Analysis on Paraffin-Based Fuels Thermal Degradation

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Abstract

Introduction: The aim of this report is to analyze how Styrene Ethylbutylene Styrene (SEBS polymer) addition in paraffin based fuels modifies their thermal degradation process. Five different mixture compositions are provided and analyzed: pure paraffin, paraffin with 5% SEBS, paraffin with 10% SEBS, paraffin with 20% SEBS and pure SEBS.

Methods: Thermogravimetric data, taken in inert environment, are provided for all five mixtures. For each, three different experimental runs were done, varying the heating rate between 5 K/min, 10 K/min and 20 K/min. From these, iso-conversional methods, such as Ozawa-Flynn-Wall, Kissinger and Ortega, are applied to retrieve the main kinetic parameters such as effective activation energy E_a and pre-exponential factor A of Arrhenius law. Finally, mixtures lifetime at fixed temperature are evaluated.

Results: It was found that although the reaction onset point is delayed, SEBS undergoes pyrolysis at a faster rate when compared to pure paraffin, resulting in a lower estimated lifetime. Therefore, SEBS addition to paraffin based fuels results in a higher reactivity, when pyrolysis only is considered. However, the burning mechanism of paraffin fuels is mainly dependant on the entrainment phenomenon, hence for this fuel kind, the observed improved gasification does not necessarily imply a faster overall regression rate.

Nomenclature

α	Conversion Degree	t_{lf}	Lifetime	A	Pre-Exponential Factor
E_a	Effective Activation Energy	ORT-M	Modified Ortega Method	k(t)	Rate Constant
γ	Heating Rate	ORT	Ortega Method	f(α)	Reaction Model
g(α)	Integral of the Reaction Model	OFW	Ozawa-Flynn-Wall Method	T	Temperature
KAS	Kissinger-Akahira-Sunose Method	R	Ideal Gas Constant	TG	Thermogravimetry

1 | Introduction

In recent years, hybrid rocket propulsion technology has seen a significant growth in attention due to some particular advantages over the more conventional (solid and liquid) propulsion architectures. In the vast majority of applications, it employs an injected liquid or gaseous oxidizer and a solid fuel grain inserted in the combustion chamber. A significant parameter in this kind of system is the solid grain regression rate, usually modeled as a function of the oxidizer mass flux rate, and in which the solid-state kinetic parameters of the fuel at hand play a strong role.

Thermal analysis methods directed towards the study of solid state reactions have been extensively studied in the past decades and numerous algorithms exist to predict the main kinetic parameters such as the pre-exponential factor A and the activation energy E_A as defined per the Arrhenius equation. Although other mechanisms may have a significant effect on the regression rate, namely droplet entrainment with liquefying fuels such as paraffin wax, the use of experimental thermal degradation data can have an important role on the assessment of the ballistic behavior of candidate novel fuels in the hybrid propulsion field.

2 | Iso-conversional Methods

In chemical kinetics, a reaction model describes the behaviour of a chemical reaction over time. It involves understanding the rate at which reactants are converted into products and the factors that influence this rate. Numerous models exist for various reaction types based on number of steps, order of reaction, temperature and catalyst dependence. Model-based methods in chemical kinetics involve the selection of an appropriate reaction model, followed by determining kinetic parameters, such as the effective activation energy E_a and the pre-exponential factor A, usually through regression fitting of non-linear experimental data.

However, this method falls short in terms of accuracy when the complexity of the reaction increases and cannot be well described by one simple and recognizable reaction model. This in turn leads us to iso-conversional methods.

Iso-conversional methods are used to study the kinetics of thermal decomposition processes, primarily by determining the effective activation energy E_a, followed by the pre-exponential factor A. These methods focus on analyzing the reaction rate at different temperatures for the same level of conversion, which is the extent of reaction α.

In this way, the kinetic parameters, E_a and A, are determined as functions of α. These methods can be applied to a wide range of materials and reactions, such as thermal decomposition or crystallization, making them very versatile. In order to apply an iso-conversional method, different experiments must be performed in which the sample undergoes different heating rates. By comparison of t he kinetic parameters for different steps/conversion range of the reaction, it becomes possible to gain insights into the reaction process complexity. There are two main types of iso-conversional methods:

1] **Differential methods** - based on the differential form of the reaction rate equation:

$$\frac{d\alpha}{dt} = f(\alpha)k(t) = f(\alpha)A \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

• *Friedman method*: this is a direct differential method that plots the natural logarithm of the reaction rate against the reciprocal of the temperature for a given conversion level α. The slope of this plot gives the activation energy E_a.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(f(\alpha)A) - \frac{E_a}{RT} \qquad (2)$$

2] **Integral methods** - based on the integral form of the reaction rate equation:

$$g(\alpha) = \frac{AE_a}{\gamma R} \int_{w_a}^{\infty} \frac{e^{-w}}{w^2} dw \qquad (3)$$

where w is defined as:

$$w = \frac{E_a}{RT} \qquad (4)$$

Since the integral reported in eq. (3) does not have an analytical solution, the available methods differ in their approximation of such term.

• *Ozawa-Flynn-Wall (OFW) method* [1]: the most widely used integral method, it employs multiple heating rates to determine the activation energy, without any assumptions on the reaction model f(α) (model-free approach). A plot is made of $\ln(\gamma)$ against $1/T_\alpha$ for a fixed conversion level α. The slope of the resulting line provides E_a:

$$\ln(\gamma) = \ln\left(\frac{A_\alpha E_\alpha}{R}\right) - \ln(g(\alpha)) - 2.315 + \frac{0.457 E_\alpha}{RT_\alpha} \qquad (5)$$

• *Kissinger-Akahira-Sunose (KAS) method*: similar to the OFW method, KAS also utilizes multiple heating rates but employs a slightly different approximation of the integral of eq. (3), which results in the following plot of $\ln(\gamma/T^2)$ against $1/T_\alpha$:

$$\ln\left(\frac{\gamma}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \ln(g(\alpha)) - \frac{E_\alpha}{RT_\alpha} \qquad (6)$$

• *Vyazovkin method*: this advanced integral method involves the optimization of the integral rate equation across multiple heating rates to calculate E_a. It minimizes the difference between the left and right sides of the integral equation for all heating rates at a given conversion level α.

• *Ortega (ORT) method* [2]: this method is based on the Vyazovkin one, but characterized by an average linear procedure which makes use of integration over small intervals of α. For small segments of $\Delta\alpha$, the temperature integral can be approximated through the "average or mean value" theorem, which considering E_a and A constant, results in the following equation:

$$g(\alpha - \Delta\alpha, \alpha) = \frac{A_\alpha}{\gamma} \Delta T exp\left(-\frac{E_\alpha}{RT_\alpha}\right) \qquad (7)$$

And consequently:

$$\ln\left(\frac{\gamma}{\Delta T_\alpha}\right) = \ln\left(\frac{A_\alpha}{\Delta g(\alpha)}\right) - \frac{E_\alpha}{RT_\alpha} \qquad (8)$$

The advantage of such method is the possibility of revealing the dependence of the effective activation energy on the degree of conversion, which can lead to a more precise solution compared to OFW and KAS methods which assumes a constant E_a. Hence, in the case of multi-step reactions this method should be taken in consideration to limit the error [3]. However, Ortega method, in the case of small $\Delta\alpha$, introduces a systematic error due to the inaccuracy of the required evaluation of $T_{\alpha-\Delta\alpha}$, which is significantly affected by noise in the measurements. In turn, errors in the evaluation of ΔT could compromise the accuracy of the evaluated kinetic parameters.

• *Modified Ortega (ORT-M) method*: as the name suggests, this method is based on the Ortega method, but characterized by a reduction on the error related to the evaluation of ΔT. The first modification is the change in the integration interval:

$$g\left(\alpha - \frac{\Delta\alpha}{2}, \alpha + \frac{\Delta\alpha}{2}\right) = \frac{A_\alpha}{\gamma} \Delta T exp\left(-\frac{E_\alpha}{RT_\epsilon}\right) \qquad (9)$$

While the second change is the evaluation of T_ϵ, which has a value between $T_{\alpha-\alpha\backslash2}$ and $T_{\alpha+\alpha\backslash2}$, further explained in [4]. Hence, the resulting equation is the same of ORT method, eq. (8), but differs in the evaluation of both ΔT_α and T_ϵ. Except for the Ozawa-Flynn-Wall method, which doesn't require a reaction mechanism due to its model-free nature, all the other integral methods make use of the compensation effect for the evaluation of the pre-exponential factor. Hence, the following equation can be used:

$$\ln(A_\alpha) = mE_\alpha + n \qquad (10)$$

From different known reaction mechanisms, E_a and A are evaluated, then through a linear fitting of eq. (10), the parameters m and n are retrieved. At this point A can be evaluated from the real value of E_a.

Finally, it is possible to evaluate the lifetime, under isothermal conditions at temperature T_0, as follows:

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT}{\gamma \exp\left(-\frac{E_\alpha}{RT_0}\right)} \qquad (11)$$

3 | Data Analysis - Pure Paraffin

In order to set a baseline, paraffin pyrolysis will first be investigated alone, through the application of iso-conversional methods to a set of thermal analysis data. Later, the results will be compared to the ones of the other mixtures, characterized by a progressive addition of SEBS.

Thermogravimetric data, taken in an inert gas environment, for three different heating rates, is presented in fig. 1 for pure paraffin mWA-C1. As expected, the increase in heating rate results in a steeper mass loss and a delayed thermal degradation due to an enhanced thermal inertia.
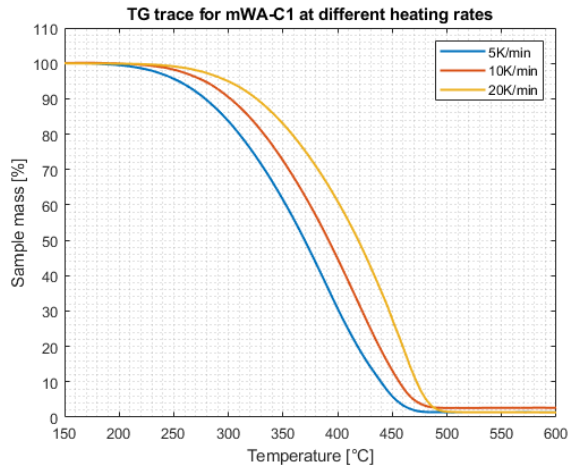
Figure 1: Thermogravimetric traces of mWA-C1

From processing of the TG data, an onset temperature of 300.6 °C is identified, as well as a temperature of 451.5°C for the reaction ending point. Both of these are in line with the thermogravimetric traces shown in the previous fig. 1. Four different iso-conversional methods were implemented for the evaluation of kinetic parameters: OFW, KAS, ORT and ORT-M. In calculations, conversion degrees α between 0.1 and 0.9 were taken in consideration. The trend of both the pre exponential factor A and the activation energy E_a, functions of α, are shown in fig. 2 and fig. 3 respectively.
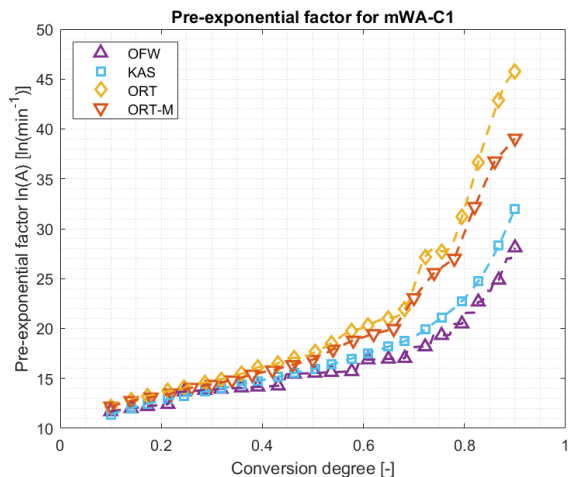
As predictable, the results are slightly dependant on the implemented method. Due to the similar approach between OFW and KAS methods, the results are almost coincident for the effective activation energy, while differ for the pre-exponential factor, since KAS, as opposed to OFW, makes use of the compensation effect. Regarding the other two methods, modified Ortega is capable of smoothing the small oscillations which affect the original Ortega method.

From the thermogravimetric traces shown in fig. 1, it is clear how a a model based on constant conversion degree, meaning no dependence on reaction extant, could not provide a suitable description for the reaction mechanism especially in the last phases of the reaction. Indeed, this results in a non constant trend for both the kinetic parameters, E_a and A, which exhibit a steep increase for a conversion degree α between 0.7 and 0.9.
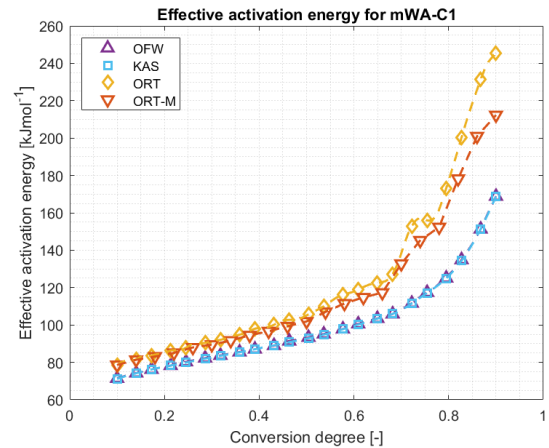

Figure 3: Effective activation energy of mWA-C1

The evaluated lifetime, illustrated in fig. 4, represents the time required to reach a prescribed conversion degree α under iso-thermal conditions. The evaluated lifetimes through both ORT and ORT-M methods are around half of the ones evaluated through OFW and KAS methods, as shown. The difference in trend is further emphasized by the divergence between methods for α greater than 0.7.

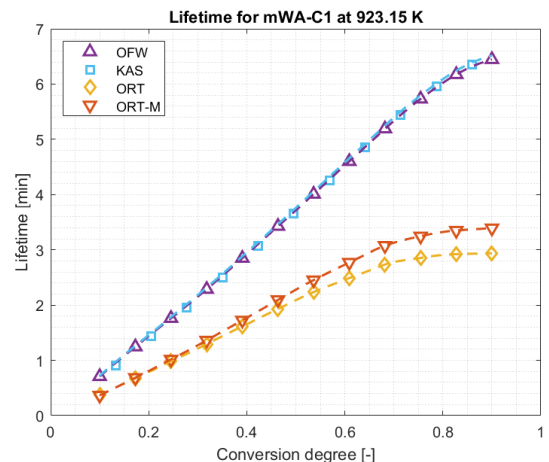Figure 2: Pre-exponential factor of mWA-C1

Figure 4: Lifetime of mWA-C1

4 | Data Analysis - SEBS Addition

With a baseline for thermal degradation of the reference paraffin fuel well established, it is now possible to analyse the effects that a performance enhancer additive may have on the kinetic parameters. The advantageous superior regression rates of paraffin wax fuels come with the drawback of poor mechanical properties, since the material is weak and brittle. Maleic anhydride grafted styrene-ethylene-butylene-styrene (SEBS-MA) is a commercial thermoplastic elastomer which has been shown to alter the rheological properties and act as a strengthening material when mixed with paraffin wax [5], making the combination an interesting candidate for a novel high-performance solid fuel.

However, the effect of this additive on the solid-state reaction kinetics of the doped paraffin fuel must be investigated. In order to do so, a series of samples were prepared, ranging the SEBS mass fraction in 5%, 10% and 20% of the total fuel. The pure block polymer was also analysed. The procedure is the same as the one described previously, in which for each species themogravimetric traces with different heating rates are taken for identical samples. The respective TG curves for each sample are shown in Figure 5 and the associated calculated reaction onset and ending temperatures indicated below in Table 1:

	T_{on} [°C]	T_{end} [°C]
mWA-C1	300.6	451.5
mWA-S05-C1	313.3	454.3
mWA-S10-C1	327.0	460.1
mWA-S20-C1	328.7	461.1
SEBS-MA	418.2	466.0

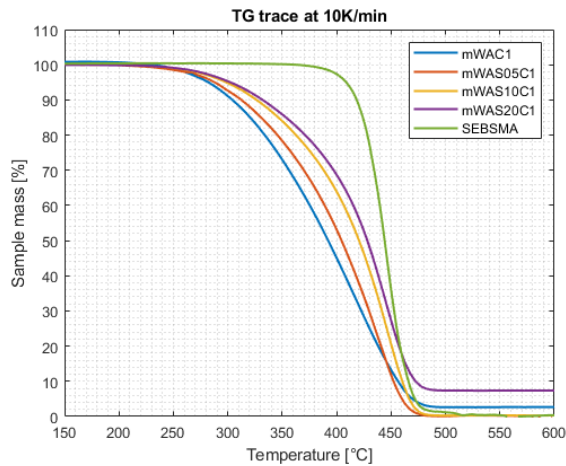Table 1: Thermal analysis results for $\gamma = 10$ K/min

Figure 5: TG traces at 10K/min for different fuels

It is immediately noticeable that the onset temperature of the decomposition reaction is delayed with increasing amounts of added polymer. However, the corresponding temperature for the end of reaction is kept approximately the same for all species, which indicates that the SEBS addition actually leads to an average decrease in the temperature interval in which the reaction occurs. This behaviour is further illustrated by the kinetic parameters results obtained through iso-convertional methods shown in Figures 6 and 7. In this section, the modified Ortega method is taken as standard due to its model generality and error minimization through the discretization of the integral.
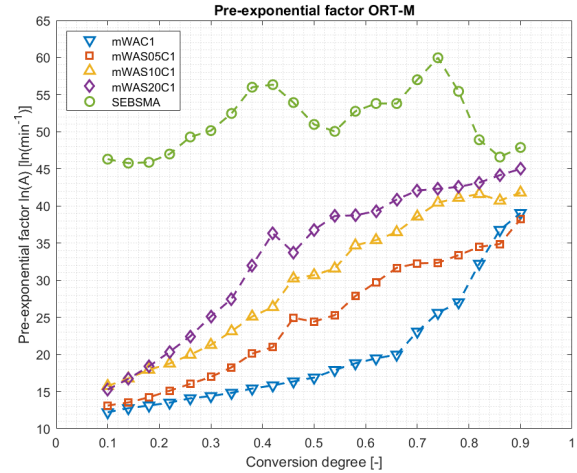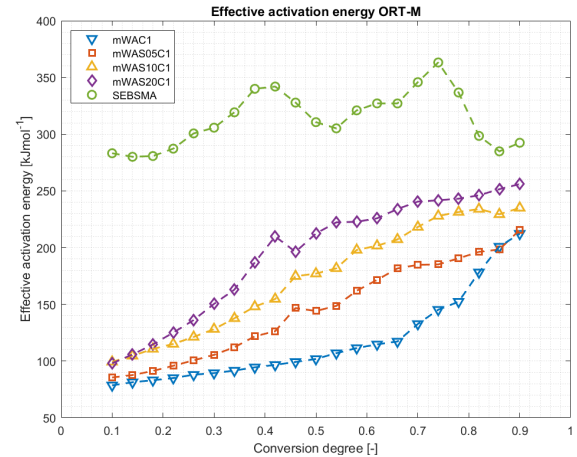
Figure 6: Pre-exponential factor - ORT-M

Figure 7: Effective activation energy - ORT-M

Under the tested conditions, a trend can be noticed of increased both pre-exponential factor and effective activation energy of the solid fuel with increasing amounts of SEBS-MA, naturally with the most markable difference being noticed in the pure polymer. It's hypothesized that the enhanced thermal stability can be attributed to the aromatic structure of the SEBS block copolymer [6][7], shown in fig. 8.
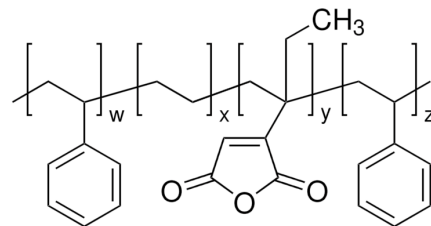
Figure 8: SEBS-MA polymer structure

Indeed, the branched aromatic structure of SEBS presents double bonds which require more energy in order to be broken, when compared to the entirety of single bonds that characterize paraffin linear structure, usually represented as $C_{50}H_{102}$. This difference explains the higher activation energy required by the thermal decomposition of SEBS.

In fig. 9, the lifetime of each of the solid fuel species, evaluated at a temperature of 625°C, is plotted as a function of conversion degree α. Lifetime can be interpreted as the thermal reactivity of the solid when subjected to isothermal conditions (recall eq. (11)). For the comparison, OFW method results were considered, since this method could be considered more conservative, computing the highest lifetime predictions, and hence the slowest reaction rates.
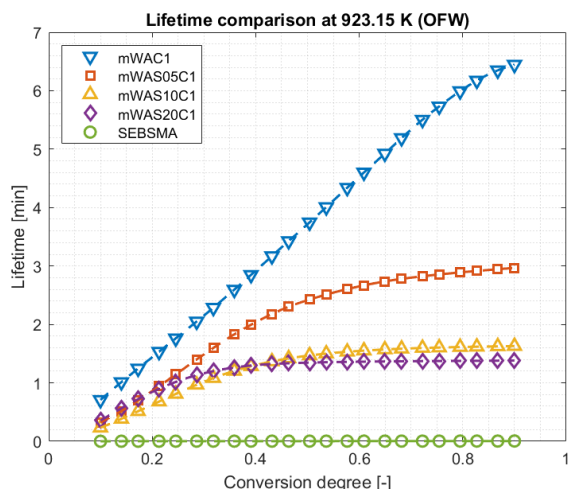

Figure 9: Lifetime comparison - OFW

The lifetime computation shows the same trend as previously discussed, in which increasing amount of SEBS-MA in the solid fuel asymptotically brings the fuel behavior close to the one of the pure polymer. Interestingly, pure SEBS shows a significantly flat trace, which indicates an increase in the rate of the global reaction between those conversion degrees. In turn, for the given conditions of the trial, it can be stated that the polymer addition improves the pyrolysis rate of the solid fuel.

It is worth noting, however, that the above drawn conclusions do not immediately translate into evidence that inclusion of SEBS-MA into a solid fuel will improve its regression performance. Hybrid propellant combustion is a complex phenomenon in which gasification due to thermal decomposition observed in the presented experiments play only a limited role. First, the presence of an oxidizing environment, which is a strong characteristic of hybrid rocket motors combustion chambers can and will affect the global reaction scheme and must be studied separately, a process know as thermo-oxidative degradation. Additionally, mass transfer effects due to droplet entrainment of liquefying fuels such as paraffin wax, as previously described during the introduction, will also contribute critically to the overall regression behavior. Therefore, caution is advised when trying to extrapolate the results of the present study into the practical applications field.

5 | Conclusion

The present study establishes the basis for the evaluation of solid state kinetic parameters related to the pyrolysis of paraffin wax hybrid fuels. The procedure is carried out through the application of classical and novel isoconversional methods, whose complexity and suitability can vary significantly, to experimental thermogravimetric data.

It was found that moderate additions of block polymer SEBS-MA to the pure paraffin fuel can delay the onset temperature of the thermal degradation reaction, while increasing the pyrolysis reaction rate once the reaction starts. In solid state kinetics terms, this translates into an increased pre-exponential factor and effectivation energy in the Arrhenius equation. This suggests that the polymer additive might make the fuel more inherently stable from a thermal standpoint and improve gasification during combustion.

Future work should focus on the study of the thermal degradation reaction of the paraffin-SEBS mixture under oxidative environments (e.g. O_2 and N_2O) and on the effect that the polymer addition will have on the rheological properties of the melted fuel, and subsequently on the entrainment phenomenom. These would provide further insights in order to better build an understanding of the impact the polymer addition has on the fuel regression rate.

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