from humid air in cold winter months.

3- Fuel Property Measurements

3-1 Density - DE40 digital density meter – ASTM – DI 298.
3-2 Distillation profile - ASTM – D86.
3-3 Sulphur content – Wavelength Dispersive XRF – ASTM – D6334.
3-4 Oxidation stability-Induction period Method-ASTM-D 525.
3-5 Vapour pressure (Reid Method) – ASTM – D323.
3-6 Vapour pressure (Dry Method) – ASTM – D5191 (for fuel- alcohol blends).
3-7 Copper strip corrosion test (3hrs, 50°c), ASTM – D130.
3-8 Vapour- Liquid Ratio of 20 ($T_{V/L=20}$) ASTM – D5188.
3-9 Vapour Lock Index (VLI = 10 VP + 7E70).
3-10 Driveability Index (DI)- ASTM- D4814-98a.
3-11 Research and Motor Octane Number (RON & MON) were determined using Octane Analyzer O.A 228 Core Lab., Serial No. 12837, USA.
3-12 Exhaust Tailpipe Emission Analyzer – Sun MGA 1200, Faculty of Engineering – Mataria – Helwan University Cairo, Egypt.

4- Test Vehicle

The test vehicle was a Sahin Car Type 1.45, Model 2001, manufactured by El-Nasr Automotive Manufacturing Co., Wadi Hoff, Helwan, Cairo, Egypt.

The technical data of the test vehicle are given in Table 3.

The test vehicle was prepared in strict accordance as reported requirements[20-22].

5- Gas Chromatographic Analysis

For the determination of aromatics in hydrocarbon-base gasoline and gasoline-butanol blends using. Agilent 6890 plus instrument with FID. Column DB-1 60 m, 0.32 mm I.D. Carrier gas N_2, flow rate 2 ml/min. Temperature programming 50-250°c.

RESULT AND DISCUSSION

The hydrocarbon base Fuel (HBF), is formulated from the locally available refinery streams reformate, isomerate and light naphtha. Specifications, antiknock index and ASTM distillation of this base gasolines are given in Table (1).

Table (2) shows GC analyses of refivery streams used for gasoline formulation. Experiments were performed on Sahine car Type 1.45. Test vehicle and engine specification are listed in Table (3). Hydrocarbon base gasoline HBF is blended with 8 and 12 volume % of iso-butanol and n-butanol. Composition and Specification of the hydrocarbon base fuel (HBF) and four HBF + n and iso butanol blends were listed in Table (4). This table shows the effects of alcohol addition on fuel specifications and GC analysis of blends, also it shows octane humber contributions by n, and iso butanol addition.

Hydrocarbon-base stock has PON value of 87.0, addition of 8.0 vol.% of n-butanol or iso-butanol contributed 2.5 and 4.0 octane numbers, while the addition of 12.0 vol. % of n-or iso-butanol, contributed 3.5 and 4.6 octane number, respectively.

The addition of n and iso butanol to hydrocarbon gasolines significantly impacts the shape of the distillation curve. Table (5) shows ASTM distillation -volatility criteria of HBF and four HBF + butanol blends.

Front end volatility, E70 is adjusted to provide : easy cold and hot starting freedom from vapour lock, low evaporative emissions. Mid range volatility, E100 is adjusted to provide; rapid warm up, smooth running, protection against carburetor icing and hot stalling, good power and acceleration. E150 is adjusted to provide; minimal fuel distillation of crankcase oil, freedom from engine deposits and good fuel economy 23.

Figures 1-4 illustrate the difference in distillation curves as a result of blending 8 and 12 volume percent of n and iso butanol to hydrocarbon base gasoline (HBF). These figures show that the addition of 8 and 12 n and iso butanol volume percent leads to increase in distillation temperature over the initial boiling points and for middle portion of the distillation curve and for final boiling points (FBP).

Data in Table (5) demonstrate that mixing n or iso butanol to gasoline increase the temperature for vapour liquid ratio of 20 ($T_{V/L=20}$) .

Also on calcutation vapour-Lock Index (VLI) addition of butanol decreased VLI values.

VLI = 10 (VP) + 7(E70)

From figures 1-4, E70, E100 and E150, values were located it can be deduced.

Also driveability index for HBF and blended gasolines were caleulated

Table (5). The calculated DI (°F) and DI (°C) values for blends are within the specified normal range between 1079 -1163(°F) and 502-543 (°C).

Table (6) shows results of tailpipe exhaust emissions of HBF, alcohol blended gasoline and for gasoline 80. Percent reduction calculated for Co_2, CO and HC emission in comparison with that of gasoline 80.

A noticed % reduction can be deduced on adding n and iso butanol to gasoline base fuel.

Conclusion

1- Addition of n or iso butanol to hydrocarbon gasolines impacts the shape of distillation curve.
2- Front end volatility (E70), mid range volatility (E100) and tail end volatility (E150) are adjusted to provide engine performance.
3- Addition of n or iso butanol increases both research and motor octane number (RON and MON).
4- Tailpipe exhaust emission shows a significant % reduction on adding n or iso butanol to hydrocarbon base gasoline.

Table 1- The main Specifications, octane number and ASTM Distillation of gasoline components

Gasoline components	Reformate	Isomerate	Light Naphtha
Specifications:-			
Density@15/4 °C g/I	0.7950	0.6515	0.6883
R.V.P Psi, Kg/cm^2	3.1 (22)	12.6 (89)	7.5 (53)
Sulphur, % wt (ppm)	0.009 (9)	0.016 (16)	0.008 (8)
Corrosion Copper strip Test 3hrs @ 50 °C	1A	1A	1A
Oxidation Stability, mint	> 480	> 480	> 480
Antiknock Index :-			
RON	94	86	68
MON	82	78	60
(R+M) / 2	88	82	64
ASTM Distillation (°C) :-			
1BP	60	32	44
5 %	82	37	56
10 %	88	39	58
20 %	96	40	60
30 %	104	42	63
40 %	111	44	66
50 %	118	46	69
60 %	125	49	71
70 %	133	53	77
80 %	144	58	82
90 %	157	69	91
95 %	166	73	102
FBP	180	79	106
Recovered, vol. %	98.8	98.5	99.0
Loss, vol. %	0.6	1.0	0.5
Residue, vol. %	0.6	0.5	0.5

Table 2- GC analyses of refinery streams used for gasoline formulation.

Composition (wt, %)	Reformate C_5 Bott.	Isomerate 30-SN-5	Light Naphtha Top C_1
iso-Butane	0.000	0.173	0.035
n-Butane	0.649	1.654	1.061
Iso-Pentane	1.721	36.542	19.776
n-Pentane	1.110	8.235	21.062
2,2-Dimethylbutane	0.31	14.142	0.686
Cyclopentane	0.139	1.523	2.266
2,3-Dimethylbutane	0.380	4.076	1.710
2-Methylpentane	2.	12.192	10.383
3-Methylpentane	1.952	6.985	7.096
n-Hexane	2.854	4.051	13.240
Methylcyclopentane	0.987	2.748	6.683
Benzene	3.468	0.000	2.281
Cyclohexane	0.075	3.866	2.981
C_7^+	83.907	3.813	10.740
Total	100.00	100.00	100.00

Table 3- Characteristics of the test vehicle and Engine

Type	Sahin Car Type 1.4s
Model	2001
Fuel	Gasoline 90 octane
Number of cylinders	Four in line
Combustion order	1-3-4-2
Engine No	6628968
Cylinder bore	80.5 mm
Cylinder stroke	67.4 mm
Compression ratio	8.3/1
Engine location	Front
Engine capacity	1400 c.c.
Maximum torque	10.7 Kgm
Maximum power output	78 HP at 5500 rpm.
Maximum speed	145 Km/h
Cooling type	Water cooled in closed circuit
Fuel supply system	Naturally aspirated carburetor.

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Table 4- Composition and Specifications of Hydrocarbon Base fuel (HBF) and four HBF + Butanol Blends.

Fuel Components	Fuel Composition, vol. %				
	HBF	HBF+8nB	HBF+12nB	HBF+8iB	HBF+12iB
Reformate	56.0	51.5	49.3	51.5	49.3
Isomerate	34.0	31.3	29.9	31.3	29.9
Light Naphtha	10.0	9.2	8.8	9.2	8.8
Oxygenate	-	8.0	12.0	8.0	12.0
Oxygenate Type	-	n-Butanol	n-Butanol	i-Butanol	i-Butanol
Total	100	100	100	100	100
Fuel specifications					
Density @15.56g/cm^3	0.7271	0.7473	0.7509	0.7472	0.7506
V.P., psi (KPa)	7.0(48.26)	6.1(42.06)	5.8(40.0)	5.9(40.68)	6.3(43.44)
Sulphur content, ppm	53	48	46	47	45
Oxygen content, wt%	-	2.33	3.49	2.33	3.49
Oxidation stabilily,min	> 480	> 480	> 480	> 480	> 480
Corrosivity (3hrs, 50C°)	1A	1A	1A	1A	1A
Gas chromatographic Analysis, wt%					
Total aromatics	26.89	24..74	23.66	24.74	23.66
Total BTEX	19.75	18.17	17.38	18.17	17.38
Benzene	2.11	1.94	1.86	1.94	1.86
Toluene	6.20	5.70	5.46	5.70	5.46
Ethylbenzene	0.93	0.86	0.82	0.80	0.82
p + m-Xylene	6.31	5.81	5.55	5.81	5.55
O - Xylene	4.20	3.86	3.69	3.86	3.69
RON	87.0	89.5	91.0	90.5	91.6
MON	80.0	85.0	88.0	87.0	88.0
(R+M)/2	83.5	87.2	89.5	88.7	89.8

Table 5- ASTM Distillation-Volatility Criteria and Driveability Indices of HBF and four HBF + Butanol Blends.

Fuel Property	Fuel Designation				
	HBF	HBF+8nB	HBF+12nB	HBF+8iB	HBF+12iB
Distillation, ASTM-D86, °C(°F)					
IBP	37(98.0)	38(100.4)	37(98.0)	40(104.0)	38(100.4)
5 %	44	50	45	49	45
10 %	54(129.2)	57(134.6)	56(132.8)	57(134.6)	56(132.8)
20 %	61	62	64	65	62
30 %	70	72	77	72	71
40 %	79	82	86	81	80
50 %	90(194.0)	91(195.8)	96(204.8)	92(197.6)	88(190.4)
60 %	100	102	104	99	95
70 %	111	112	116	106	101
80 %	129	131	131	120	117
90 %	151(303.8)	155(311.0)	155(311.0)	140(284.0)	145(293.0)
95 %	167	171	176	172	170
F.B.P	183	184	184	183	184
Volatility Criteria					
E70, vol. %	30	28	23	28	30
E100, vol. %	60	59	55	62	68
E150, vol. %	89	90	90	92	89
$T_{V/L=20}$ (°F)	144.72	149.90	152.20	150.92	147.70
VLI (10VP+7E70)	693	617	561	603	644
Driveability Index (DI)					
DI (°F)	1079	1147	1163	1098	1093
DI (°C)	502	523	543	512	509

Table 6- Tailpipe Exhaust Emission of HBF, HBF-Butanol Blends and Gasoline 80.

Fuel Designation	CO_2, vol. %	% Change
HBF	10.71	+ 0.37
HBF-8nB	10.63	+ 1.12
HBF-12nB	10.58	+ 1.58
HBF-8iB	10.18	+ 5.30
HBF-12iB	10.10	+ 6.05
Gasoline 80*	10.75	-
	CO, vol. %	
HBF	6.22	-2.05
HBF-8nB	5.93	-6.61
HBF-12nB	4.41	-30.55
HBF-8iB	4.36	-31.34
HBF-12iB	3.61	-43.15
Gasoline 80*	6.35	-
	Hc, ppm	
HBF	983	-0.61
HBF-8nB	805	-18.60
HBF-12nB	713	-27.91
HBF-8iB	627	-36.60
HBF-12iB	615	-37.82
Gasoline 80*	989	-

* Gasoline marketed in Cairo, Egypt, 80 pump octane

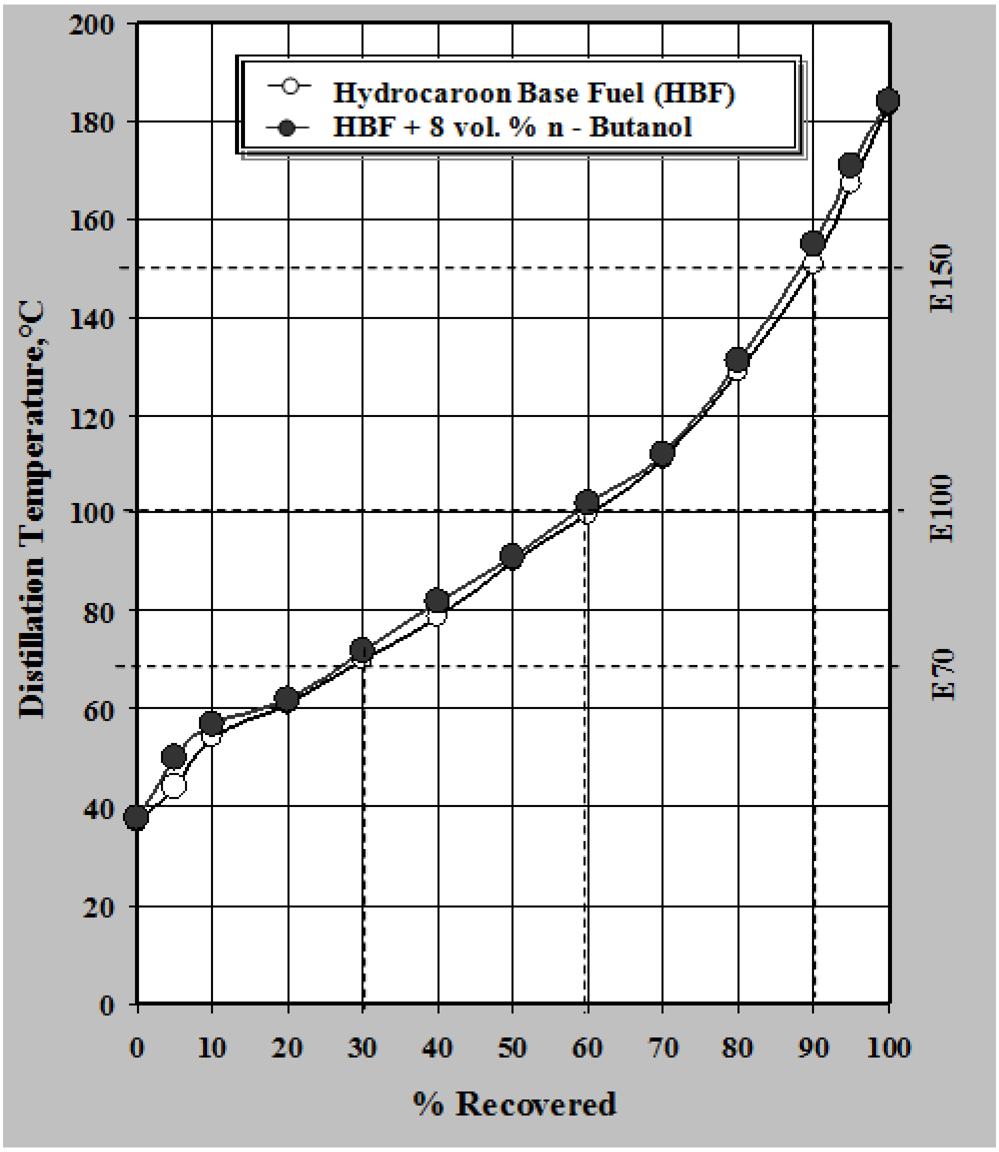

Figure 1- Distillation Profile of HBF and HBF + 8 vol. % n-Butanol

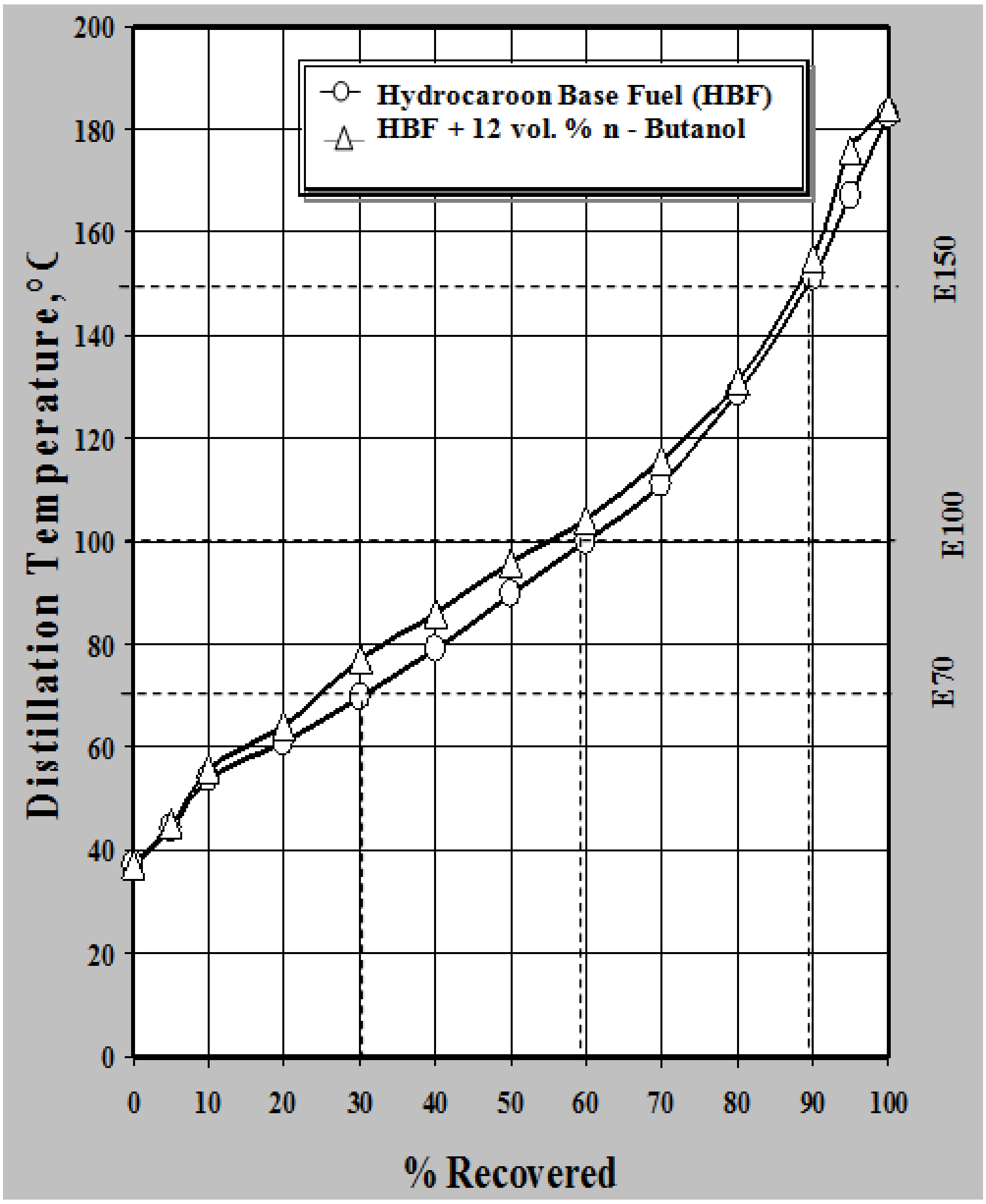

Figure 2- Distillation Profile of HBF and HBF + 12 vol. % n-Butanol

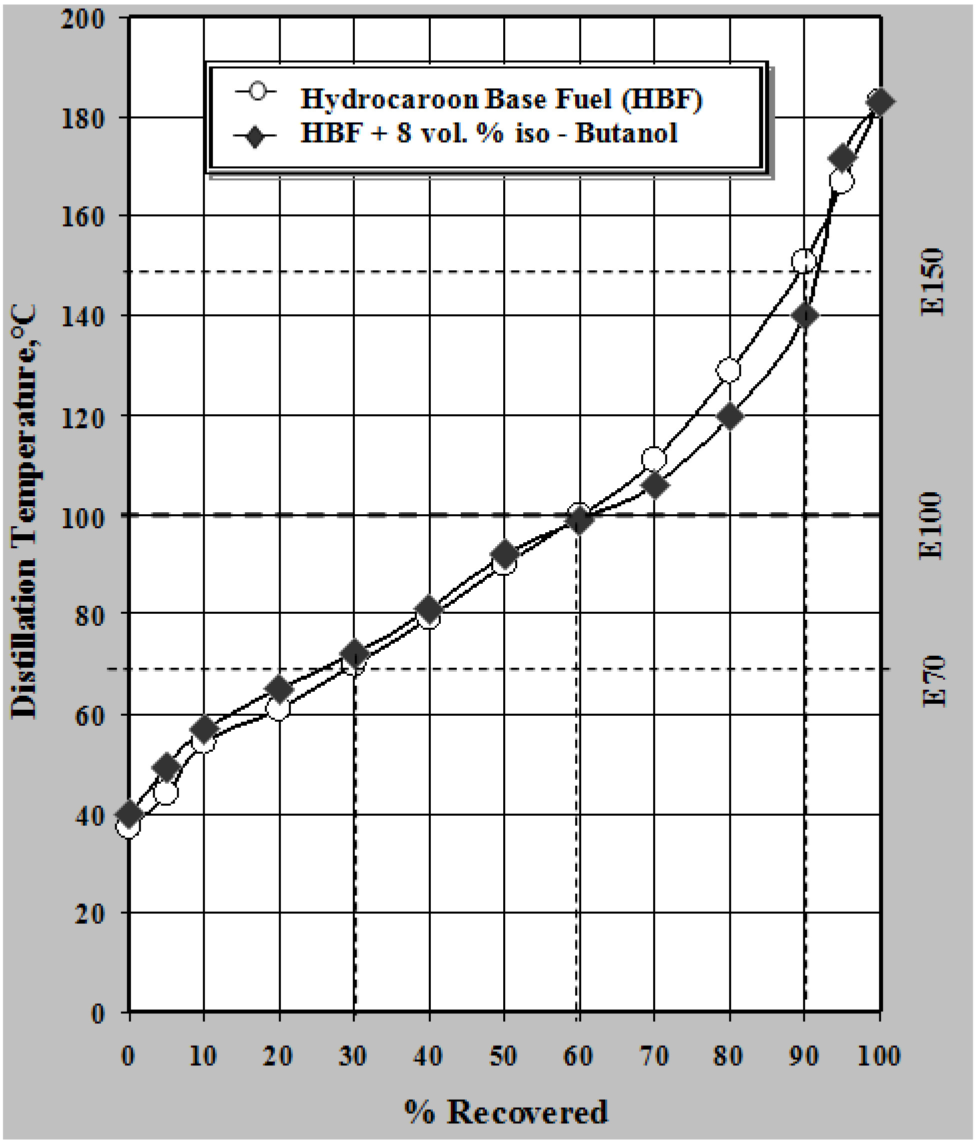

Figure 3- Distillation Profile of HBF and HBF + 8 vol. % iso Butanol

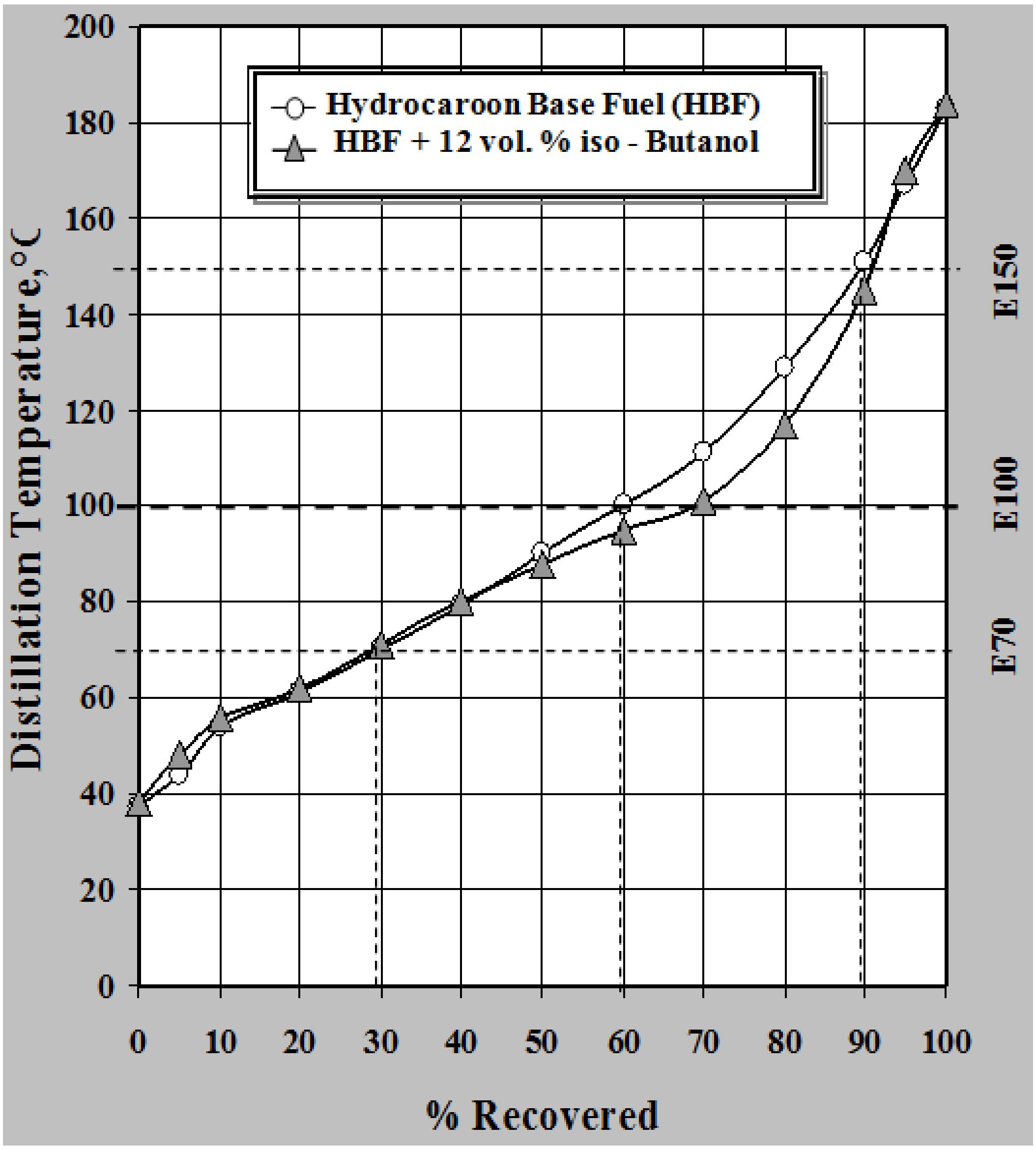

Figure 4- Distillation Profile of HBF and HBF + 12 vol. % iso -Butanol

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