

# Volatility Criteria and Specifications of Some Gasoline-Ester Blends

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Article history: Received 19 November 2013, Accepted 10 December 2013, Published 23 December 2013.

**Abstract:** Hydrocarbon-base gasoline was formulated volumetrically from three local refinery streams: reformate, isomate and light naphtha. The formulated gasoline fuel was blended with four different percentages (v/v) of each of the employed oxygenates, ethyl acetate, iso-butyl acetate and n-butyl acetate. The prepared blends were stored refrigerated along with the ester-free base gasoline. Fuel properties were measured using standard test methods and gas-chromatographic analysis. Changes in volatility criteria associated with the addition of each ester at 2, 4, 6 and 8 vol% were evaluated through measurements of distillation characteristics, vapour pressure, vapour-liquid ratio and vapour-lock index. The effects of the added esters on other specifications, were studied.

**Keywords:** gasoline- ester blends; fuel oxygenates; volatility criteria.

## 1. Introduction

Alcohols and ethers are the commonly used oxygenate additives in gasoline to assist in octane rating increment and better combustion quality [1]. C<sub>1</sub>-C<sub>4</sub> alcohols are attractive oxygenates, however, some of them proved to have bad combustion quality that increases emission of aldehyds and acetic acid or less environmentally benign fuel additive [2-4]. Methyl tertiary butyl ether (MTBE) was considerably thought as health risk threat [5] and biodegradation of other alkyl ether oxygenates, have

been investigated [6]. Researchers have looked ahead for better exhaust emission and more efficient combustion. Several other oxygenates have been attempted and evaluated as gasoline additives. Transformation of glycerol into fuel oxygenates by etherification and esterification are among chemical reactions to produce antiknock additives and octane boosters for gasoline fuel [7-10]. Also synthesis of bioadditives to petrol fuel, through acetylation of glycerol, have been reported [11,12]. Through the dual fermentation biorefinery (DFB) process, methyl acetate, ethyl acetate and isopropyl acetate, were prepared as blending oxygenates and proved to be better octane boosters than alcohols and ethers [13]. More recent studies reported that 10% ethyl acetate-gasoline blend gave octane number contribution very close to that achieved by 10% ethanol blend of the same gasoline composition [14, 15]. Also, several patents have appeared in literature using esters as blending gasoline additives [16, 17].

In the present study, three esters namely, ethyl acetate, n-butyl acetate and iso-butyl acetate, were used as blending oxygenates in hydrocarbon- base gasoline to study the effects of these esters on volatility criteria, octane number, driveability index, and other specifications of the resulted fuel blends.

## 2. Materials and Methods

### 2.1. Refinery Streams

Three petroleum distillates namely reformate, isomerate and light naphtha, were kindly supplied by Cairo Petroleum Company-Mostorod Refinery, Cairo, Egypt. Table 1 lists gas chromatographic (GC) individual analysis along with some properties of these distillates as received from the producer.

### 2.2. Gasoline Formulation

Hydrocarbon-base gasoline (BG) was formulated volumetrically from neat refinery streams: reformate (70%), isomerate (20%) and light naphtha (10%). This hydrocarbon BG was blended with 2, 4, 6 and 8 volume % of each of ethyl acetate, iso- butyl acetate and n-butyl acetate to get twelve gasoline-ester blends. Designations of the formulated base gasoline and gasoline-ester blends are given in Table 2. For example; BG-2EA, indicates a gasoline- ethyl acetate blend that consists of 2 volume % ethyl acetate and 98 volume % gasoline. Properties of the employed esters (oxygenates) are listed in Table 3. The formulated blends (4 liter each), were kept refrigerated in well-stoppered labeled containers. An ice-box was used to keep these blends refrigerated when sent for 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.

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

COMPOSITION (Wt. %)	Reformat 21C <sub>1</sub> Bott	Isomerase 30-SN-5	L.Naphtha TOP C <sub>7</sub>
Iso- Butane	0.09	0.34	0.00
n- Butane	0.42	3.78	0.00
iso- pentane	2.00	38.15	13.07
n- Pentane	1.67	11.24	17.33
2,2- Dimethylbutane	0.35	12.47	0.37
Cyclopentane	0.12	1.45	1.75
2,3- Dimethylbutane	0.33	3.88	1.33
2-Methylpentane	2.28	11.11	8.33
3- Methylpentane	1.78	6.34	5.46
n- Hexane	2.45	4.14	13.13
Methylcyclopentane	0.75	2.33	6.15
Benzene	3.65	0.01	2.26
Cyclohexane	0.11	3.10	4.36
C <sub>7</sub> <sup>+</sup>	84	1.66	26.46
<b>Total</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
<b>Sp. Gravity<sub>60/60</sub><sup>o</sup>F</b>	0.7931	0.6471	0.67528
<b>Sulphur, (ppm)</b>	114	76	118
<b>RON</b>	93.8	86.2	58.2
<b>MON</b>	83.5	83.8	56.1
<b>(RON+MON)/2</b>	88.7	85.0	57.2

**Table 2:** The Formulated Gasoline-Ester Blends

Added Ester	Vol. %	HC-BG Vol.% @	Designation
Ethyl acetate CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	0.0	100	BG
	2.0	98	BG-2EA
	4.0	96	BG-4EA
	6.0	94	BG-6EA
	8.0	92	BG-8EA
n-Butyl acetate CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	2.0	98	BG-2BA
	4.0	96	BG-4BA
	6.0	94	BG-6BA
	8.0	92	BG-8BA
iso-Butyl acetate CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	2.0	98	BG-2IBA
	4.0	96	BG-4IBA
	6.0	94	BG-6IBA
	8.0	92	BG-8IBA

@ HC-BG = hydrocarbon base gasoline.

**Table 3:** Properties of the Employed Esters (Oxygenates)

Property	Ethyl Acetate	n-Butyl acetate	iso-Butyl- acetate
<b>Chemical formula</b>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>
<b>Formula weight</b>	88.105	116.16	116.16
<b>Density, g/cm<sup>3</sup></b>	0.9068	0.880	0.875
<b>Purity, %</b>	99.9	99.0	96.0
<b>Appearance</b>	Colourless liquid	Colourless liquid	Colourless liquid
<b>Melting point, °C</b>	-83.6	-77.0	-99.0
<b>Boiling point, °C</b>	77.1	127.0	118.0
<b>Oxygen content, wt %</b>	36.4	27.6	27.6
<b>Solubility in H<sub>2</sub>O @20°C(g/L)</b>	85.3	10.0	Slightly soluble
<b>Volatility</b>	high	medium	medium
<b>Odour</b>	sweet	fruity ester	fruity ester
<b>Toxicity</b>	nontoxic	nontoxic	nontoxic
<b>CAS number*</b>	141-78-6	123-86-4	110-19-0

\* cas = chemical abstracts service

### 2.3. Fuel Property Measurements

2.3.1. Relative density - DE40 digital density meter, ASTM-D1298[18].

2.3.2. Distillation profile- ASTM – D86[19].

2.3.3. Sulphur content Wavelength Dispersive XRF-ASTM-D6334[20].

2.3.4. Calorific value- ASTM D240[21].

2.3.5. Oxidation Stability Induction Period Method- ASTM- D525[22].

2.3.6. Copper strip corrosion test (3 hrs, 50 °C) ASTM-D130[23].

2.3.7. Vapour Pressure (Reid Method) - ASTM-D323[24].

2.3.8. Dry vapour pressure equivalent (DVPE)-ASTM-D5191[25].

2.3.9. Vapour- Liquid Ratio of 20 ( $T_{V/L=20}$ ) ASTM- D4814[26].

2.3.10. Vapour Lock Index : ( $VLI = 10 VP + 7E70$ ).

2.3.11. Driveability Index (DI) - ASTM- D4814-98a[27].

2.3.12. Research Octane Number (RON) ASTM-D2699[28].

### 2.4. Gas chromatographic Analysis

For the determination of aromatics in ester-free and ester- blended gasoline fuels using Agilent 6890 plus instrument with flame ionization detector (FID). Column: DB-1, 60m, 0.320 mm I.D, 5 µm film thickness Injector: 280 °C, Detector 300 °C, Oven temperature programming: 50 °C (5min), 6 °C/min to 250°C, 250°C (10 min), carrier gas N<sub>2</sub>, flow rate 2 ml/min.

### 3. Results and Discussion

#### 3.1. Base Stock and Ester Blending

The hydrocarbon-base gasoline was formulated volumetrically from three local refinery streams: reformat (70%) isomerate (20%) and light naphtha (10%). The formulated base stock gasoline was blended with 2, 4, 6, and 8% by volume of each of ethyl acetate, iso-butyl acetate and n-butyl acetate to get twelve gasoline-ester blends in three groups. Each of the resulting blends along with the ester-free base stock was subsequently analyzed by gas-chromatography for aromatic content and the performance of each fuel was evaluated through the determined specifications. Composition and specifications of the formulated hydrocarbon-base gasoline (BG) and the twelve gasoline-ester blends are listed in Tables 4A, 5A and 6A.

**Table 4A:** Composition and Specifications of Gasoline- Ethyl Acetate Blends

Fuel Components	Fuel blend Composition, vol. %				
	BG	BG-2EA	BG-4EA	BG-6EA	BG-8EA
<b>Reformat</b>	70.0	68.6	67.2	65.8	64.4
<b>Isomerate</b>	20.0	19.6	19.2	18.8	18.4
<b>Light Naphtha</b>	10.0	9.8	9.6	9.4	9.2
<b>Ethyl acetate</b>	0.0	2.0	4.0	6.0	8.0
<b>Total</b>	100	100	100	100	100
<b>Aromatics, wt %</b>					
<b>BTEX, wt %</b>	37.5	36.8	36.0	35.2	34.5
<b>Benzene</b>	33.6	32.8	32.0	30.4	29.9
<b>Toluene</b>	3.7	3.6	3.3	3.2	3.0
<b>Ethyl benzene</b>	10.8	10.5	10.3	10.2	10.3
<b>Xylene (m&amp; p)</b>	3.8	3.5	3.6	2.9	2.8
<b>o -Xylenes</b>	10.6	10.5	10.2	9.6	9.4
	4.7	4.7	4.6	4.5	4.4
<b>Fuel Specifications</b>					
<b>Density @ 15.56 g/cm<sup>3</sup></b>	0.7465	0.7493	0.7537	0.7561	0.7592
<b>Sulphur content, ppm</b>	94	91	91	87	85
<b>Oxygen content, wt %</b>	0.0	0.867	1.725	2.579	3.420
<b>Hydrogen/carbon ratio</b>	0.1669	0.1655	0.1641	0.1627	0.1612
<b>Calorific value, kj/kg</b>	56483	55765	55047	54330	53612
<b>Oxidation stability, min</b>	> 480	-	> 480	-	> 480
<b>Octane number (RON)</b>	83.0	83.2	84.0	84.6	85.6
<b>Corrosivity (3hrs, 50°C)</b>	1	1	1	1	1

**Table 4B:** Distillation Characteristics and Volatility Criteria of Gasoline- Ethyl Acetate Blends.

Fuel Properties	Fuel blend Designations				
	BG	BG-2EA	BG-4EA	BG-6EA	BG-8EA
<b>Distillation, ASTM-D86, °C (°F)</b>					
<b>IBP</b>	38	38	38	38	38
<b>10 vol.% evaporated</b>	62(144)	63(145)	61(142)	60(140)	58(136)
<b>20 vol.% evaporated</b>	80	80	79	80	80
<b>30 vol.% evaporated</b>	93	91	91	92	90
<b>40 vol.% evaporated</b>	102	101	98	100	98
<b>50 vol.% evaporated</b>	112(234)	110(230)	110(230)	109(228)	106(223)
<b>60 vol.% evaporated</b>	124	120	122	125	118
<b>70 vol.% evaporated</b>	132	134	135	134	129
<b>80 vol.% evaporated</b>	145	148	147	148	140
<b>90 vol.% evaporated</b>	165(329)	165(329)	164(327)	162(324)	159(318)
<b>FBP</b>	183	184	181	181	180
<b>Driveability Index (°C)</b>					
	594	592	591	587	574
<b>Driveability Index (°F)</b>					
	1243	1241	1240	1232	1211
<b>Volatility Criteria</b>					
<b>Vapour Pressure, psi(kPa)</b>	6.2(42.7)	6.8(46.9)	6.9(47.6)	7.0(48.3)	7.1(49.0)
<b>E70, vol. %</b> (recovered up to 70 °C)	15	16	17	17	15
<b>E100, vol. %</b> (recovered up to 100 °C)	38	40	42	40	42
<b>E150, vol. %</b> (recovered up to 150 °C)	84	82	82	83	85
<b>T<sub>V/L=20</sub> (°F)</b> (vapour liquid ratio of 20)	157.76	154.42	153.51	151.98	149.60
<b>VLI (vapour lock index).</b>	532	581	595	602	602

### 3.2. Composition and Specifications

The composition and specifications of the formulated base gasoline (BG) and the investigated ethyl acetate (EA), iso-butyl acetate (IBA), and n-butyl acetate (BA) blends are listed in Tables 4A, 5A and 6A. Aromatics are fuel molecules which are good octane components of gasoline. Aromatics are products of catalytic reforming that is why reformat distillate is the highest octane gasoline stream (Table 1). Aromatic content in BG is 37.5 wt % which decreases as the concentration of added ester increases. The aromatic limit in gasoline is a function of the final boiling point (FBP) of gasoline. The FBP limit in gasoline provides the best means to limit heavy aromatic molecules which are the reason for combustion chamber deposits. Gasoline and gasoline-ester blends in this study have boiling range from 38 to 190 °C, Individual aromatic analyses shown in Tables 4A, 5A and 6A include benzene, toluene, ethyl benzenes and xylenes. Total aromatic content includes trace of C<sub>9</sub> + aromatics and other

hydrocarbon-types. Findings from the US-AQIR and the European EPEFE programmes showed that of all the fuel properties tested, aromatic level had the largest effect on exhaust benzene emissions. Because benzene is a known human carcinogen, the control of benzene in gasoline has been recognized by regulators in many countries as an effective way to reduce human exposure to benzene [29, 30].

**Table 5A:** Composition and Specifications of Gasoline- iso-Butyl Acetate Blends

Fuel Components	Fuel blend Composition, vol.%				
	BG	BG-2IBA	BG-4IBA	BG-6IBA	BG-8IBA
<b>Reformate</b>	70.0	68.6	67.2	65.8	64.4
<b>Isomerate</b>	20.0	19.6	19.2	18.8	18.4
<b>Light Naphtha</b>	10.0	9.8	9.6	9.4	9.2
<b>iso-Butyl acetate</b>	0.0	2.0	4.0	6.0	8.0
<b>Total</b>	100	100	100	100	100
<b>Aromatics, wt %</b>					
<b>BTEX, wt %</b>	37.5	36.8	36.0	35.2	34.5
<b>Benzene</b>	33.6	32.9	31.6	30.9	29.0
<b>Toluene</b>	3.7	3.6	3.4	3.2	3.0
<b>Ethyl benzene</b>	10.8	10.7	10.5	10.6	10.5
<b>Xylene (m&amp; p)</b>	3.8	3.8	3.5	3.3	3.1
<b>o -Xylenes</b>	10.6	10.3	10.0	9.8	9.6
	4.7	4.5	4.2	4.0	3.8
<b>Fuel Specifications</b>					
<b>Density@15.56 g/cm<sup>3</sup></b>	0.7465	0.7543	0.7548	0.7572	0.7601
<b>Sulphur content, ppm</b>	94	94	90	87	88
<b>Oxygen content, wt %</b>	0.0	0.639	1.278	1.910	2.539
<b>Hydrogen/carbon ratio</b>	0.1669	0.1658	0.1648	0.1637	0.1626
<b>Calorific value, kj/kg</b>	56483	56055	55628	55201	54774
<b>Oxidation stability, min</b>	> 480	-	> 480	-	> 480
<b>Octane number (RON)</b>	83.0	83.0	83.3	84.3	85.0
<b>Corrosivity (3hrs, 50°C)</b>	1	1	1	1	1

**Table 5B:** Distillation Characteristics and Volatility Criteria of Gasoline-iso-Butyl Acetate Blends

Fuel Properties	Fuel Designations				
	BG	BG-2IBA	BG-4IBA	BG-6IBA	BG-8IBA
<b>Distillation, ASTM-D86, °C (°F)</b>					
<b>IBP</b>	38	38	38	38	38
<b>10 vol.% evaporated</b>	62(144)	63(146)	64(147)	64(147)	62(144)
<b>20 vol.% evaporated</b>	80	76	79	84	81
<b>30 vol.% evaporated</b>	93	90	93	95	95
<b>40 vol.% evaporated</b>	102	100	102	105	104
<b>50 vol.% evaporated</b>	112(234)	114(237)	114(237)	112(234)	112(234)
<b>60 vol.% evaporated</b>	124	121	120	125	118
<b>70 vol.% evaporated</b>	132	130	129	132	124
<b>80 vol.% evaporated</b>	145	140	138	143	135
<b>90 vol.% evaporated</b>	165(329)	156(313)	155(311)	152(306)	150(302)
<b>FBP</b>	183	181	180	188	187
<b>Driveability Index (°C)</b>	594	601	600	598	600
<b>Driveability Index (°F)</b>	1243	1256	1251	1247	1239
<b>Volatility Criteria</b>					
<b>Vapour Pressure, psi(kPa)</b>	6.2(42.7)	6.4(44.1)	6.5(44.8)	6.6(45.5)	6.6(45.5)
<b>E70, vol. %</b> (recovered up to 70 °C)	15	15	15	16	18
<b>E100, vol. %</b> (recovered up to 100 °C)	38	40	40	37	37
<b>E150, vol. %</b> (recovered up to 150 °C)	84	87	88	85	91
<b>T<sub>V/L=20</sub> (°F)</b> (vapour liquid ratio of 20)	157.76	157.85	158.04	158.12	158.51
<b>VLI (vapour lock index).</b>	532	564	553	567	581

Based on environmental requirements, refiners and marketers can decide to put the necessary changes in gasoline specifications to control the environmental impact of oxygenated gasolines concerning fuel economy and emissions reduction [31-35]. In the present study, gasoline-ester blends are research grade test fuels having relative densities within the conventional motor gasoline range. Densities of these test fuel blends increased with increasing the volumetric concentration of added esters (Tables 4A, 5A and 6A). Relative densities were measured by a standard method (**ASTM-D1298**). It has been found that the studied gasoline-ester blends contain very little sulphur content as determined by wavelength dispersive XRF method (**ASTM-D6334**), but this can be harmful because sulphur on combustion forms sulphur oxides, which when dissolved in water becomes sulphuric acid. This corrosive sulphur compound attacks metal parts of the engine or the fuel system. This characteristic is tested by the Copper Strip Corrosion test, a severe discolouration or pitting of the polished strip indicates the presence of corrosive sulphur compounds in the fuel (**ASTM-D130**).



**Table 6A:** Composition and Specifications of Gasoline- n-Butyl Acetate Blends

Fuel Components	Fuel blend Composition, vol.%				
	BG	BG-2BA	BG-4BA	BG-6BA	BG-8BA
<b>Reformat</b>	70.0	68.6	67.2	65.8	64.4
<b>Isomate</b>	20.0	19.6	19.2	18.8	18.4
<b>Light Naphtha</b>	10.0	9.8	9.6	9.4	9.2
<b>n-Butyl acetate</b>	0.0	2.0	4.0	6.0	8.0
<b>Total</b>	100	100	100	100	100
<b>Aromatics, wt %</b>					
<b>BTEX, wt %</b>	37.5	36.8	36.0	35.2	34.5
<b>Benzene</b>	33.6	32.8	31.5	30.4	28.8
<b>Toluene</b>	3.7	3.5	3.4	3.4	3.0
<b>Ethyl benzene</b>	10.8	10.7	10.5	10.3	10.4
<b>Xylene (m&amp; p)</b>	3.8	3.8	3.5	3.1	3.2
<b>o -Xylenes</b>	10.6	10.3	10.0	9.8	8.7
	4.7	4.5	4.1	3.8	3.5
<b>Fuel Specifications</b>					
<b>Density@15.56 g/cm<sup>3</sup></b>	0.7465	0.7537	0.7561	0.7584	0.7621
<b>Sulphur content, ppm</b>	94	93	90	88	83
<b>Oxygen content, wt %</b>	0.0	0.643	1.288	1.919	2.548
<b>Hydrogen/carbon ratio</b>	0.1669	0.1658	0.1648	0.1637	0.1626
<b>Calorific value, kj/kg</b>	56483	56058	55634	55201	54786
<b>Oxidation stability, min</b>	> 480	-	> 480	-	> 480
<b>Octane number (RON)</b>	83.0	83.0	83.3	83.7	84.3
<b>Corrosivity (3hrs, 50°C)</b>	1	1	1	1	1

### 3.2.1. Ester Addition and Calorific Value

Calorific values of ester-free gasoline and ester blended ones were determined (ASTM-D240-02). In Figure 1 ester addition resulted in linear decrease in calorific values of Gasoline-ethyl acetate, Gasoline-iso-butyl acetate and Gasoline-n-butyl acetate blends. It is well-known also that the calorific value of any fuel depends on the hydrogen / carbon ratio (H/C ratio) of this fuel. Data in Tables 4A-6A show that H/C ratio decreases as the added ester increases. A linear relationship is obtained (Figure 2) between the calorific value and the H/C ratio of the investigated gasoline-ester blends (data points of iso-and n-butyl acetates are almost identical). The decrease in H/C ratio is mainly due to the increase of oxygen- to- fuel ratio in these oxygenated gasoline blends (Figure 3). R-square values of these relations indicate the reliability of the fits.

**Table 6B:** Distillation Characteristics and Volatility Criteria of Gasoline-n-Butyl Acetate Blends

Fuel Properties	Fuel blend Designations				
	BG	BG-2BA	BG-4BA	BG-6BA	BG-8BA
<b>Distillation, ASTM-D86, °C (°F)</b>					
<b>IBP</b>	38	38	38	38	38
<b>10 vol.% evaporated</b>	62(144)	63(145)	63(145)	63(145)	61(142)
<b>20 vol.% evaporated</b>	80	82	80	79	80
<b>30 vol.% evaporated</b>	93	92	93	93	90
<b>40 vol.% evaporated</b>	102	100	104	103	101
<b>50 vol.% evaporated</b>	112(234)	112(234)	110(230)	108(226)	107(225)
<b>60 vol.% evaporated</b>	124	122	124	123	122
<b>70 vol.% evaporated</b>	132	130	133	130	130
<b>80 vol.% evaporated</b>	145	141	140	140	140
<b>90 vol.% evaporated</b>	165(329)	160(320)	157(315)	153(307)	151(304)
<b>FBP</b>	183	184	184	185	187
<b>Driveability Index (°C)</b>	594	596	590	582	572
<b>Driveability Index (°F)</b>	1243	1245	1233	1217	1211
<b>Volatility Criteria</b>					
<b>Vapour Pressure, psi(kPa)</b>	6.2(42.7)	6.4(44.1)	6.5(44.8)	6.2(42.7)	6.0(41.4)
<b>E70, vol. %</b> (recovered up to 70 °C)	15	18	15	15	16
<b>E100, vol. %</b> (recovered up to 100 °C)	38	38	37	38	38
<b>E150, vol. %</b> (recovered up to 150 °C)	84	84	86	87	89
<b>T<sub>V/L=20</sub> (°F)</b> (vapour liquid ratio of 20)	157.76	156.14	156.05	156.60	156.91
<b>VLI (vapour lock index).</b>	532	546	560	539	526

### 3.2.2. Ester Addition and Oxidation Stability

The test is a measure of the stability of gasoline during long term storage. Oxidation results in the formation of gums, deposits and sludges. In this test (**ASTM-D525**), the sample is heated in a sealed vessel with oxygen and the time measured before it starts to absorb the oxygen (i.e oxidize and form gum). The induction period measured equate the safe storage time of the hydrocarbon- base and ester-blended gasolines. The current-level specified in Egypt is 480 minutes. In New Zealand and Japan, 240 minutes induction period is accepted [36]. The European standards require 360 minutes induction period. Absence of cracked stream in gasoline formulation may lead to more stable fuel in storage [37, 38].

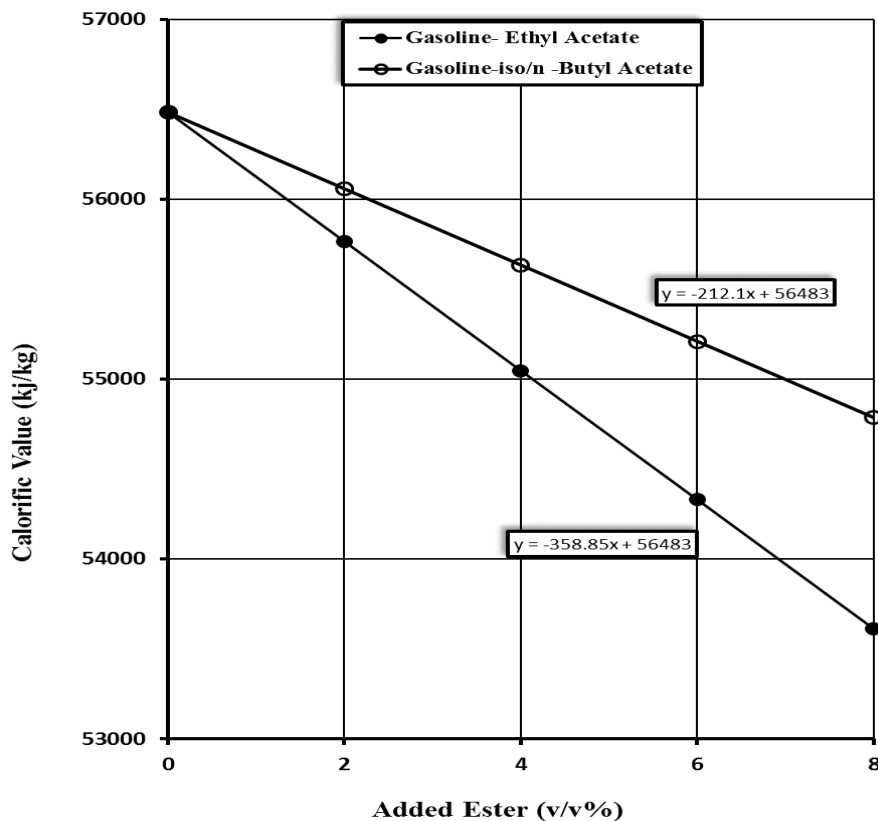


Fig. 1. Relationship between Calorific Value and Added Ester in the Blends

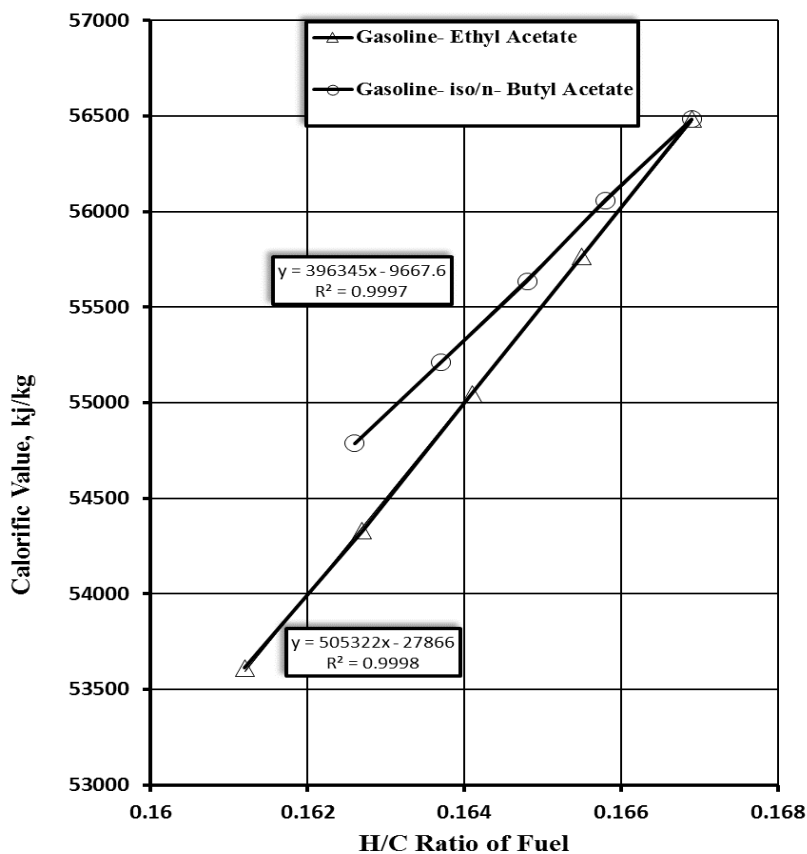
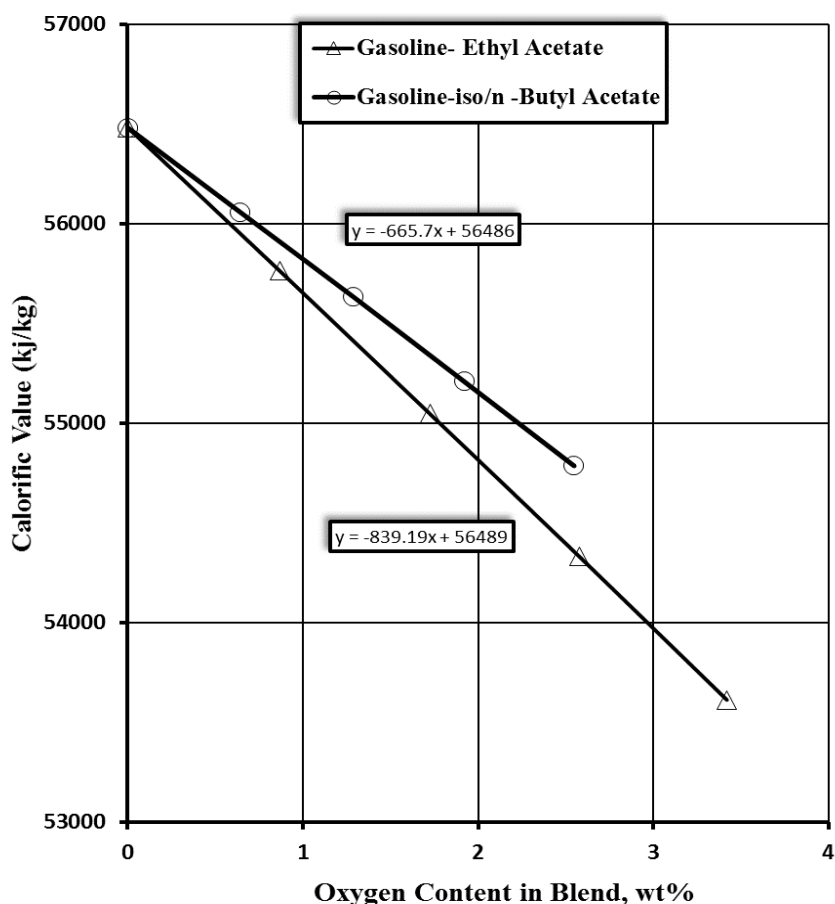


Fig. 2. Relationship between Calorific Value and H/C Ratio of the Fuel Blends

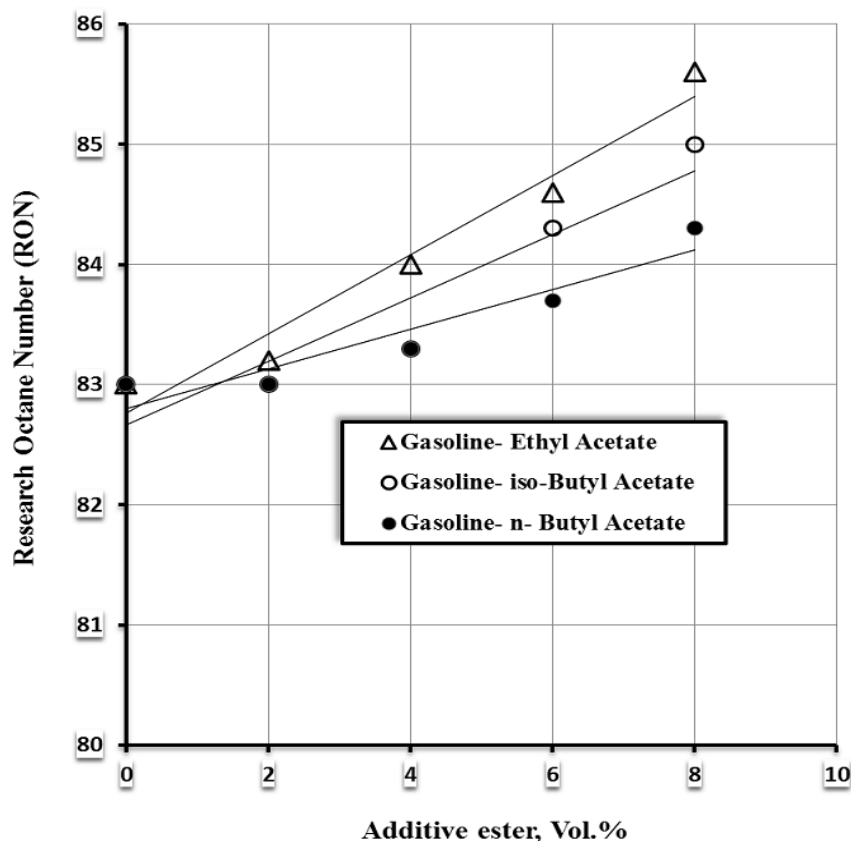


**Fig. 3.** Relationship between Calorific Value and Oxygen Content in the Blends

### 3.2.3. Ester Addition and Octane Number

It can be seen from research octane number (RON) data of gasoline-ester blends listed in Tables 4A, 5A and 6A, that the octane benefits are detected only above 4.0 volume percentage of the blended esters (Figure 4). The octane value contributions of 4, 6 and 8 vol.% ester addition reached 0.3, 0.7, 1.3 for n-butyl acetate, 0.3, 1.3, 2.0, for iso-butyl acetate and 1.0, 1.6, 2.6, for ethyl acetate, respectively. The maximum attainable RON values, were achieved at 8.0 vol. % of ester addition (**ASTM-D2699**). The contribution of the employed ester oxygenates is reasonable if compared with the contribution of some ether or alcohol oxygenates which have been previously investigated in our Oxygenated Gasoline Program, Egyptian Petroleum Research Institute (EPRI). Hydrocarbon base stock gasoline consists of 70.0 vol. % reformat, 13 vol. % isomerate and 17.0 vol. % light naphtha. RON of this fuel equals 84.3. Blending 4, 6, and 8 vol. % ethanol into this gasoline contributed 1.4, 2.2, and 3.4 octane numbers, i.e., the resulting blends have RON values of 85.7, 86.5 and 87.7, respectively [39]. Another hydrocarbon base stock gasoline which consists of 56.0 vol. % reformat, 34.0 vol. % isomerate, and 10 vol. % light naphtha. This composition has RON value of 86.9. Blending of 4.0, 8.0 and 12.8 vol. %

ethyl tertiary butyl ether (ETBE) into this gasoline contributed 0.3, 1.0, and 1.9 octane numbers giving RON values of 87.2, 87.9, and 88.8 for the gasoline-MTBE blends, respectively[40].



**Fig. 4.** Effect of Ester Addition on Research Octane Number (RON) of the Blends

### 3.3. Volatility Criteria of Ester Blends

#### 3.3.1. Driveability and volatility of ester blends

Driveability describes how an engine starts, warms up, and runs. Driveability problems include hard starting, backfiring, rough idling, poor throttle response, and stalling. The key gasoline characteristics for good driveability is volatility [41]. Volatility is important because gasoline must be vapourised before it can burn in the combustion chamber of an engine. Gasoline blenders in refinery, formulate gasoline to vapourise easily in winter. Gasoline that vapourises easily allows a cold engine to start quickly and warm up smoothly. Warm weather gasoline is blended to vapourise less easily to prevent engine vapour-lock and to control evaporative emissions that contribute to air pollution [42,43].

It is important to note that there is no single best volatility for gasoline. Volatility must be adjusted for the altitude and seasonal temperature of the location where the gasoline will be used [44]. Three properties are used to measure gasoline volatility: distillation profile, vapour pressure and vapour-liquid ratio. A fourth property, driveability index, is calculated from the distillation profile.

Instead of vapour-liquid ratio, a vapour lock index (VLI) is used to control hot fuel handling problems [41].

### 3.3.2. Distillation profile and volatility of ester blends

From distillation profile, fuel characteristics could be determined. Figure 5 is the distillation profile of the investigated hydrocarbon-base stock gasoline in this study. This constructed profile illustrates the location of a set of “T” points or “E” points.  $T_{10}$ ,  $T_{50}$ , or  $T_{90}$ , is the temperature at which 10%, 50% or 90% by volume of fuel distilled. Also E70, E100, or E150, is the volume percentage of gasoline fuel distilled at 70, 100, or 150 °C [45, 46]. Through distillation profile and the location of these distillation characteristics, some specific aspects of gasoline fuel performance could be correlated (ASTM-D86). For example  $T_{10}$ , the front-end volatility, is the 10% evaporated temperature must be low enough to provide: easy cold starting, freedom from vapour-lock.  $T_{50}$ , the mid-range volatility, is the 50% evaporated temperature, must be adjusted to provide: rapid warm up and smooth running, good power and acceleration, protection against carburetor icing and hot stalling.  $T_{90}$ , the tail-end volatility, is the 90% evaporated temperature.  $T_{90}$  is adjusted to provide: good fuel economy, freedom from engine deposits, and minimal fuel dilution of crankcase oil.

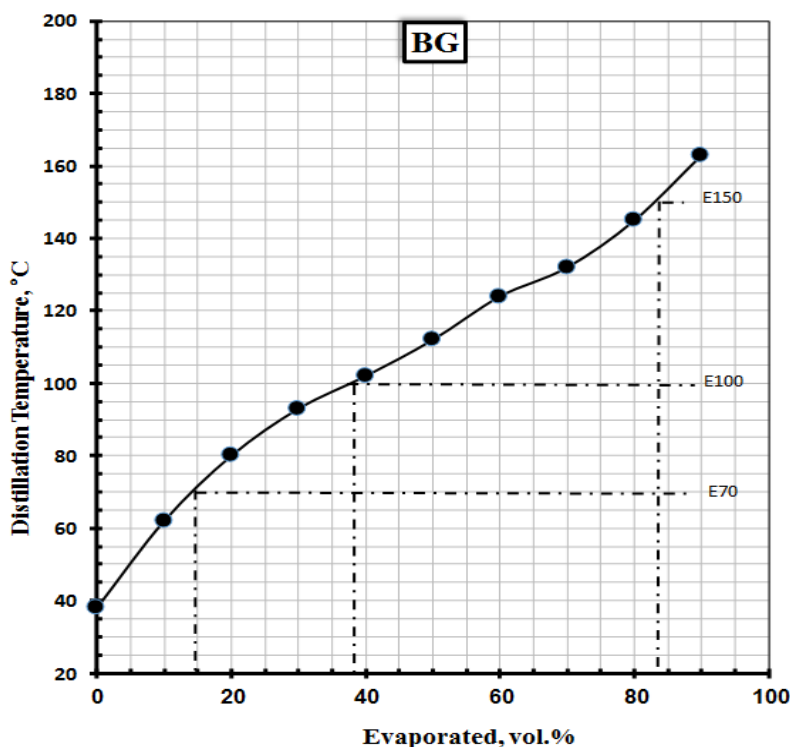


Fig. 5. Distillation Profile of BG alone (Illustrative figure)

For better illustration of the effect of ester addition on the shape of distillation profile, Figure 5 is an illustrative one for hydrocarbon-base gasoline (BG) along with three other couples of distillation profiles. Figure 6 for BG and BG-8EA blend, Figure 7 for BG and BG-8IBA blend, and Figure 8 for BG and BG-8BA blend. These Figures illustrate the difference in distillation profiles as a result of

blending 8 vol. % ethyl acetate (EA), iso-butyl acetate (IBA) or n-butyl acetate (BA), into 92 vol. % of hydrocarbon-base gasoline (BG). More significant change in the shape of BG-8EA distillation curve (Figure 6) was noticed and the decrease in distillation temperatures from  $T_{40}$  to  $T_{90}$  gave indication that blending up to 8 vol. % ethyl acetate substantiates that increase in volatility. Blending 8 vol. % of IBA into BG, Figure 7 shows a distinct change in the shape of distillation curve from  $T_{60}$  to  $T_{90}$  i.e. at the tail-end volatility. Less produced change in the shape of BG-8BA distillation curve except at  $T_{90}$  (Figure 8), which can cause a limited change in the volatility of the blend.

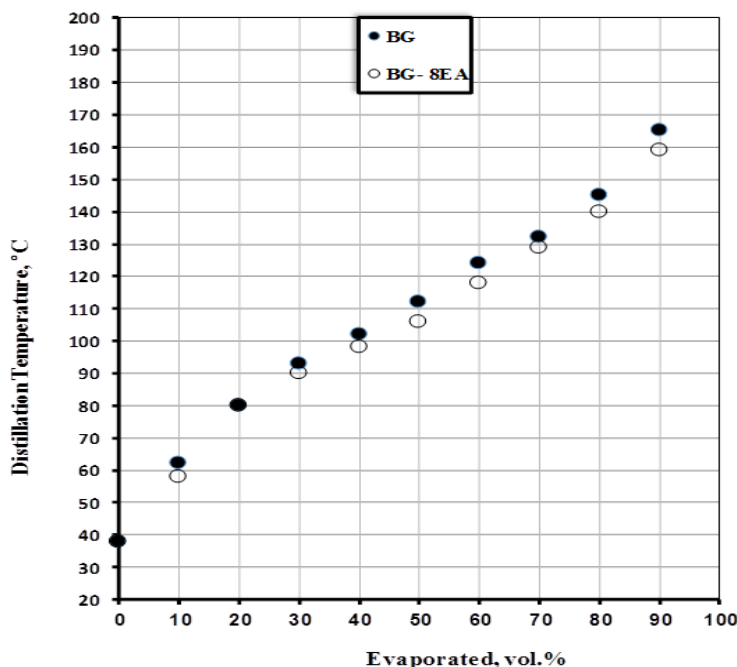


Fig. 6. Distillation Profile of BG and BG-8EA blend

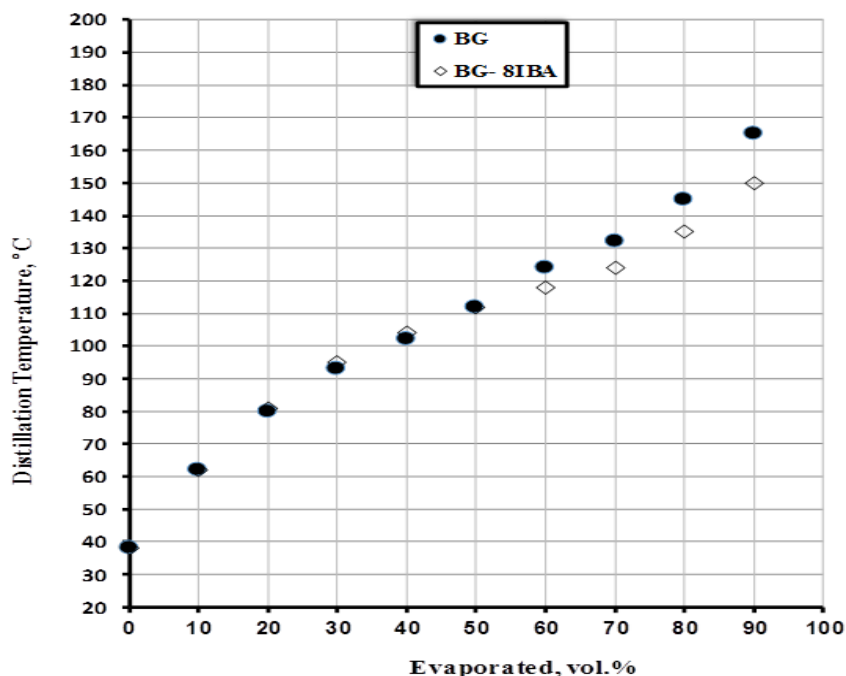


Fig. 7. Distillation Profile of BG and BG-8IBA blend

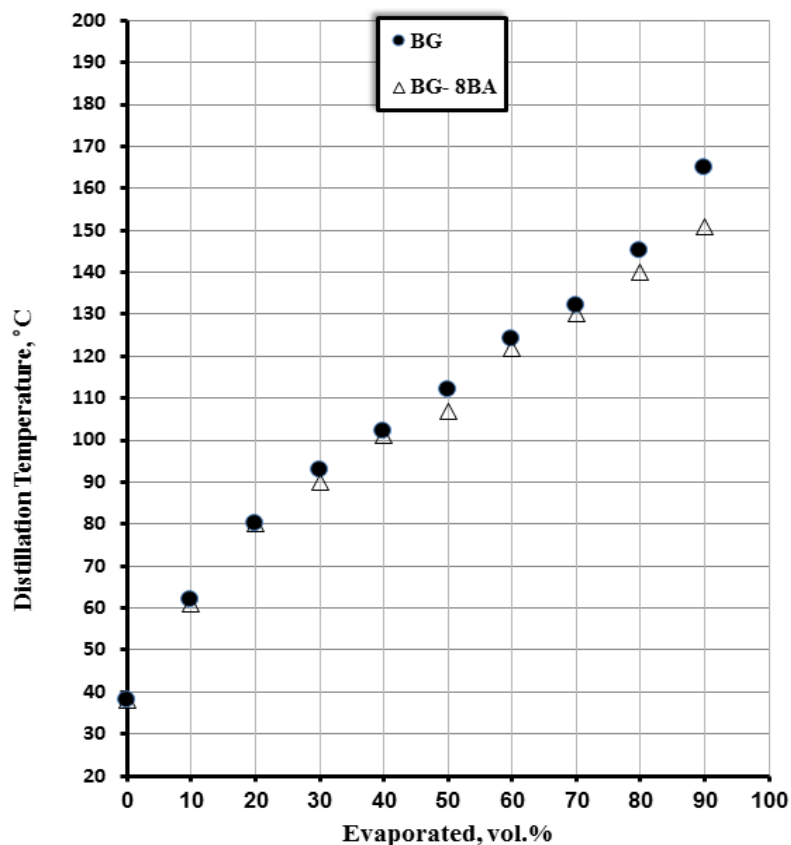


Fig. 8. Distillation Profile of BG and BG-8BA blend

### 3.3.3. Driveability Indexes of ester blends

Distillation characteristics,  $T_{10}$ ,  $T_{50}$  and  $T_{90}$  affect vehicle performance. A relationship exists between distillation temperatures and driveability index (DI) as expressed in equation 1 using the temperatures in degrees Fahrenheit [47, 48].

$$DI (^{\circ}F) = 1.5 (T_{10}) + 3.0 (T_{50}) + T_{90} \quad (1)$$

DI varies with gasoline composition, for the hydrocarbon-base gasoline, the normal range is 850 to 1300. Lower DI values 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 [27, 29]. Applying equation 1 for the formulated base gasoline is within the specified normal range i.e., 1243.

An oxygen correction factor has been introduced for gasoline-oxygenate blends. The developed equation 2 in degrees Celsius and equation 3 in degrees Fahrenheit

$$DI (^{\circ}C) = 1.5 (T_{10}) + 3.0 (T_{50}) + T_{90} + 1.33 (\text{oxygenate vol. \%}) \quad (2)$$

$$DI (^{\circ}F) = 1.5 (T_{10}) + 3.0 (T_{50}) + T_{90} + 2.4 (\text{oxygenate vol. \%}) \quad (3)$$

Driveability indexes, of gasoline-ester blends, containing 2%, 4%, 6% and 8% by volume of



ethyl acetate, n-butyl acetate and iso-butyl acetate, were calculated using the developed equations and the obtained values are listed in Tables 4B, 5B and 6B. Blending from 2 to 8 vol% of the employed esters into hydrocarbon- base gasoline, kept their DI values within the specified range.

#### 3.3.4. Effect of ester addition on $T_{50}$ value

The effect of ester addition on  $T_{50}$  value of fuel blends in this study, tends to reach a minimum for the gasoline when blended with 2-8% by volume of any of the employed esters. In previous studies, blending 1-10% by volume ethanol resulted in lowering  $T_{50}$  value of hydrocarbon-base gasoline, i.e. decrease the 50% evaporated distillation temperature of ethanol-free gasoline base stock [39]. Lowering  $T_{50}$  value means increasing the volatility of gasoline-oxygenate blend.

Data in Tables 4B, 5B and 6B, show that none of the twelve gasoline-ester blends, has a  $T_{50}$  value below the minimum of 66 °C (150 °F) specified in ASTM-D4814. Prior to blending with ester,  $T_{50}$  value of hydrocarbon-base gasoline was 112 °C (234 °F). ASTM-D4814-09b specifies that gasolines which may be blended with oxygenate must meet a minimum  $T_{50}$  of 77 °C (170 °F) prior to blending. Results of the present study reveal that after blending the hydrocarbon-base gasoline (BG) with 2, 4, 6 and 8% by volume of any of the employed esters,  $T_{50}$  values of the resulting fuel blends, were found in the ranges: 234-223; 237-234 and 234-225 °F for gasoline-ethyl acetate; gasoline-iso-butyl acetate and gasoline n-butyl acetate blends, respectively. Careful inspection of data in Tables 4B-6B, show that blending butyl acetates gave insignificant impact on the volatility of the resulting blends (i.e., ester addition does not lower  $T_{50}$  value of the blend), whereas, ethyl acetate gave considerable impact on the volatility of the blends using gasoline of the same composition. DI values listed in Tables 4B, 5B and 6B, show that increasing ester concentration from 2% to 8% resulted in a decrease in DI values from 1243 to 1211 in ethyl acetate and n-butyl acetate blends, whereas DI decreased from 1243 to 1239 in iso-butyl acetate blends. These DI ranges are still within the specified ASTM normal range which permit good driveability performance for vehicles fueled with any of the investigated gasoline-ester fuel blends. (Figures 9, 10 and 11)

#### 3.3.5. Vapour pressure of ester blends

Data listed in Tables 4B, 5B and 6B show twelve gasoline ester blends in three groups along with the reference hydrocarbon-base gasoline. Figure 12 shows three lines which illustrate the effect of increasing the concentration of added ester on vapour pressure of the investigated gasoline-ester blends. For the concentration range 2% - 8% of added ester, the vapour pressure of gasoline-ethyl acetate and gasoline-iso-butyl acetate blends, two trend lines which run parallel, can be seen in the figure. The abrupt increase, in the vapour pressures of gasoline- ethyl acetate blends, is higher than that observed for gasoline-iso-butyl acetate ones. In case of gasoline-n-butyl acetate blends, vapour

pressure rises with the addition of 2 and 4 volume% of this ester. At higher concentrations, the vapour pressure of the blends decreases. In all the investigated blends, the partial vapour pressure contributed by the hydrocarbon-base gasoline-fraction is constant, the vapour pressure difference in blends is due to the partial vapour pressure generated by the ester mole fraction in blend.

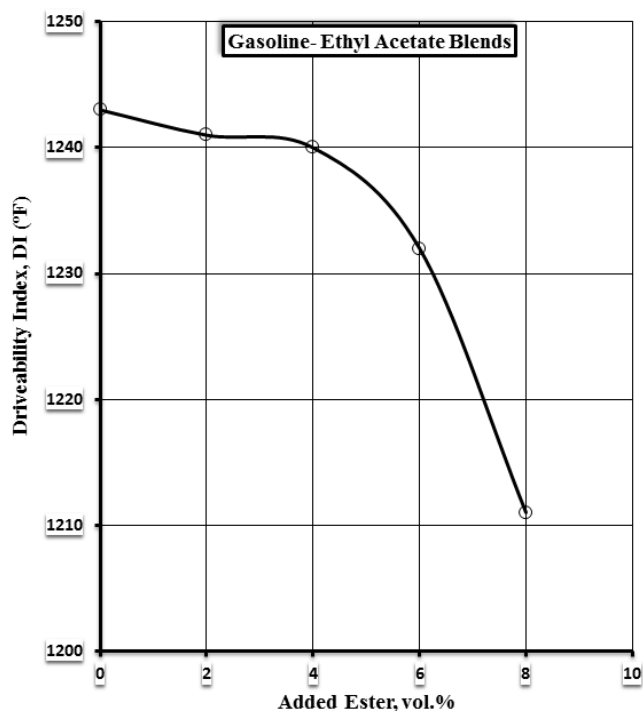


Fig. 9. Effect of Ethyl Acetate Addition on Drivability Index of Fuel Blends



Fig. 10. Effect of n-Butyl Acetate Addition on Drivability Index of Fuel Blends

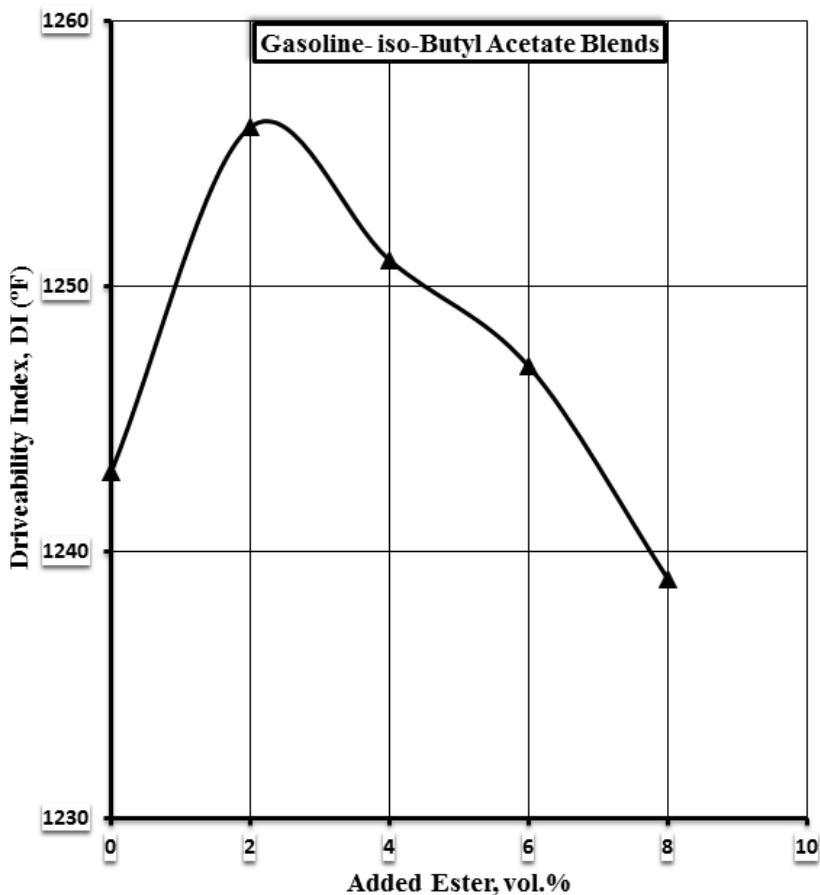


Fig. 11. Effect of Iso-Butyl Acetate Addition on Drivability Index of Fuel Blends

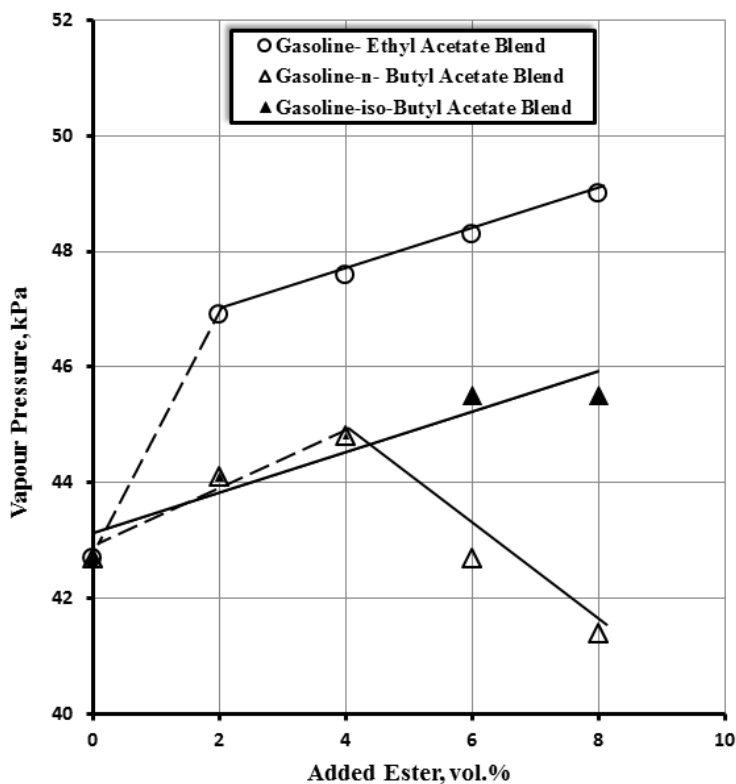


Fig. 12. Effect of Ethyl- and Butyl Acetate Addition on Vapour Pressure of Hydrocarbon- Base Gasoline

### 3.3.6. Vapour-Liquid ratio of ester blends

The preferred measure of vapour-locking tendencies of gasolines is expressed in terms of vapour-liquid ratio, or V/L. It is a more precise evaluation of relative vapour- locking qualities of gasolines than Reid vapour pressure (ASTM-D323). V/L ratio describes the volume of vapour relative to liquid that a gasoline forms (at equilibrium at 760 mm Hg pressure and any stated temperature). ASTM- D2533 has standardized a procedure for measuring directly the 20= V/L ratio of a gasoline sample at any temperature.

In the present study, temperature for V/L = 20 (°F or °C) was calculated through the linear equation method (ASTM - D4814) which provide the temperature in °C or °F from equation 4 or 5

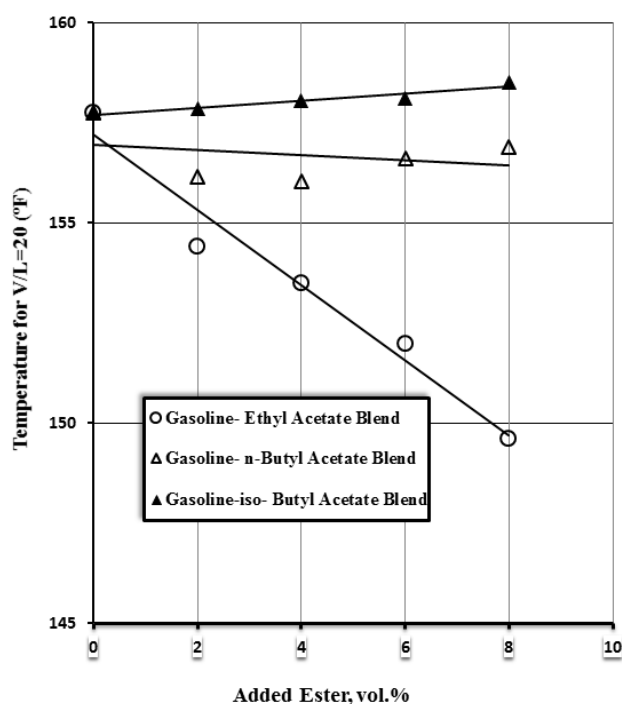
$$T_{V/L=20}(^{\circ}\text{F}) = 114.6 - 4.1 (\text{VP}) + 0.20 T_{10} + 0.17 T_{50} \quad (4)$$

where VP = psi,  $T_{10}$  and  $T_{50}$ , °F

$$T_{V/L=20}(^{\circ}\text{C}) = 52.47 - 0.33 (\text{VP}) + 0.20 T_{10} + 0.17 T_{50} \quad (5)$$

where VP = kPa,  $T_{10}$  and  $T_{50}$ , °C

Temperature (°F) for vapour- liquid ration of 20 ( $T_{V/L=20}$ ) were estimated for ester-free and ester-blended fuels, the obtained results are listed in Tables 4B, 5B and 6B. Data pictured in Figure 13 demonstrates that blending ethyl acetate and hydrocarbon-base gasoline at concentrations of 2, 4, 6 and 8 % by volume, significantly depresses the temperature for a vapour-liquid ratio of 20 ( $T_{V/L=20}$ ). It can be seen that this depression is a linear function of added ester. On the contrary, blending butyl acetate in hydrocarbon-base gasoline, at the same concentrations, gave insignificant impact on temperature for V/L=20 values as shown in Figure 13.



**Fig. 13.** Effect of Ethyl- and Butyl Acetate Addition on Temperature for V/L =20 of Hydrocarbon-Base Gasoline

Table 7 lists the ASTM – D4814-09b vapour lock Protection class requirements of the six vapour lock protection classes. All the measured  $T_{V/L=20}$  values, shown in Tables 4B, 5B and 6B, are above the ASTM values. It can be concluded that blending either ethyl or butyl acetate in hydrocarbon-base gasoline at concentrations of 2-8% by volume should not pose a problem for meeting the minimum temperature (°F) for a vapour liquid ratio of 20. ASTM-D4814-09b specification for gasoline-fuel has several vapour lock control specifications which apply at various months of the year and with geography. These specifications protect the consumer from vapour lock problems in summer time.

**Table 7:** ASTM-D4814-09b Vapour Lock Protection Class Requirements

Vapour Lock Protection Class	Minimum Temperature (°F) for a Vapour Liquid (V/L) Ratio of 20
1	129
2	122
3	116
4	116
5	105
6	95

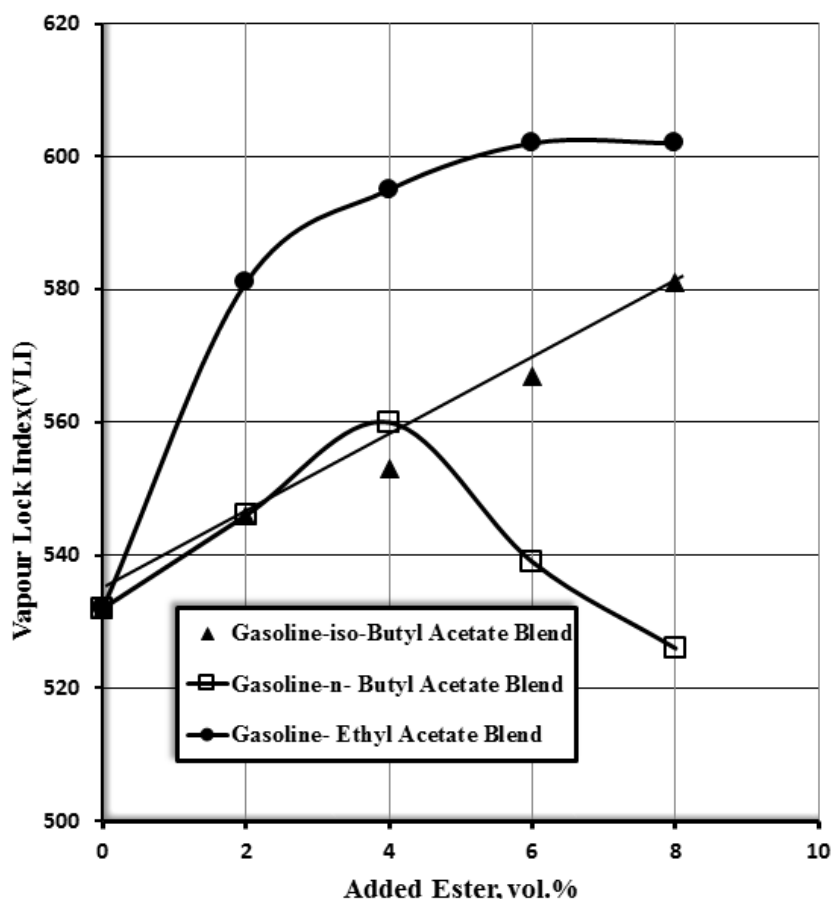
### 3.3.7. Vapour Lock Index of ester blends

In warm weather, gasoline which vapourises too easily will form bubbles of vapour in the fuel system which can prevent the easy flow of fuel. This is called vapour lock and the engine will stop because it is not receiving enough fuel. VLI is used to control vapour lock and other hot handling problems [41].

VLI is calculated using vapour pressure in kPa and the percent evaporated at 70 °C (158 °F) from the distillation profile, as follows

$$VLI = 10 (VP) + 7 (E70) \quad (6)$$

VLI varies with the season, the normal range is 800 to 1250. Lower values provide greater protection against vapour lock and hot fuel handling problems. Hydrocarbon-base gasoline has VLI value of 532. After blending with 2, 4, 6 and 8 vol. % of any of the employed esters, VLI values of the obtained blends do not exceed 602 (Tables 4B, 5B and 6B) which indicate that the evaluated gasoline-ester blends have the least tendency to cause vapour lock problem. The relation between VLI and added esters approaches linearity in case of iso- butyl acetate addition, Figure 14.



**Fig. 14.** Effect of Ethyl- and Butyl Acetate Addition on Vapour Lock Index of Hydrocarbon- Base Gasoline

#### 4. Conclusions

From this study the following conclusions can be drawn.

- 1) Ethyl acetate and butyl acetate proved to be good oxygenate gasoline additives.
- 2) The investigated gasoline-ester blends show good oxidation stability which permits safe storage time.
- 3) RON contribution of the blended ester oxygenates is reasonable if compared with that achieved with alcohol or ether oxygenates.
- 4) Linear decrease in calorific value of the obtained blend when plotted against ester- oxygenate concentration or oxygen content in the blend.
- 5) Insignificant change in the shape of distillation curve of butyl acetate blends, whereas the change observed in ethyl acetate blends substantiate that increase in volatility.
- 6) The investigated ester-free and ester- blended fuels, have driveability indexes within the specified normal range which permits good driveability and better cold start.

- 7) Neither the ester-free nor the ester-blended fuels, have  $T_{50}$  value below the minimum specified in ASTM-D4814.
- 8) Addition of 2-8 vol.% of ethyl acetate or iso-butyl acetate in the hydrocarbon-base gasoline, increases the vapour pressure of the obtained fuel blends.
- 9) Blending 2-8 vol. % of ethyl acetate into hydrocarbon base gasoline, significantly depresses the  $T_{V/L=20}$  ( $^{\circ}$ F) values, this depression is a linear function of added ester.
- 10) All the measured  $T_{V/L=20}$  values, are above the minimum temperature of vapour lock protection specified by the ASTM-D4814.
- 11) The evaluated gasoline-ester blends gave vapour lock index (VLI) values not exceeding 602 which indicate that these blends have the least tendency for vapour-lock problems.

## Acknowledgements

We would like to thank the Academy of Scientific Research and Technology- Egypt for the financial support. Thanks are extended to the Egyptian Petroleum Research Institute (EPRI), Cairo Oil Refining Co. and Mostorod Refinery Laboratories, for their valuable assistant.

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