# EXPERIMENTAL DETERMINATION OF DISTILLATION CURVES OF ALCOHOLS/GASOLINE BLENDS AS BIO-FUEL FOR SI ENGINES

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***Abstract:*** The use of oxygenates as a gasoline blend is one of production methods for high octane gasoline and reduction of harmful compounds amount in exhaust gas. Distillation curves are presented for single monohydroxy alcohols and gasoline mixtures containing 3-15% by volume of ethanol, 1-butanol and i-butanol (2-methyl-1-propanol) which can be obtained from renewable sources. The influence of various concentrations of these alcohols on the distillation characteristics of base gasoline were investigated. Most alcohols form mixtures with gasoline exhibiting near-azeotropic behavior near its boiling point that significantly affect the shape of the distillation curves. In addition, distillation curves for a variety of dual-alcohol blends are presented, containing 10-20% by volume of two alcohols.

**Key words**: DISTILLATION, GASOLINE, BLENDS, ETHANOL, 1-BUTANOL, I-BUTANOL

## *1.Introduction*

Constantly increasing fossil fuel prices led humanity to the search for alternative biofuels. Biofuel is a type of fuel which is derived from biological sources. The use of alcohols as blends of gasoline for ignition engines is very actual problem which is applied in the fields of fuel production and its applications. By the late 1990s ethanol had emerged as the predominant alcohol for blending with gasoline and flexible fuel vehicles were designed instead for ethanol blends. Currently ethanol is the most commonly used biofuel worldwide [1–4], however there is an increased interest in other alcoholic fuels especially 1-butanol and isobutanol [5, 6]. The fuel mixtures with these oxygenates in same cases have better properties than the regular gasoline. As oxygenates ethanol and 1-butanol are very usable mainly because they easily can be produced from biomass [7–9]. In addition to that they also meet the essential requirements for oxygenates which can be described as a high octane number, low toxicity and good performance [10]. Currently there is a great attention for the iso-butanol biosynthesis from the biomass of as well as the applications of this alcohol as a gasoline blend [11–14]. Moreover, the use of bio-based products in fuels is a strategic government resolution in most European countries.

Alcohols consists from hydrogen, carbon and oxygen - these compounds are oxygenates**.** Various researches have shown that the use of oxygenates not only increases combustion efficiency but also reduces the amount of CO, $NO_x$ and unburned fuel in the exhaust gas by about 40% thus reducing smog [15, 16]. The first-ranked monohydroxylic alcohols have high octane number which leads to the fact that they not only improve the combustion of gasoline, but also enhance the octane properties of its mixture. In the EU and US gasoline blends with 10% ethanol by volume (E10) are common, however one drawback ethanol has is that it is a very hygroscopic liquid thus it quite easily absorbs water from the surroundings. To minimize the risk of water-induced phase separation in the ethanol-gasoline blends, anhydrous ethanol is blended into gasoline at the terminal prior to shipping to retail gas stations.

With the development of second-generation biofuels it is possible that alcohols other than ethanol will enter the market. The usage of gasoline and 1-butanol mixtures in the spark ignition engines increase the detonation resistance, achieve higher gas compression and higher thermodynamic efficiency compared with the pure gasoline suggesting that 1-butanol as a higher quality oxygenate is more efficient than ethanol [17–21]. In addition, there is an increasing interest in gasoline that contains alcohol concentrations different from currently applied worldwide.

Prior to such an introduction, a detailed knowledge of the physical and chemical properties of alcohol-gasoline blends is required and their performance in engines and impact on emissions needs to be tested. It was found that gasoline with 10% ethanol blends reduce air polluting substances about 28%. The concentration of the CO emissions decreases as the ethanol content increase at the fuel blend due to the oxygen presence in the fuel molecules [22]. The investigation of a gasoline and 10% ethanol blend by volume confirm that a mixture can be used without engine modifications. One of the most important characteristic of gasoline it's volatility which is assessed by fractional composition of the distillation. When ethanol and methanol are blended with gasoline a positive azeotropic mixture is formed [23–26]. The ASTM D86 (EN: ISO3405) distillation curve represents the temperature of the fuel vapor versus the volumetric fraction of the fuel sample distilled. In a mixture, an azeotrope would manifest itself as a flat portion of the distillation curve at the boiling temperature of the azeotrope [23, 24]. While this is a necessary condition to verify that an azeotrope is present it should also be noted that a flattening of the curve can also be observed for azeotropic mixture dominated by one component. The fractional distillation composition is expressed in two ways: when the monitored temperature (°C) of distilled gasoline fractions and percentage (%) of the total gasoline up to temperature (E70, E100, E150) according to the standard ASTM D86 (EN: ISO3405) BS EN 228: 2013.

While knowing the temperature $t_{10}$ (°C) of analyzed gasoline's 10% distillation, an estimation can be done to calculate the lowest ambient temperature $t_p$ (°C) at which cold engine can be started [27]. This is calculated by using formula 1:

$$t_p = 0{,}5t_{10} - 50{,}5 \quad (1)$$

The lowest ambient temperature $t_g$ (°C) at which the vapor jams can be formed is calculated according to the formula 2:

$$t_g = 2t_{10} - 93 \quad (2)$$

The distillation curve provides insight into the boiling range of the fuel and can be used to predict its operation in engines. The low temperature region of the curve (up to 70 °C) E70 can be related to the startup of the engine, engine warm-up, evaporative emissions, and vapor lock (for carbureted vehicles). The middle range of the curve (70-100°C) E100 can be related to warm-up, acceleration, and cold-weather performance, while the top range of the curve (above 150°C) E150 relates to propensity for combustion deposits and oil dilution [28]. Although there is substantial interest in the potential use of different alcohols in blends with gasoline, the published database concerning distillation curves for alcohol-gasoline mixtures is incomplete. Some distillation curves for the mixtures of ethanol [29–30] and butanol blends with gasoline have been reported. The distillation curves of small quantity isobutanol blends have not been reported and only about 30%, 50% and 70% concentration of isobutanol mixtures with gasoline are reported [31]. Also, there is little data available concerning the behavior of mixtures of two or more alcohols (e.g., ethanol and butanol) with gasoline. In order to have a better understanding of the volatility of alcohol-gasoline blends and their utility as motor vehicle fuels, distillation curves for gasoline and blends of 3-15% ethanol, 1-butanol and i-butanol with gasoline were determined (Table1). In addition, we present distillation curves for dual-alcohol blends containing 10-20% by volume of two alcohols ethanol and 1-butanol, or ethanol and i-butanol, as well as 1-butanol and i-butanol in gasoline (Table 2). The applied of monohydroxylic alcohols, ethanol, 1-butanol and i-butanol (2-methyl-1-propanol) and their compositions in gasolines production were studied in this work. The influence of various concentrations of these alcohols on the main characteristics of base gasoline were investigated.

## *2. Prerequisites and means for solving the problem*

The fractional distillation composition is expressed in two ways: when the monitored temperature (°C) distilled of 10, 50, 90, 97% share of gasoline fractions and percentage (%) of the total gasoline, up to 70, 100, 150°C temperature (E70, E100, E150). According to the requirements of ASTM D86 (EN:ISO 3405) BS EN 228:2013 standard,distillation characteristics must comply with the E70 - 22-50% by volume; E100 - 46 to 71% by volume, E150 - not less than 75% by volume. In this study the following stocks were used:

1. Base gasoline from ORLEN Lietuva (non-commercial, oxygenate-free, without additives)
2. Dry ethanol from Biofuture and "MG Baltic"
3. 1-Butanol and i-butanol from Sigma-Aldrich.

Distillation points of gasoline with alcohols were measured by a computer-controlled ,,OptiDist" apparatus (PAC) (Figure 1).


***Fig. 1*** *,,OptiDist" apparatus.*

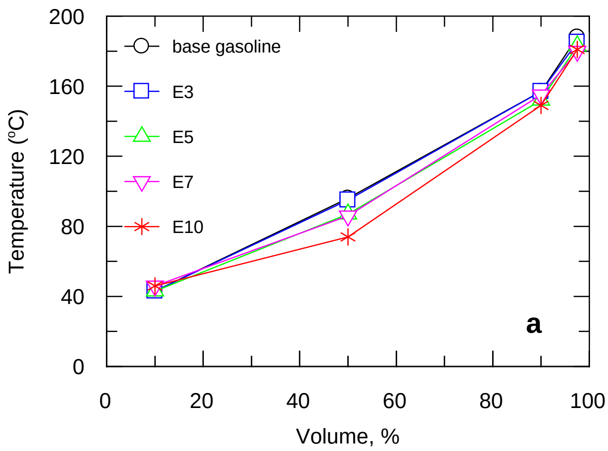
## *3. Results and discussion*

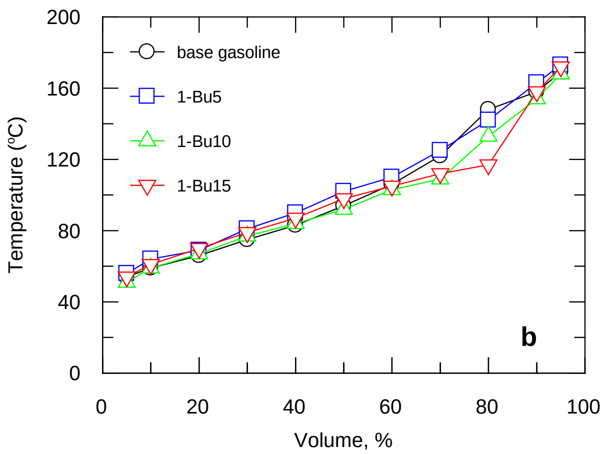
The fuel distillation curves reveal information on its opportunities to be deployed in the ignition engines. Various mixtures of base gasoline with single-alcohol blends and dual-alcohol blends of bio-fuels were investigated. The alcohol content in gasoline was constantly adjusted based on the oxygen quantity in the fuel, therefore mixtures with small quantities of alcohol were selected. The composition of all the mixtures is summarized, respectively in Table 1 and in Table 2.

***Table 1:*** *Single-alcohol blends with base gasoline.*

| Mixture | Gasoline (% by vol.) | Ethanol (% by vol.) | 1-Butanol (% by vol.) | i-Butanol (% by vol.) |
|---|---|---|---|---|
| E3 | 97 | 3 | | |
| E5 | 95 | 5 | | |
| E7 | 93 | 7 | | |
| E10 | 90 | 10 | | |
| 1-Bu5 | 95 | | 5 | |
| 1-Bu10 | 90 | | 10 | |
| 1-Bu15 | 85 | | 15 | |
| i-Bu3 | 97 | | | 3 |
| i-Bu5 | 95 | | | 5 |
| i-Bu7 | 93 | | | 7 |
| i-Bu10 | 90 | | | 10 |

The distillation curves of oxygenate-free gasoline A 92 with different volumes of ethanol (0%, 3%, 5%, 7% and 10%) are shown in Figure 2a; mixtures with butanol-1 (0% 5%, 10%, 15%) are shown in Figure 2b band mixtures with i-butanol (0%, 3%, 5%, 7%, 10%) are shown in Figure 2c.



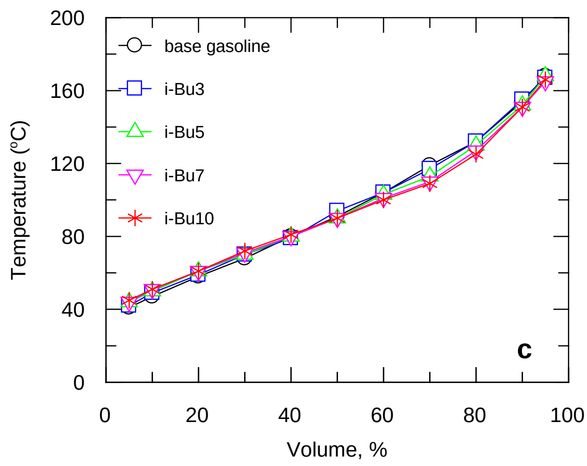



*__Fig. 2__ Distillation curves of base gasoline mixtures with ethanol (__a__), 1-butanol (__b__) and i-butanol (__c__).*

From the figures above it is noted that distillation temperatures of gasoline mixtures with ethanol or 1-butanol increase more slowly than the base gasoline from T20 to T70 and T100 to T160. The distillation curves for i-butanol blends are very similar to the ones of base gasoline. These observations indicate that ethanol and 1-butanol can form an azeotropic mixtures with the gasoline hydrocarbons. Investigation of ($t_{10}$) temperature trend shows that cold engine starts in a temperature of -55°C. From ($t_{50}$) temperature it is seen that engine has a better warming up properties as well as a reduced fuel consumption. This improves engine dynamism, e.g. facilitation of the transition from one mode to another. Temperatures $t_{90}$, and $t_{97,5}$ affect the economy of the engine and friction. The higher the temperature ($t_{90}$), the higher fuel quantity is consumed by the engine [27]. It was found that higher ethanol blend temperatures ($t_{10}$) and ($t_{50}$) slightly decrease (shown in the mixtures Fig. 2a). The increased concentration of 1-butanol (Fig. 2b) shows that the temperatures ($t_{10}$) and ($t_{50}$) are slightly increasing, but for i-butanol Fig. 2c the temperatures ($t_{10}$) and ($t_{50}$) are very similar to the trends of base gasoline. During the test distillation curves, the results showed that the increased oxygenate concentration in the mixtures of different alcohols decreases the temperatures ($t_{90}$), and ($t_{97,5}$).

The different composition of ethanol, 1-butanol and i-butanol were used as a dual-alcohol blends for gasoline. Full data of gasoline blends presented in Table2.

***Table 2:** Dual-alcohol blends with base gasoline.*

| Mixture | Gasoline (% by vol.) | Ethanol (% by vol.) | 1-Butanol (% by vol.) | i-Butanol (% by vol.) |
|---|---|---|---|---|
| E5, 1-Bu10 | 85 | 5 | 10 | |
| E10, 1-Bu5 | 85 | 10 | 5 | |
| E10, 1-Bu10 | 80 | 10 | 10 | |
| E3, i-Bu7 | 90 | 3 | | 7 |
| E5, i-Bu5 | 90 | 5 | | 5 |
| E7, i-Bu3 | 90 | 7 | | 3 |
| 1Bu10, i-Bu5 | 85 | | 10 | 5 |
| 1Bu10, i-Bu7 | 83 | | 10 | 7 |
| 1Bu10, i-Bu10 | 80 | | 10 | 10 |

The results showed (Figure 3a) that the distillation curve of ethanol–1-butanol–gasoline from T15 to T60 is higher than gasoline, and from T140 is below. Only the ending distillation has a very similar look compared to the basic gasoline distillation curve, and $t_{10}$, $t_{90}$, $t_{97,5}$ are the same as those of gasoline, while $t_{50}$ is lower. The distillation of mixtures ethanol–i-butanol–gasoline from T40 to T140 takes place at lower temperatures than gasoline, but distillation from the beginning to the T40 and from T140 is same again (Figure 3b). In conclusion $t_{10}$, $t_{90}$, $t_{97,5}$ are the same as those of gasoline, only $t_{50}$ is lower.

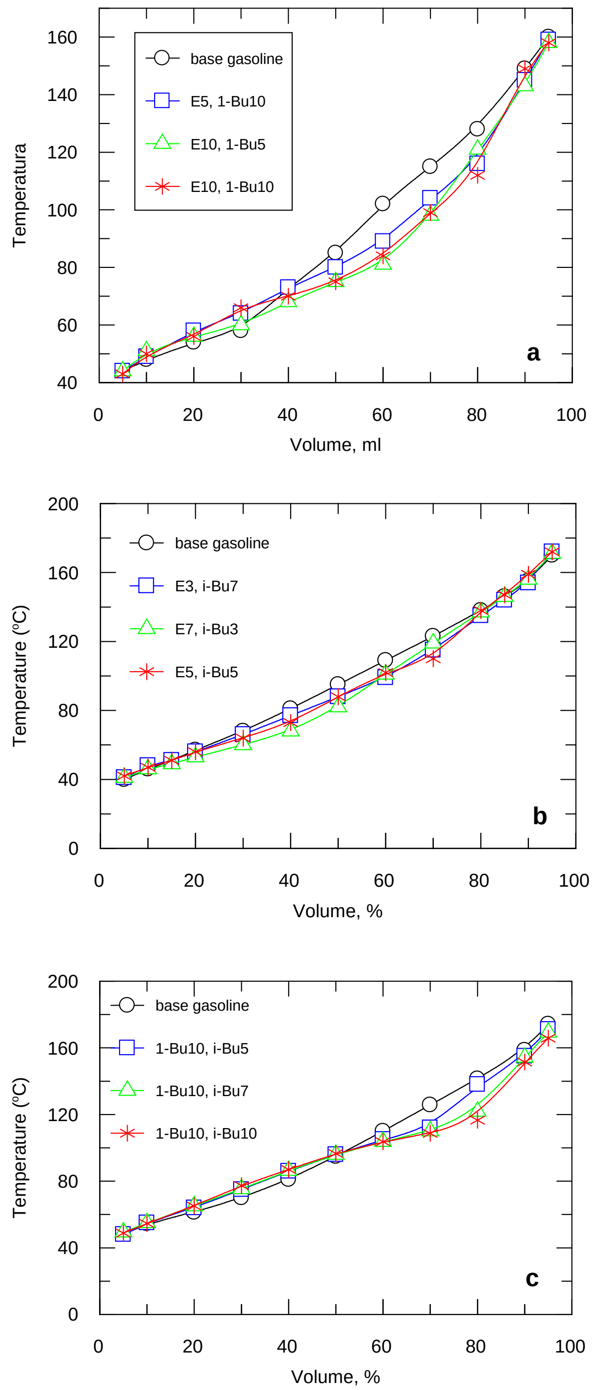



*__Fig. 3__ Distillation curves of base gasoline blends with ethanol ÷ 1-butanol (a), ethanol ÷ i-butanol (b) and 1-butanol ÷ i-butanol (c).*

For the gasoline mixtures shown in Figure 3c distillation curves from T50 to T90 are located higher than base gasoline distillation curve. Based on T90 we can note that the mixtures boil at a lower temperature than the base gasoline and the temperature of distillation depends from the concentration of alcohols. In conclusion the mixtures in comparison with base gasoline have temperatures of $t_{10}$, $t_{90}$, $t_{97,5}$, while $t_{50}$ temperatures are the same.

## 4. Conclusion

As conclusions of the experiments performed and described above the following points are made:

1. Experimental results showed that gasoline mixtures with both ethanol and butanol have the same tendency bend at the points of their blended alcohol boiling temperature – this is the feature of azeotropic mixtures.
2. The results showed that a gasoline blend with two different alcohols provides better influence towards engine operability than a gasoline blend containing higher concentration of one alcohol (a gasoline blend with 15% butanol versus a gasoline blend with 10% ethanol and 5% butanol). This is based on distillation trend in a region of T20-T70 results.
3. Currently worldwide ethanol is the most commonly used oxygenate, however positive experiment results with blends of two different alcohols or higher-chain alcohols such as butanol or i-butanol draw a positive view for the future as these alcohols could be used more advantageously than only ethanol itself.

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