



EVALUATION OF METHODOLOGIES EMPLOYED TO ANALYSIS FOR FUEL BLENDS APPLIED TO SPARK-IGNITION ENGINES

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Abstract. *Ethanol-Gasoline blends have great application potential in the world. In Colombia, there is little experience with ethanol-gasoline blends research, and knowledge on its properties which is essential for new engine development. According to experts in the automotive sector, Brazilian flex-fuel vehicles that are run on blends have lower efficiency when compared to engines that are run on gasoline, taking into account that ethanol has the potential to have higher efficiency. Therefore it is necessary to gather engineering knowledge to the development and calibration of engines that work with ethanol-gasoline blends. There is still a need to characterize mixtures of these two components in order to contribute to the optimization of the process of obtaining energy during the combustion process, depending on the ethanol amount in the gasoline. The most commonly used thermal analysis techniques are thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry. These techniques are quick and efficient to obtain kinetic parameters of fuels in the combustion process, depending on the heating rate or the temperature rate. In this paper, it is performed a brief literature review concerning the experimental studies focused on the evaluation of fuel blends, especially the ethanol/gasoline blends that are run on the thermogravimetry tests. The obtained results allowed a better understanding of the fuel blends kinetics for the optimization of the engine's design and the development of more accurate simulation models.*

Keywords: *fuel mixtures, internal combustion engine, thermal analysis techniques, ethanol.*

1. INTRODUCTION

Ethanol and biodiesel are fundamental parts of the energy basket of any country to reduce their dependence on fossil fuels and greenhouse gases generated in the transport sector. They also bring social benefits in the development of the field with biofuel crops where Latin America shows great potential (Masiero – Lopez 2008).

There is still much uncertainty about the availability of some countries to produce biofuels without affecting vegetable products from the food chain in a sufficient scale to make their production economically feasible and in necessary amounts to have a positive impact on the environment. In conclusion, the future of biofuels in a medium and long term is going to be ethanol blends with fossil fuels in low and medium volume percentages.

Biofuels derived from plants are being used in blends as viable supplements to petroleum fuels, but have an open way for a possible replacement with a few technical changes in the combustion equipment (engines, burners).

It is also important to evaluate aspects of the combustion of biofuels, and to compare them with conventional fuels, including ignition, oxidation and potential toxic emissions.

The chemical kinetic processes of biofuels blends combustion are similar to those of petroleum fuels, and their end products are primarily carbon dioxide and water, although there are many intermediate species produced during the combustion of biofuels that are not present in the combustion of conventional fuels. Furthermore, unlike fossil fuels, they contain oxygen within their primary fuel molecules, which can have different intermediate species, and the types and reaction pathways of ignition processes and oxidation may also produce different chemical contaminants in the emissions (Westbrook et al 2011).

The most widely used biofuel blends with conventional gasoline to be used in spark ignition engines are ethanol and methanol, while other types of biofuels derived from vegetable oils (biodiesel) are very useful as a complement, or as a replacement of conventional fuels in combustion diesel engines.

In short and medium terms, the ethanol mixed with gasoline is the most promising biofuel to be worldwide used in light passenger vehicles. This is due to the availability of ethanol, the "flex fuel" engine technology and a few changes that must be made to conventional Otto cycle engines to use small amounts of ethanol in the gasoline, up to 15% or 20%.

The global needs of ethanol as fuel to reduce the dependence on fossil fuels, to mitigate greenhouse gases, and the potential shown by biofuel-producing countries, has great relevance for understanding the physical and chemical

properties of ethanol and gasoline mixtures. Thus, knowledge on these parameters enables a better understanding of the effect of the ethanol percentage in the mixture with gasoline for the engine's performance.

Better understanding gasoline-ethanol blends is going to be, in a near future, essential to develop devices that highly improve the combustion's efficiency of these blends, resulting in the mitigation of pollutants into the atmosphere in the cities with the highest density of vehicles and thus, in general, reducing greenhouse gases.

Gasoline and ethanol are widely studied individually, and their physicochemical characteristics are well-defined. However, there is still a need to characterize mixtures of these two components in order to contribute to the optimization of the process of obtaining energy during the combustion, depending on the ethanol content in the gasoline.

One of the most important properties for the engine's combustion in any fuel is the ignition delay which is associated with some undesirable characteristics, such as engine noise, high stress and generation of greenhouse gases (Heywood 1988).

Ignition delay is the time period between the fuel inlet to the combustion chamber and the start of combustion. This period consists of two parts: physical and chemical delay.

The physical delay occurs when the fuel is sprayed and mixed with the combustion air which, in the case of combustion with carburetors and injected systems, the mixture is in the intake port. This time fraction is relatively large, which is the opposite of direct injection engines where the delay is much shorter.

Chemical delay is the time it takes to break down heavy hydrocarbon fractions into lighter fractions before the combustion. The speed with which these light fractions are generated is the parameter that defines the combustion start. These reactions occur when the fuel is mixed with oxygen.

Because of the two periods overlap, it is very difficult to define when one ends and when the other one begins, so that the two of them together form the pre-ignition time which determines the ignition delay (Heywood 1988).

According to Conconi-Crnkovic (2013), the ignition delay is strongly related to the activation energy, thus it is an important parameter for evaluating the quality of fuels. For the lower activation energy, the combustion will be easier. Given this direct relation, it can make a quality classification of the different fuels based on their activation energy periods.

Thermal analysis techniques have been used as tools in understanding the process of combustion and pyrolysis, which allow studying their kinetic characteristics, among others, to be used in the simulation of fuel combustion. The most frequently used techniques are Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). TG, DTA and DSC assays are quick and efficient in determining the kinetic parameters of the process of fuel combustion, depending on the heating rate or the temperature rate.

Thermal analysis TG, DTG and DSC techniques are widely used in the analysis of the activation energy of a fuel because they are easy tests with fast results and a low cost.

Since very little is known about the combustion kinetics of fuel blends, mainly regarding gasoline/ethanol blends, this paper presents the determination of activation energy of gasoline, ethanol and their blends. Thermogravimetric analyses were performed and the model-free kinetic was applied to the fuels evaluated in the region of thermal decomposition. In addition, prior to the thermogravimetric tests, a brief literature review was conducted.

2. EXPERIMENTAL

2.1 Materials and Procedures

Gasoline samples from Petrobrás S.A. and commercial anhydrous ethanol (99.5%) were used. Five fuel samples were evaluated, considering different percentages of gasoline and ethanol. The thermogravimetric experiments were performed in a Shimadzu TGA-51H analyzer and under non-isothermal conditions, with temperature ranging from room temperature up to 150°C, applying three different heating rates (10, 20, and 30 °C min⁻¹) in dynamic air atmospheres. Samples of 15±0.5 mg were used in all experiments.

Ethanol can be blended with gasoline to form ethanol-gasoline blends, identified by an 'E' followed by the volumetric percentage of ethanol in the blend (E5, E10, and E85 are common blends).

The samples used for the present thermogravimetric analysis was pure gasoline (E0), anhydrous ethanol (E100) and three gasoline/ethanol blends in the proportion of 75:25 (E25), 50:50 (E50) and 25:75 (E75).

2.2 Kinetic Method

Activation energy of gasoline, ethanol, and their blends were obtained using non-isothermal thermogravimetric (TG) experiments and applying the Model-Free Kinetics.

The reaction rate of a chemical reaction depends on conversion, temperature and time. Conversion is defined as in Eq. (1), where m is the sample mass that varies with time, m_0 is the initial sample mass and m_∞ is the final sample mass.

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

The activation energy (E_α) is obtained as a function of the conversion, given by Eq. (2), where T is the temperature, $g(\alpha)$ is the reaction model, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. The subscript α represents the value related to a given conversion (α).

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R} \frac{1}{T_\alpha} \quad (2)$$

In Eq. (2), there is still a dependence from model $g(\alpha)$ but one of the main advantages of this method is that it isolate the function $g(\alpha)$ in the linear coefficient and estimating E_α as a function of α without choosing the reaction model. Therefore, the determination of this function in a complex process is very difficult (Wendlandt 1986) and when it is incorrectly assumed, it may lead to errors in determining the kinetic parameters (Benjumea *et al* 2011).

To apply the Model-Free Kinetics method it is necessary to obtain at least three different heating rates (β) and respective conversion curves evaluated from the TG curves measured (Vyazovkin *et al* 1996). For each α value, $\ln(\beta/T_\alpha^2)$ is plotted against $1/T_\alpha$. The method of least squares (linear regression) is then applied to establish the straight lines whose slopes ($-E_\alpha/R$) provide the values of activation energy.

3. RESULTS AND DISCUSSION

3.1 Literature Review

Thermogravimetric techniques have been widely accepted in the study of the kinetics of fossil fuels combustion for a long time, but nowadays, biofuels are used instead.

At the beginning of the twentieth century, it was described an instrument that would analyze the effect of heat on a substance. This instrument is known as thermobalance which contained a torsional quartz microbalance inside in an electric furnace for analyzing the weight loss as a function of temperature by heating zirconia and other minerals. The first commercial thermobalance emerged in the United States, and was built by the laboratories of Niagra Electronics in 1949. In this case, the employed analysis technique is thermogravimetry (temperature and gravimetry: measuring the change in mass) (Oliveira 2010).

Tadema (1956) is recognized in literature review as one of the first researchers to use thermal analysis to study the effects of combining different crude oils and clays in combustion. The author shows that there are two main reactions at a low temperature and a high temperature when the DTA technique is applied in petroleum crude oils.

In Brazil, there have been various works with crude oils, with special attention to the research work of Crnkovic *et al* (2012). They analyze the activation energy for three heavy crude, applying TG / DTG and DTA curves. It was observed that there are three sets of reactions that occur in three different ranges of temperature.

Thermogravimetry is universally applied in analytical problems, including the study of petroleum-derived products. Furthermore, many of these products are validated with the thermal analysis (Leiva *et al*, 2005).

In the case of liquid fuels derived from petroleum, as diesel, kerosene, gasoline and others, there are very few works with thermogravimetric analyses for these fuels. Rustshev (1990) summarizes the main works in this area, concluding that there is a great use of thermogravimetry combined with other techniques for the analysis of these fuels.

In the area of renewable fuels or biofuels, it has many thermal analysis studies on biodiesel derived from vegetable oils. Oliveira (2010) investigated the behavior of some biodiesel from three different crop sources in two different types of atmosphere, nitrogen and oxygen.

One of the most studied sources of oil for biodiesel production is the *jatropha curcas*. This fuel is analyzed by different researchers using thermal analysis. The most representative authors in these works are: Singh Chouhan *et al* (2013), Freire *et al* (2009), Jain & Sharma (2012), and Rodriguez *et al* (2011). They analyze the physical stability, the activation energy, cloud point, cold flow, among other characteristics of the biofuel.

Crnkovic *et al* (2012), Oliveira (2010), Jain & Sharma (2010) have some works on thermal analysis for biodiesel deriving from oil animal. They showed that these biodiesel has features like cloud point, cold flow, and is poorer than biodiesel derived from vegetable oils.

Another biofuel with worldwide potential application is ethanol. Nevertheless, there are few studies that investigate the thermal stability of ethanol or their mixtures with diesel, gasoline or biodiesel.

Li, Su *et al* (2012) conducted research on second generation ethanol from a cellulosic bamboo material. This paper shows the process of preparing bamboo cellulosic material which is irradiated with ultrasound in an ethanol solution to dilute lignin. Afterwards, soluble fractions of lignocellulose ethanol were obtained. These fractions were subjected to

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various tests, including TG and DTG to comparatively obtain their thermal stability. The irradiated samples show higher thermal stability and a higher content of lignin when compared to non-irradiated ones.

Laza, Berczky (2011) studied mixtures of seed oils and ethanol, analyzing the thermal stability of the mixtures and changes in viscosity. In all studied cases, the oxidative degradation begins at a temperature which is below the thermal degradation. The TGA and DTG curves confirmed that part of the ethanol, which has a lower boiling point, is kept in the mixture even above 100° C. Therefore, the ethanol has no other effect on the evaporation of the mixture rather than to lower the viscosity.

Pau Soto (2005) deals with Combustions rates in a chemical kinetic analysis of ethanol-gasoline blends. According to this author, "The activation energy is a conventional magnitude, determined by slower processing steps which are those that limit the speed of the reaction throughout the whole. Therefore, as the oxidation reactions in the combustion process in engines must develop sufficiently high speeds, ethanol is burned faster than gasoline, favoring the combustion process, since gasoline has complex chemical reactions."

Considering that very little is known about the combustion process of alternative fuels, like gasoline-ethanol blends, mainly regarding the pre-ignition chemical reactions and taking into account that there are still few studies that show the determination of kinetic parameters for biofuels and their mixtures with gasoline, a thermogravimetric analysis was carried out by the authors.

3.2 Activation Energy Determination

Samples of gasoline, ethanol, and three gasoline/ethanol blends in the proportion of E25, E50 and E75 were evaluated. Figures 1a and 1b show the TG (thermogravimetric) and DTG (Derivative thermogravimetric) curves with a heating rate of 15 °C min⁻¹ for all samples. These figures show the curves for only one heating rate in order to present the different behavior of thermal decomposition. However, for other heating rates (10 and 20 °C min⁻¹), similar profiles were obtained.

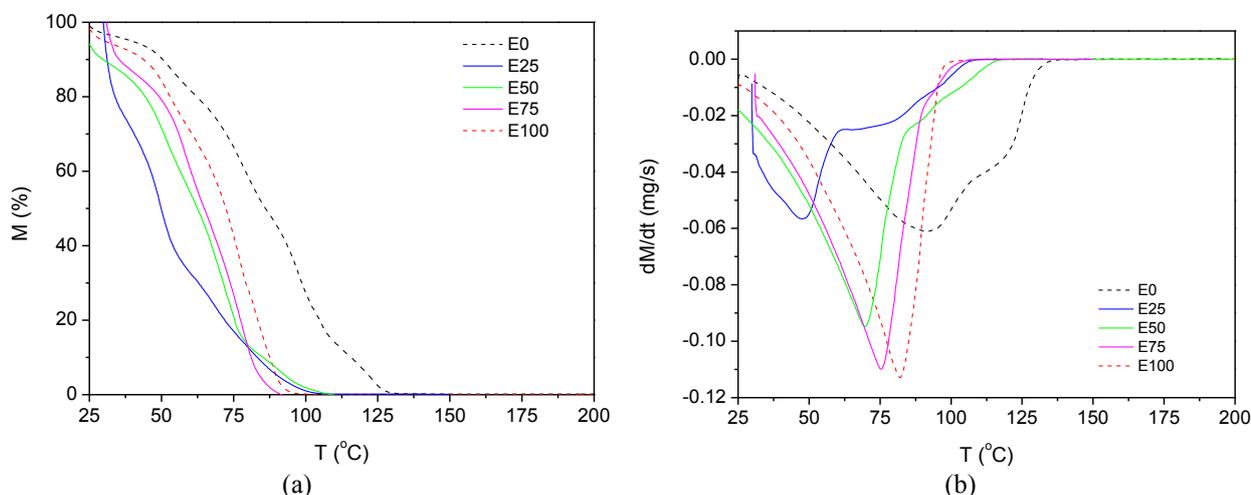


Figure 1. (a) TG and (b) DTG curves for all samples at heating rate of 15 °C min⁻¹. Sample mass of (15±0.5) mg was used in air atmosphere at 100 ml min⁻¹.

In these non-isothermal experiments, two region of thermal decomposition can be observed and distinguished for the ethanol sample. The thermal decomposition of gasoline and other three blends was observed within two reaction regions. The different decomposition regions for the samples were distinguished through DTG curves, in which a series of peaks are obtained. When compared to gasoline, it is observed that the addition of ethanol into the gasoline has led to a decrease in the onset and burnout temperatures, and the lowest temperatures were observed to sample E25.

The activation energy of the thermal decomposition can be associated with the quality of the fuel in the ignition step of a combustion process.

Figure 2 shows the conversion plotted in function of temperature for all different heating rates of gasoline, ethanol and their three blended samples. To examine the thermal stability of the samples, all fractions showed analogous degradation profiles. It is possible to observe that all conversion curves were shifted to a higher temperature with an increasing heating rate, but it also depends on the ethanol content.

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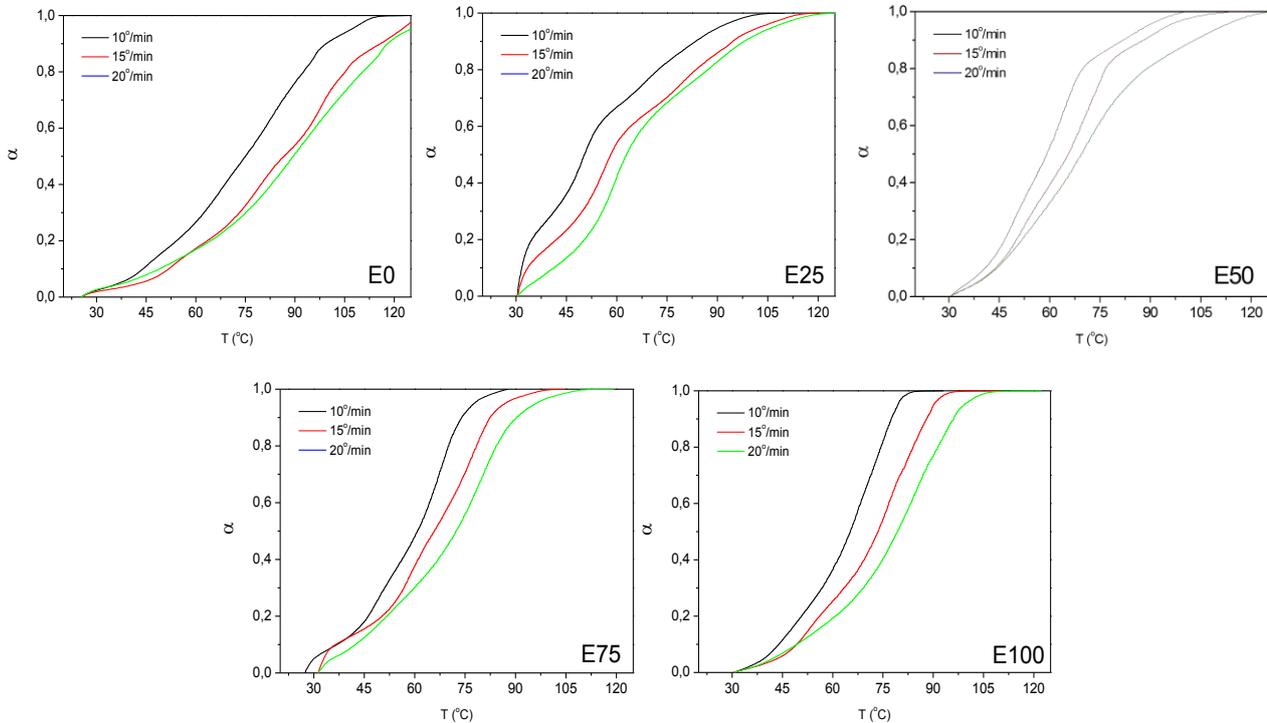


Figure 2. Conversion plotted against temperature for all the fuel samples. Conversion range normalized for 0 to 1.

The thermal degradation curves in fig. 2 show a constant ethanol evaporation profile because it is a pure element. It just depends on the heating rate defined in each test. Curves of mixtures of gasoline and ethanol show different stages of evaporation due to gasoline being a composite of many different elements that possess complex chemical reactions, according to Pau Soto's report (2005).

By plotting $\ln(\beta/T\alpha^2)$ against $1/T\alpha$, one obtains a line with a slope of $-E\alpha/R$, and a different line with independent slope is obtained for each level of conversion. Table 1 shows the activation energy values corresponding to these conversions degrees. Based on this principle and applying the least squares method, the activation energy can be plotted as a function of the conversion in all samples, as shown in Figure 3.

To the activation energy values shown in Table 1, they are taken only in a range between 10% and 90% of the conversion curve; due to scattered values, out of this range, are not taken into account to avoid affecting the average value.

Table 1: Standard deviation, minimum and maximum values of activation energy for all fuel samples, considering α range from 0.1 to 0.9.

Parameters	Activation Energy (kJ/mol)				
	Gasoline	Ethanol	E25	E50	E75
Mean value	40.86	45.80	39.43	64.05	58.67
Standard deviation	4.95	10.30	3.96	30.16	18.81
Minimum value	32.51	33.93	30.76	26.52	38.49
Maximum value	55.58	83.46	45.65	145.26	119.39

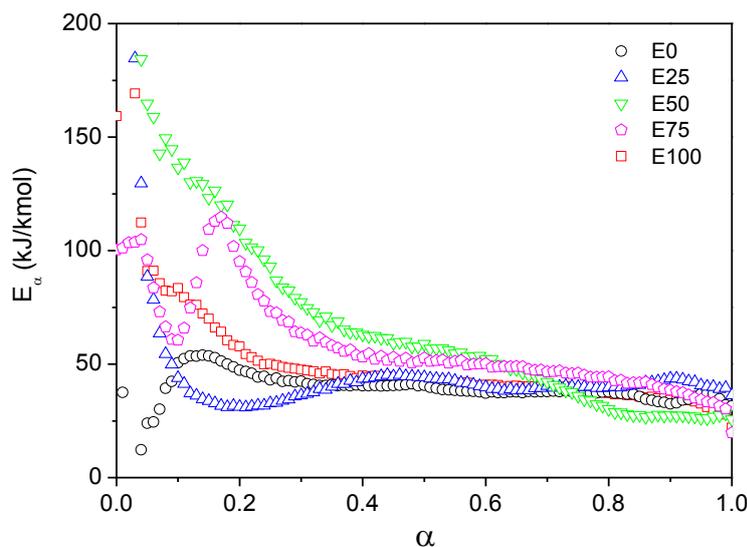


Figure 3. Activation energy against conversion for all fuel samples.

Fig. 3 shows that there are two well-demarcated regions for changing the activation energy into the conversion value. At the first stage for all samples containing ethanol, high values of activation energy are shown, while this value begins low and then increases at one-fifth of the test for pure gasoline, as it can be seen in fig. 3. Then, it remains constant until the end. These kinetic energy high values are consistent with the antiknock property of ethanol in gasoline blending, allowing an increase in the compression ratio of the engine to obtain higher efficiency in the combustion, which is a well-known feature of this biofuel (Anderson et al, 2012).

Pure gasoline reaches the maximum activation energy ($55.58 \text{ kJ mol}^{-1}$) at a conversion of 0.12 with a slight decrease run afterwards, reaching the mean activation energy of $40.86 \text{ kJ mol}^{-1}$.

For gasoline-ethanol mixtures, it is observed a very dynamic behavior in the initial values of the activation energy. This is possibly because the kinetic model does not fit the behavior of these mixtures very well, especially in its initial phase where it has a high tendency to evaporate at room temperature. Research should be conducted with these mixtures to try and find or develop a better model that defines the behavior in the early stages of thermal decomposition, in which the ignition processes are dominated by chemical changes. Additionally, more detailed studies of the gasoline-ethanol blends would be required to perform a deeper analysis of the complete thermal behavior of fuels with increasing ethanol content. Current trends, such as requirements to increase the usage of biofuels (that means increasing ethanol content in blends with gasoline), requires more research on this topic in order to develop efficient engines that use gasoline-ethanol blends.

Because there is little literature sources of thermal analysis by thermogravimetry in ethanol-gasoline blends, it is not possible to compare the results of the investigation. It is only possible to analyze the kinetic behavior of the combustion of these mixtures in comparison with other studies, using the relation between the activation energy and the ignition delay. This property of the combustion of ethanol-gasoline blends is studied by means of other methods rather than the thermogravimetry.

4. CONCLUSIONS

TG and TGA curves provide general information on the overall reaction kinetics, rather than individual reactions. It can be used as a tool for the comparison of gasoline-ethanol blends kinetic data. The results presented in this paper represent a range of different thermal behaviors regarding the response of various physical parameters with the addition of ethanol into the base gasoline. The kinetics of thermal decomposition reactions of these blends are complex and the process involves a large number of reactions in the thermal degradation and phase change, mainly in the early stages.

Different values of the activation energy of gasoline, ethanol and some of these mixtures were determined. It is observed that the used model does not match the thermal characteristics of the fuels tested in a low temperature range, close to room temperature. The model is suitable to represent the thermal behavior between 10% and 90% of conversion.

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