



## Research Paper

## Thermal behavior and kinetics assessment of ethanol/gasoline blends during combustion by thermogravimetric analysis

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## HIGHLIGHTS

- Kinetic parameters of thermal decomposition events were obtained.
- Thermal analysis was used as a tool for understanding combustion processes.
- Blends would be classified using thermogravimetric analysis technics.
- Synergistic effect of ethanol mixed with gasoline was studied and defined.
- Relative error and activation energy values were used to analyze the synergy.

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## ABSTRACT

The use of ethanol as a fuel or as an additive blended with gasoline is very important for most countries, which aim to reduce the heavy dependence on fossil fuels and mitigate greenhouse gases emission. An increased use of ethanol-gasoline blends has placed great relevance on acquiring knowledge about their physical and chemical properties. Thus, knowledge of such properties favors a better understanding of the effect of the percentage of ethanol/gasoline blends on engine performance. Thence, the present study has established a correlation between activation energy and synergetic effects, obtained by a thermal analysis, and ethanol content in gasoline for different blends in order to use this technique as a tool to classify these blends in the process in order to obtain useful energy in spark ignition engines. For such a purpose, a kinetic study has been conducted through a simultaneous thermal analysis system – TGA (thermogravimetry analysis) and DTA (differential thermal analysis) by following the methodology of non-isothermal tests. Thermogravimetric tests were performed and fuel activation energies for gasoline, ethanol, and percentages of 5, 10, 15, 20, 25, 30, 50, and 75% (%v) ethanol mixed with gasoline, which was achieved by the model free kinetics. The analysis results suggest that the theoretical curves characteristics of the thermal decomposition of ethanol-gasoline blends are rather different due to their ethanol content. Furthermore, it was observed significant interactions and synergistic effects, especially regarding those with low ethanol percentage. In conclusion, the thermal analysis techniques can be used as a tool for liquid fuel rating.

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## 1. Introduction

Energy is one of the most important factors that promote economic and industrial development. Fossil fuel combustion accounted for over 80% of primary energy use in the world in 2013 [1]. Global population growth has increased population mobility, and the production and consumption of goods, whose

transportation means are considerable concerns as regards future energy strategies.

Oil cost variations and a desire to improve energy security in countries with limited oil resources are common concerns [2]. If compared to gasoline, ethanol has a greater octane number and latent heat of vaporization, which allows obtaining higher compression ratio and, consequently, increased thermal efficiency and a decrease in the emission of gases which are harmful to the environment [3]. Ethanol has a higher burning rate which can also help increase combustion efficiency and minimize energy loss [4,5].

Alcohols mixed with gasoline are interesting alternatives to reduce pollutant emissions and fossil fuel consumption. This is

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because they contain oxygen in their molecule, are highly volatile fuels, furthermore, blends with hydrated ethanol have small amounts of water in their composition, which allows reducing the temperature in the combustion chamber, thus improving efficiency and reducing the emission of NO<sub>x</sub> [6]. Moreover, low-carbon alcohols (ethanol) lead to nearly zero particulate matter emissions [2]. These characteristics are generally favorable for good combustion.

Overall needs for both reducing the dependence on fossil fuels and mitigating greenhouse gases emission have led to seeking highly relevant knowledge in order to understand the ethanol content effect of ethanol-gasoline blends on their physicochemical properties and engine performance. In the short and medium term, ethanol mixed with gasoline is the biofuel with the greatest potential to be used worldwide in light passenger vehicles [6]. This scenario is due to the technology which has been used in current flexible fuel engines and small changes that must be made in conventional Otto cycle engines so as to adapt them to the use of lower ethanol content in gasoline, which may vary from 10% to 20% [7].

According to the development of future availability of ethanol scenarios in the United States, it was estimated that large increases from 4 to 7 points in gasoline RON (Research Octane Number) will be possible by increasing the ethanol content of the blend to 10% [8]. The use of ethanol-gasoline blends has become a reality in many countries, such as the United States, Brazil, Colombia, Thailand, India, China, and Canada [9], which manufacture vehicles with flexible fuel technology in their internal combustion engines that can use blends with up to 85% (USA) and 100% (Brazil) of hydrous ethanol or gasoline [7], while blends with low ethanol content require the use of anhydrous ethanol. All countries that have been using such blends have plans to increase the ethanol content in the gasoline, either as additive or fuel [9].

In pure fuels, a different set of reactions and chemical species must be determined individually in order to describe the reaction mechanism. Moreover, when different fuels are mixed, there may be cross-reactivity of intermediate species, which makes it necessary to include other additional reaction mixtures in the engine [10]. In addition, ethanol content in gasoline affects the vapor pressure of the fuel. Blends with low ethanol content, between 1% and 30%, are more volatile than pure gasoline, and even more volatile than pure ethanol [11].

Particular interest should be given to knowing whether ethanol-gasoline blends have the same behavior as the one observed in the vapor pressure to obtain energy, as it would indicate the use of smaller quantities of gasoline in the blends with low ethanol content to obtain the same amount of energy. The previous behavior can be defined as the synergistic effect of ethanol-gasoline blends.

It is considered the application of thermal analysis techniques, such as the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) which have been widely accepted in the study of fossil fuels and biofuel combustion [12]. This technique has also been widely used to obtain the kinetic parameters of thermal decomposition events [13–17] and to conduct an analysis of the synergism between blends [18–21].

There are some studies in literature on thermal analysis to evaluate the synergism of solid fuel blends in the combustion of different blends, e.g. coal and biomass [18], biomass and plastic mixtures [19], oil shale semi-coke and torrefied cornstalk [20]. However, the study of synergism through liquid fuels is still little explored in literature, and works on the interaction effect on the thermal decomposition of ethanol-gasoline blends were not found<sup>1</sup>.

In this context, the development of a methodology for testing ethanol-gasoline blends by using thermal analysis techniques in order to classify the blends according to their most important characteristics for the combustion process emerges as one of the main aims of this work. The thermal analysis can be used as a tool for understanding combustion processes, which is considered economic, quick and simple in comparison with other tests for fuel rating [22].

## 2. Materials and methods

### 2.1. Sample preparation

Gasoline type A (Table 1) is one produced by oil refineries, which is delivered directly to distributors without being mixed with ethanol. It is a mixture of naphtha in quantities that meet the product specification laid down by the ANP. The present work uses gasoline type A, which was kindly provided by REVAP which is one of Petrobras refineries.

The term ethanol refers to ethyl alcohol that is marketed in two forms, hydrated (95% to 96%) and dry ( $\geq 99.5\%$ ). The anhydrous ethanol (Table 1) used for the tests performed in this work was purchased from a commercial laboratory (Table 1).

The percentage proportion (%v) of ethanol in ethanol-gasoline blends is commonly preceded by the letter E, i.e. mixture E5 is composed of 5% ethanol and 95% gasoline (%v). Samples of pure gasoline type A (E0), pure ethanol (E100), and their blends were used at a proportion of 5% to 75% ethanol to form blends E5, E10, E15, E20, E30, E50, and E75.

### 2.2. Thermal analysis

Thermal analysis experiments were performed through a TA Instruments high-resolution system (SDT Q600), which allows conducting TGA and DTA tests simultaneously. The thermogravimetric analysis (TGA) measures the weight loss of a sample as a function of increasing temperature, whose result is represented by the TGA curve (weight  $\times$  temperature). DTG curve (derivative of the TG curve) represents the change rate in the sample weight. The differential thermal analysis (DTA) measures the temperature difference between a sample and a reference material as a function of temperature in the process of weight loss while samples and materials are being subjected to a controlled temperature program [23].

For high-volatility materials, mass measurement is critical and the initial sample mass for all tests should be with an amazing degree of accuracy. To improve its accuracy, a precision pipette (10  $\mu$ L) and a crucible with a lid were used. In addition, both the initial temperature of the test and the environment temperature were controlled. Initially, the sample was added to the crucible with a mass of around 5% higher. Once the volatilization of the sample has reached the desired mass, the test was started.

Prior to testing, the samples were stored under refrigeration  $5 \pm 0.5$  °C and the initial temperature of test was set at 18 °C. The

**Table 1**  
Fuel properties of Brazilian gasoline type A and ethanol.

| Properties            | Ethanol <sup>a</sup> | Gasoline <sup>b</sup> |
|-----------------------|----------------------|-----------------------|
| Degree GL             | 99.5                 | 0                     |
| Ant knock index (AKI) | 106                  | 90.9                  |
| Density               | 0.79 kg/L (20 °C)    | 0.743 kg/L (20 °C)    |
| Lower heating value   | 27 MJ/kg             | 44 MJ/kg              |
| Heat of vaporization  | 904 J/g              | 346.7 J/g             |

<sup>1</sup> The key words used in the research were: Ethanol-gasoline blends, synergics, interaction, TGA, DTG.

<sup>a</sup> QUIMESP. Analysis report. Absolut alcohol.

<sup>b</sup> PETROBRAS. Analysis report. Certificate 2630 – 15 G.

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