

UNIVERSIDAD POLITÉCNICA DE MADRID

Escuela Técnica Superior de Ingenieros de Minas y Energía



Numerical and Computational Modelling of Solid Fuels Flammability

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Roberto Paredes Gallo

MSc Energy Engineer

Madrid, 2025



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**Doctoral Degree in Research, Modeling and Analysis of
Environmental Risk**

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Under the supervision of:
Dr. Blanca Castells Somoza

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Title: Numerical and Computational Modelling of Solid Fuels Flammability

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Doctoral Programme: Research, Modeling and Analysis of Environmental Risk

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External Reviewers:

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Thesis Defense Date:

A Andrea Paredes

Acknowledgements

A Blanca Castells Somoza, mi directora de tesis, me gustaría darle las gracias por recorrer este largo camino conmigo. Camino que comenzó con la tutela de mi trabajo final de carrera, pasando por ser mi jefa y socia, la tutela de mi trabajo final de máster y ahora tesis, para cerrar el ciclo siendo un gran apoyo, compañera y amiga. Estoy tremendamente agradecido por todo lo que me has ido enseñando durante estos años y por luchar siempre para darme y que me den el lugar que merezco.

A Isabel Ámez Arenillas me gustaría darle las gracias por ser también la otra importante parte del proceso, por su amabilidad y generosidad conmigo, así como por transmitirme su conocimiento y de igual forma, luchar siempre por mí.

A Sergio Barón Sanz, agradecer su apoyo, risas y, en algún que otro momento, supervisión. Creo que todo el mundo es conocedor de los ojos que tenía al conocerte, de corderito, y que gracias a eso hayamos formado una gran amistad y formes parte de mi vida.

A Marcelo F. Ortega Romero, agradecer su apuesta por mí, su generosidad, su “siempre está todo bien”, por enseñarme a ver la vida de otra forma, sin tanto estrés y disfrutando del proceso.

A María Chiquito Nieto y a Lina María López Sánchez, agradecer su entera predisposición a ayudarme desinteresadamente. Gracias por compartir conmigo vuestro conocimiento en un área que, hasta entonces, era totalmente desconocida para mí y ha sido motivo de curiosidad y motivación para seguir aprendiendo.

A mis amigos, todos aquellos que no entendían qué le pasaba a mi cabeza cuando, máster tras máster y ahora doctorado, les decía que quería seguir estudiando. Les quiero agradecer el “bullying” recibido, pues ahora gracias a eso tendrán que dirigirse a mi como “Dr. Paredes”.

A mis padres, agradecer prácticamente todo. Gracias a ellos empecé el grado en la Escuela y me han dado la oportunidad de poder seguir estudiando, así como todo su apoyo, comprensión y miradas de admiración por ver todo lo que he ido consiguiendo.

A Andrea, el amor de mi vida, esta tesis también es tuya, porque si no fuese por ti, tu constante apoyo, tu sacrificio y tu forma de quererme, yo no tendría ni la mitad de lo que tengo ahora. Gracias.

Abstract

The flammability risk assessment of solid fuels has become a major research topic in the contemporary industrial landscape, marked by safety regulations and environmental considerations. In this doctoral thesis, the flammability and explosivity characteristics of solid fuels were examined in depth, to create novel numerical and computational models to improve industrial safety procedures.

To assess ignition sensitivity and explosion severity, the study technique consisted of a methodical investigation of biomass and coal samples using thermogravimetric analysis and standardised test protocols. The research produced several methodological advances in industrial safety assessments as a result of this extensive methodology.

One novel development was the creation of a new technique for differential analysis of thermogravimetric curves to predict the minimum ignition temperature of dust layers. This new method, which resulted in a significant improvement in testing efficiency and optimisation of resources, used only 60 mg of sample material and produced excellent accuracy with an error of 2.25% compared to experimental results.

In addition, a strong correlation between the ignition temperature of the powder layers and the amount of hemicellulose present was determined in this study, providing important new information on biomass composition and ignition properties. The study provided important new information on the role of hemicellulose as an inert heat sink through the release of CO₂ and the production of flammable volatiles by cellulose and lignin. This relationship, which has an $R^2 = 0.98$, represents a breakthrough in the knowledge between flammability risk and substance composition.

On the other hand, in order to characterise the tendencies to spontaneous combustion using numerical techniques, the research presents a new index, the RB Index. This new index provides a better understanding of the risk factors for self-heating in industrial environments. A complex method was also developed to simulate the minimum ignition temperature of dust clouds using an optimised five-parameter expression related to inherent material characteristics.

In the same way, a new index was also developed to quantify the oxidative potential of solid fuels as high-energy explosives. This index provided a more accurate way of assessing the oxidative potential in industrial materials from the immediate analysis values, achieving a correlation of $R^2 = 0.99$, compared to conventional oxygen balance techniques.

The TNT equivalent method was also employed to simulate maximum overpressure results in the 20-litre sphere using the Viper::Blast software. This method showed a high accuracy of the peak pressure value. On the other hand, the accuracy of the $(dP/dt)_{max}$ parameter was increased by almost 80% by implementing an empirical Ψ factor of 1.65.

Beyond the theoretical advances, the practical consequences of this study provide industrial facilities with new approaches to risk assessment and risk management. Therefore, this research contributes to the theoretical understanding of solid fuel combustion behaviour and offers feasible and realistic solutions for industrial safety applications. The combination of computational simulation, numerical modelling and experimental validation creates a solid basis for further studies and real-world industrial safety management applications.

Resumen

La evaluación de los riesgos de la inflamabilidad de los combustibles sólidos se ha convertido en un tema de investigación determinante en el panorama industrial contemporáneo, marcado por las normativas de seguridad y las consideraciones medioambientales. En esta tesis doctoral se examinaron a fondo las características de inflamabilidad y explosividad de los combustibles sólidos, con el objetivo de crear modelos numéricos y computacionales novedosos para mejorar los procedimientos en materia de seguridad industrial.

Para evaluar la sensibilidad a la ignición y la severidad a la explosión, la técnica de estudio consistió en una investigación metódica de muestras de biomasa y carbón mediante análisis termogravimétricos y protocolos de ensayo normalizados. La investigación produjo varios avances metodológicos en las evaluaciones de seguridad industrial como resultado de esta extensa metodología.

Un desarrollo novedoso fue la creación de una nueva técnica de análisis diferencial de curvas termogravimétricas para predecir la temperatura mínima de ignición de las capas de polvo. Este nuevo método, que supuso una importante mejora en la eficacia de las pruebas y la optimización de los recursos, utilizó sólo 60 mg de material de muestra y produjo una excelente precisión con un error del 2,25% en comparación con los resultados experimentales.

Además, en este estudio fue determinada una fuerte correlación entre la temperatura de ignición de las capas de polvo y la cantidad de hemicelulosa presente, ofreciendo nueva información importante sobre la composición de la biomasa y las propiedades de ignición. El estudio aportó nueva información importante sobre la función de la hemicelulosa como sumidero de calor inerte a través de la liberación de CO₂ y la producción de volátiles inflamables por parte de la celulosa y la lignina. Esta relación, que tiene un valor $R^2 = 0,98$, supone un gran avance en el conocimiento entre el riesgo de inflamabilidad y la composición de la sustancia

Por otro lado, con el objetivo de caracterizar las tendencias a la combustión espontánea mediante técnicas numéricas, la investigación presenta un nuevo índice, el Índice RB. Gracias a este nuevo índice se comprenden mejor los factores de riesgo de autocalentamiento en entornos industriales. También se creó un método complejo para simular la temperatura mínima de ignición de las nubes de polvo mediante una expresión optimizada de cinco parámetros relacionada con las características inherentes al material.

De la misma forma, también fue desarrollado un nuevo índice para cuantificar el potencial oxidativo de los combustibles sólidos como explosivos de alta energía. Este índice proporcionó una forma más precisa de evaluar el potencial oxidativo en materiales industriales a partir de los valores del análisis inmediato, alcanzando una correlación de $R^2 = 0,99$, en comparación con las técnicas convencionales de balance de oxígeno.

También se empleó el método del equivalente TNT para simular los resultados de presión máxima en la esfera de 20 litros utilizando el programa Viper::Blast. Este método mostró una gran exactitud en cuanto al valor de la presión máxima. Por otro lado, se aumentó la precisión del parámetro $(dP/dt)_{max}$ en casi un 80% al implementar un factor Ψ empírico de 1,65.

Más allá de los avances teóricos, las consecuencias prácticas de este estudio proporcionan a las instalaciones industriales nuevos enfoques para la evaluación y gestión de riesgos. Por todo ello, esta investigación contribuye al conocimiento teórico del comportamiento de la combustión de combustibles sólidos y ofrece soluciones factibles y realistas para aplicaciones en materia de seguridad industrial. La combinación de simulación computacional, modelización numérica y validación experimental crea una base sólida para estudios posteriores y aplicaciones de gestión de la seguridad industrial en el mundo real.

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List of Publications

This research led to the following publications:

- **Paredes, R.**, Amez, I., León, D., & Castells, B. (2025). Multifactorial analysis of the relationship between combustion propagation in solid fuels and the BZ burning class number. *Biomass and Bioenergy*, 193, 107519. <https://doi.org/10.1016/j.biombioe.2024.107519>
- **Paredes, R.**, Amez, I., León, D., & Castells, B. (2024). Biomass minimum ignition temperature prediction through differential study of thermogravimetric analysis. *Journal of Loss Prevention in the Process Industries*, 92, 105486. <https://doi.org/10.1016/j.jlp.2024.105486>

In addition, the following publications were published:

- Castells, B., **Paredes, R.**, León, D., & Amez, I. (2025). Kinetic and Thermodynamic Insights into Sewage Sludge Torrefaction: Energetic Optimization and Safety Considerations. *Energy Nexus*, 100377. <https://doi.org/10.1016/j.nexus.2025.100377>
- Amez, I., Castells, B., León, D., & **Paredes, R.** (2025). Study of quaternary hydrogen and biogas mixtures: An industrial safety approach. *Fuel*, 381, 133663. <https://doi.org/10.1016/j.fuel.2024.133663>
- Amez, I., **Paredes, R.**, León, D., Bolonio, D., Pantelakis, D., & Castells, B. (2024). New Experimental Approaches for the Determination of Flammability Limits in Methane–Hydrogen Mixtures with CO₂ Inertization Using the Spark Test Apparatus. *Fire*, 7(11), 403. <https://doi.org/10.3390/fire7110403>

Chapter 1

Background and Literature Review

1.1. STRUCTURE AND RESEARCH CONTENT OF THE STUDY

The structure and research content of this thesis are shown in Figure 1.1, followed by a brief description of the contents of each chapter.

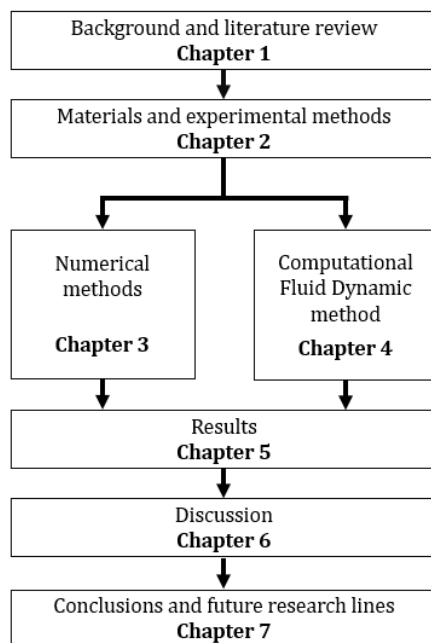


Figure 1.1. Structure and main contents of the thesis

Chapter 1 provides an introductory background on the global situation of conventional and renewable fuels, as well as the inherent physicochemical characteristics of each group. In addition, it introduces flammability and explosion risks in terms of industrial safety. Self-ignition phenomena are studied in detail, including thermal analysis methods to assess ignition susceptibility. Different tests to determine the ignition sensitivity and severity of the explosion of solid fuels are also presented. Finally, the state of the art in the field of explosions is reviewed, with special emphasis on the TNT equivalent method and its modelling by computational fluid dynamics.

Chapter 2 presents the materials and methods used to achieve the objectives proposed above. This chapter delves into the physical properties, the thermogravimetric analysis, with special emphasis on the characteristic points related to flammability, and an explanation of the determining experimental tests: minimum ignition temperature of dust layer, minimum ignition temperature of dust cloud and explosion severity.

Chapter 3 presents the numerical methods used to evaluate aspects related to composition, reactivity, and chemical kinetics using the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), and Friedman methods, reaction thermodynamics, and combustion parameters based on various determining indices. In addition, it presents the numerical methods developed to predict the experimental tests mentioned above.

Chapter 4 details the computational modelling of the explosion severity of solid fuels using Viper::Blast, detailing the geometry design, meshing with sensitivity analysis and boundary and processing conditions.

Chapter 5 presents the results obtained through experimental tests and those obtained from numerical and computational modelling.

Chapter 6 presents discussions based on a comparative analysis of the results collected in Chapter 5.

Chapter 7 presents the main conclusions drawn from this study and future research lines.

1.2. CONVENTIONAL AND RENEWABLE FUELS

The energy sector is currently at a historic turning point owing to growing environmental challenges and the need to ensure long-term energy security. Conventional fuels, mainly of fossil origin, have formed the basis of industrial development since the mid-19th century. However, their contribution to climate change and their finite nature have prompted research and the development of various renewable alternatives.

This section examines the characteristics, properties, and applications of the main types of fuels, both conventional and non-conventional or renewable, with emphasis on their chemical composition, transformation processes, and energy potential. It begins with biomass-based renewable fuels, detailing their conversion processes, followed by an analysis of conventional fossil fuels, starting with coal and continuing with other hydrocarbon derivatives.

1.2.1. Biomass

Renewable energies are becoming increasingly important in response to concerns about the environment and the security of the energy supply. Over the last few decades, climate change has become one of the main societal issues. The gradual increase in greenhouse gas (GHG) emissions since the Industrial Revolution [1,2] has had catastrophic consequences in the form of polar ice melting, ecosystems collapsing, biodiversity loss, and other devastating natural disasters [1,2]. In this regard, many governments have collaborated in summits and agreements to tackle this obstacle together. In particular, plans for transition to climate “neutral” society in the European Union (EU) were agreed upon for three important periods: 2020, 2030 and 2050. The latter is predicted to fulfil a net zero greenhouse gas emission economy [3,4].

Therefore, renewable energies have proven to be the principal way to curtail energy dependence on fossil fuels [5]. However, it is not simple to find a working alternative to fossil fuels, particularly when managing variations in non-renewable energy, because there are quite a large number of energy sources relying on external aspects preventing them from being able to handle peak demand. In this context, biofuels can play the role of one of the pillars due to the production characteristics of fossil fuels: their generation is weather-independent, and delivery beyond gas, liquid, and solid matter could be biogas, biodiesel or bioethanol, and solid biomass [3,6].

In the context of a global climate emergency, the use of solid biofuels is a sustainable approach because biogenic carbon dioxide (CO₂) is released during biomass conversion processes, making these processes carbon-neutral when using biomass [7]. Hence, if produced sustainably, bioenergy can deliver large net emission reductions [8,9]. In addition, solid biofuels offer a favourable benefit-cost ratio due to their low-cost raw materials. They also hold the potential to enhance the energy mix due to their adaptability and versatility [10,11].

However, the bioenergy industry faces a variety of challenges [12], such as complex supply chains and the low bulk density of many raw materials, as well as significant variations in feedstock properties. Moreover, the high moisture content and low energy density of several types of biomass present limitations that should be properly addressed to consider biomass as a viable energetic substitute. Furthermore, certain materials have high ash and chlorine contents, which can cause deposit formation and corrosion [12].

Biomass is the only renewable source of fixed carbon and is an essential factor in meeting the needs of fuel and consumer goods [13]. Biomass is a solid, non-fossil, and complex organic-inorganic biogenic product, generated by natural and technogenic processes and includes [14] natural components originated by the growth of terrestrial and aquatic vegetation by photosynthesis or generated through the digestion of animal and human food, and technogenic products derived from the processing of the natural components mentioned above.

One of the classifications of biomass varieties as fuel sources can be divided into various groups according to biodiversity, source and origin, as shown in Table 1.1.

Table 1.1. Biomass classification [15]

Biomass group	Varieties and species
Wood and woody biomass	Coniferous or deciduous; Angiospermous or gymnospermous; Stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmills and others from various wood species.
Herbaceous biomass	Grasses and flowers, straws, and other residues.
Aquatic biomass	Marine or freshwater algae; macroalgae or microalgae; seaweed, kelp, lake weed, water hyacinth, etc.
Animal and human waste biomass	Bones, meat-bone meal; various manures, etc.

Lignocellulosic biomass (LCB), also known as lignocellulose, is the most abundant renewable material on Earth. Its composition is complex, generally composed of polysaccharides, phenolic polymers and proteins that constitute the essential part of the cell walls. LCB has a special complex structure, in which cellulose (carbohydrate polymer) is "trapped" in a dense structure formed by hemicellulose (another carbohydrate polymer) and lignin (an aromatic polymer), as shown in Figure 1.2.

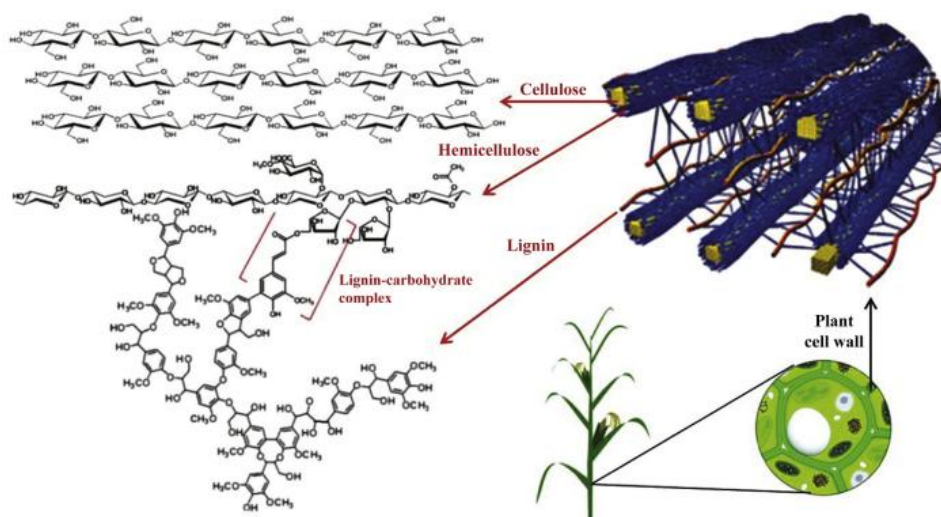


Figure 1.2. Structure of lignocellulosic biomass [16]

The ultimate objective of the characterisation of lignocellulosic biomass is its use in biorefineries and, therefore, its conversion into biofuels and bioproducts. This conversion can be performed via biochemical and thermochemical processes.

1.2.1.1. Biochemical processes

Biochemical processes use microbes to transform biomass into biofuels and bioproducts, with the most commonly used methods being anaerobic digestion (AD), fermentation, and composting. The main limitation of this series of methods is their inability to process biomass feedstocks with a longer hydraulic retention time (HRT) and the emission of greenhouse gases (GHGs) during the process.

Anaerobic digestion (AD)

Anaerobic digestion involves the conversion of biomass to biogas by microorganisms in the absence of oxygen. This biogas contains between 55-65% methane (CH_4) and 35-45% carbon dioxide (CO_2), as well as traces of hydrogen sulphide (H_2S), hydrogen (H_2) and ammonia (NH_3), among other substances.

Fermentation

Fermentation consists of three main steps. In pretreatment, the lignin layer that encapsulates the cellulose fibres formed by unique complex sugars is mainly broken down into long chains so that the cellulose is accessible to the microbial community to act on it [17]. Enzymatic hydrolysis, where cellulose and hemicellulose that have not been broken down during pretreatment, are forced to convert into sugars during such hydrolysis. This process produces solutions that can be fermented to produce ethanol ($\text{C}_2\text{H}_6\text{O}$), methanol (CH_4O), butanol ($\text{C}_4\text{H}_{10}\text{O}$) and biochemicals [18]. Finally, in the conversion process, yeast converts simple sugars from the hydrolysis process into ethanol, butanol, methanol, and fatty acids, among others [19].

Composting

Composting consists of the degradation of organic substances under aerobic conditions to produce compost that can be used as a fertiliser. The main drawback of this process is that the lignin layer present in lignocellulosic biomass inhibits easy access to cellulose and hemicellulose, which contain microorganisms and their enzymes that are responsible for the faster decomposition of complex biomass [20].

1.2.1.2. Thermochemical Processes

In contrast, thermochemical processes convert biomass into biofuels and bioproducts in the presence of heat and other chemicals. The four main processes are pyrolysis, hydrothermal liquefaction (HTL), gasification and direct combustion.

Pyrolysis

Pyrolysis is a process that consists of the thermochemical decomposition of biomass in the absence of oxygen, with an operating temperature in the range of 300–800 °C. In this process, biomass is converted into bio-oil, biochar and synthesis gas also known as syngas [21].

Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) converts biomass into bio-oil and chemicals in the presence of an aqueous medium (water). The optimum operating conditions are as follows: pressure of 4-25 MPa and temperature of 250–375 °C in the reactors according to diverse authors [22,23]. In this process, biomass is broken down into smaller unstable compounds and reunited to form bio-oil [24].

Gasification

Gasification is the process by which biomass is partially oxidised to produce syngas, along with impurities (tar), at temperatures between 800-1,500 °C. After mandatory dehydration at 100 °C, the biomass is crushed and homogenised before being introduced into the gasifier, where the aforementioned oxidation occurred [25].

Direct combustion

The direct combustion process involves the production of heat energy by burning biomass in an open or controlled environment.

1.2.2. Coal

Coal is the result of the accumulation of organic and inorganic matter and its subsequent transformation over geological time through the carbonisation process, becoming a fossil fuel with a relatively high energy density [26]. The energy density increases as the carbonisation process progresses, which explains the wide variation in the quality of the existing coal. To increase the energy density, the inorganic matter content must be reduced using any of the techniques established for this purpose.

On the other hand, one of the classifications of coals is as follows: peat, lignite, sub-bituminous coal, bituminous coal, anthracite, graphite, cannel coal and coking coal. The most common are lignite, bituminous coal and anthracite [27]. The structural models of these may be viewed to notice their ordering in Figure 1.3.

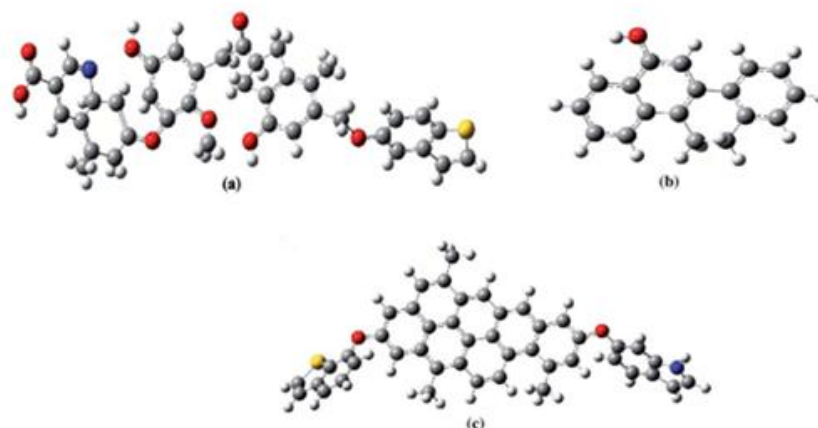


Figure 1.3. Structural models of a) lignite coal, b) bituminous coal and c) anthracite [28]

The ultimate objective of characterising coal, similar to that of biomass, is to obtain heat energy through combustion or chemical production. Delving into the second group, it can be observed in Figure 1.4 chemicals derived from coal.

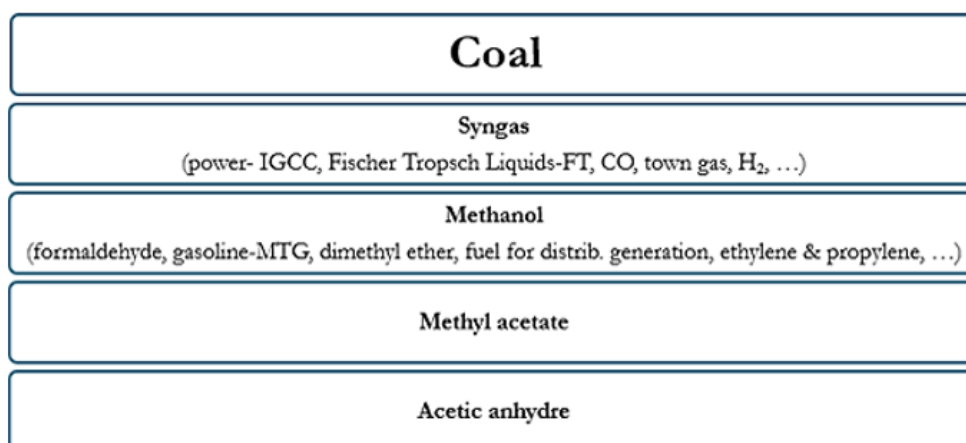


Figure 1.4. Scheme of the production of chemicals from coal [29]

Chemicals produced directly from gasification include syngas, methanol, hydrogen, and carbon monoxide, which are subsequently derived from various chemical products such as oleophynes, acetic acid, formaldehyde, ammonia, and urea. In Table 1.2, a brief description of the most common chemicals, as well as their production reactions, is detailed.

Table 1.2. Chemical, brief description and conversion from syngas [29]

Chemical	Brief description	Conversion or derived from syngas
Methanol	Produced by the conversion of syngas, natural gas, coal, off-gas refinery or oil. In addition, if it can be used directly as fuel, it can be converted into gasoline by following the following process: methanol → dimethyl ether → ethylene → oligomerization → gasoline.	$2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH}$
Hydrogen	Various methods are used for the production of hydrogen, although the most common is the so-called steam methane reforming.	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Ammonia	During coal pyrolysis (gasification), nitrogen bound to the fuel is transformed into ammonia.	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
Acetic acid and derivatives	Can be produced indirectly by carbonylation of methanol over rhodium or iridium catalysts.	$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$
Formaldehyde	Can be produced indirectly by dehydrogenation and partial oxidation of methanol using a sulphur catalyst.	$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$ $\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$

1.3.FUELS FLAMMABILITY RISKS

The risks associated with the fuel's flammability are a factor to be carefully analysed in the field of process safety and the prevention of occupational risks. However, the frequency of this type of accident continues to increase over time. Between 2002 and 2024, there were several accidents involving fires and explosions at industrial biomass and coal facilities and storage sites, as reported in Table 1.3.

Incidents at biomass facilities commonly arise from boiler fires, spontaneous ignition of fermenting woodchips or sawdust heaps, or explosions caused by wood dust. On the other hand, coal-related explosions often occur in mines due to the release of firedamp-methane, a flammable gas.

Table 1.3. Biomass and coal industrial incidents [30–40]

Date	Place	Accident
2024	Quetta, Pakistan	Twelve miners dead in coal mine explosion.
2023	Palotina, Paraná (Brazil)	Eight workers killed and 11 injured in silo explosions at agribusiness.
2023	Satatausa, Colombia	Twenty-one workers dead in coal mine explosion.
2022	Baden-Württemberg, Germany	Deflagration at a biomass thermal power station.
2021	Schameder, Germany	Three workers were injured in a wood chip silo explosion.
2021	Siberia, Russia	Fifty-two workers dead in methane explosion.
2018	Madhya Pradesh, India	One killed and one dead in fluid bed dryer fire.
2015	Macclesfield, UK	Dust explosion, 4 people killed.
2014	Yorkshire, UK	Fire in wood chip pile. 3,000 tonnes of wood chips destroyed. 10 days to extinguish.
2013	Minnesota	Explosion and fire in biomass storage.
2013	Port of Tyne	Wood pellets fire in the conveying system.
2012	Netherlands	Dust explosion, wood pellets.
2011	Sonae, Merseyside	Fire in wood chip storage hopper, burned for over a week. 1 fatality.
2002	Sonae, Merseyside	Dust explosion. MDF production plant. 17 m diameter hole blown in the building wall. 1 serious injury.

Most dusts used in the industry are combustible. However, an explosion can occur if a series of requirements are met. First, it is necessary to consider the conditions conducive to ignition which, according to the tetrahedron of flammability, are the existence of fuel, oxidiser, source of ignition and continuity in the reaction, as observed in Figure 1.5.a.

Once the theory of ignition has been developed, the transition to the explosion phenomenon occurs similarly, as long as the existence of the flammability tetrahedron conditions is met and the dust is suspended, confined and the concentration is the minimum feasible for the explosion to occur, as observed in Figure 1.5.b.

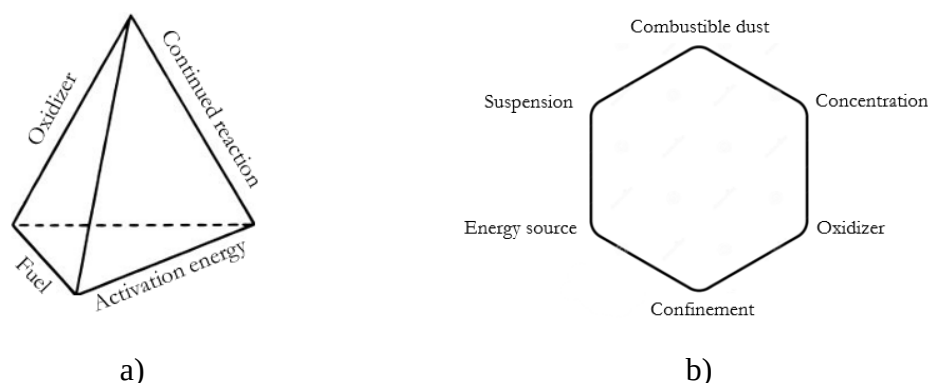


Figure 1.5. a) Tetrahedron of flammability and b) Explosion hexagon [41,42]

In the first instance, dust must be combustible, as mentioned above. To determine this, it must be assessed whether the dust explodes while remaining in a scattered cloud and can be demonstrated by the "Screening Test (Go/No-go test)" according to ISO/IEC 80079-20-2 [43].

In addition, the dust should be suspended and intimately mixed with an atmosphere of oxidising gas suitable to allow oxidation to occur on the surface of the particles. Owing mainly to the availability of oxygen around each particle, the combustion process is very fast, resulting in a dust explosion and pressure effects.

Moreover, the minimum explosive concentration (MEC) must be known. The sensitivity of the dust cloud to ignition, and also the resulting explosion violence, increases as the concentration of the dust cloud above the MEC is increased until an optimal concentration is reached. If the dust cloud concentration is higher than optimal, it may result in a point where no propagation occurs because the atmosphere is too rich in fuel.

The sensitivity to ignition in a dust cloud and the severity of the resulting explosion increased with decreasing particle size. This is because a smaller particle size increases the surface area per unit mass, thus increasing the oxidation potential. Therefore, the particle size of the powder is a crucial determinant of its thermo-kinetic behaviour in

ignition and flame propagation phenomena. The influence of particle size on flammability can be quantified using various mass and energy-transfer mechanisms.

On the one hand, the minimum ignition energy (MIE) exhibits an empirical dependence on the particle diameter (d_p or d_{50}) that follows the relation $MIE \propto d_p^n$, where the exponent ranges from 1 to 3 depending on the physicochemical composition of the material [44]. This correlation is derived from the fact that ignition occurs when a critical volume of material reaches the pyrolysis temperature, a phenomenon controlled by thermal diffusion

In contrast, according to the above, the specific surface area available for heterogeneous reactions increases exponentially as $A_s = 6/(\rho_p \times d_p)$, in increasing the release of volatiles per unit mass and establishing more favourable concentration profiles to reach flammability limits. The atmosphere must be able to withstand the combustion of the dust cloud; that is, the atmosphere must contain sufficient oxidising agents. Generally, oxygen in air is the preferred oxidant, although chlorine, fluorine, nitrogen oxide, nitric oxide, and nitrogen tetroxide are common.

Finally, ignition must provide sufficient energy to initiate flame propagation [45]. The most common ignition sources are listed in the UNE EN-1127-1 standard and are set out below [46]:

- Hot surfaces.
- Arc Flashes.
- Flames and hot gases.
- Sparks generated by the mechanical equipment.
- Electrical systems.
- Cathodic corrosion protection.
- Static electricity.
- Lightning strike.
- Electromagnetic fields.
- Electromagnetic radiation.
- Ionising radiation.
- Ultrasound.
- Adiabatic compression and circulating gases.
- Chemical reaction.

Among the various ignition mechanisms of solid fuels, auto-ignition is particularly critical because it does not require the presence of external energy sources to initiate combustion. This process occurs when the rate of heat generation due to exothermic reactions (oxidation at low temperatures, microbiological activity, or fermentation) exceeds the rate of heat dissipation to the surroundings, causing a progressive accumulation of energy that culminates in the spontaneous ignition of the substance.

This phenomenon is intrinsically linked to the composition of the substance, particularly to parameters such as moisture, volatile matter, fixed carbon, and ash, thus determining its susceptibility to spontaneous ignition. Similarly, the ratio of volatile matter content to fixed carbon is a key indicator of the reactivity of the material, where higher values are associated with greater ease of releasing combustible gaseous compounds at relatively low temperatures, thus increasing the likelihood of self-ignition.

1.3.1. Spontaneous Ignition

The phenomena of self-ignition or spontaneous combustion can be differentiated between the processes that occur in coal and biomass. This is due to the fundamental differences in the physicochemical properties and reactivity mechanisms of these fuels, which significantly affect their auto-ignition behaviour. Furthermore, the growing trend towards co-firing and co-processing of coal and biomass in industrial facilities requires a thorough understanding of how these materials behave both independently and synergistically in spontaneous combustion scenarios.

On the one hand, the self-ignition of coal piles is primarily due to chemical and physical processes [47], while in the case of biomass, self-heating or self-ignition also involves a microbial process that plays a critical role in heat accumulation in the early stages, particularly between 0-75 °C [48].

In the case of coal, and according to numerous authors, spontaneous combustion occurs when the air supply is sufficient to carry out the coal oxidation process and the air velocity is insufficient to dissipate the heat generated [49–53].

Thus, according to Liu et al. (2023) [47] and Zhang et al. (2021) [54], the self-combustion of coal can be divided into three differentiated states, as shown in Figure 1.6:

- The spontaneous combustion latency.
- The self-heating stage.
- The combustion stage.

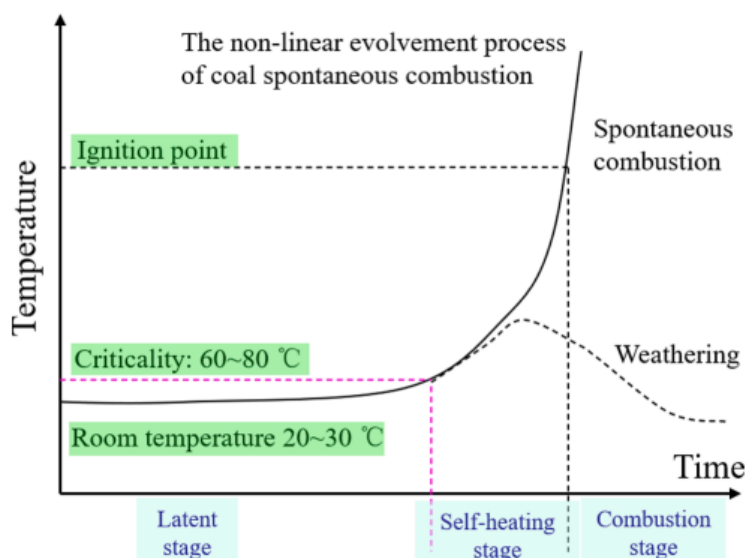


Figure 1.6. Three-stage classification of coal spontaneous combustion [54]

They are all combinations of oxidation reactions of active groups, including free radicals and functional groups. The coal is ‘broken’ due to external actions, which trigger fractures at the molecular level of the coal and, consequently, increase the number of free radicals [55].

The molecular breakdown of coal accelerates its natural oxidation because these free radicals can occur on the surface of the coal particles or, conversely, in the cracks of the coal itself. In an oxidising atmosphere, the free radicals react rapidly to generate peroxide radicals through an exothermic reaction, e.g. by releasing heat.

In this reaction, peroxide radicals further decompose into various reactive groups and secondary radicals. However, in this first stage of exothermic reactions, the heat released is absorbed by the intrinsic moisture of the coal; hence, in the initial oxidation phase, the temperature of the coal may drop or remain stable. Nevertheless, once the evaporation of moisture is complete, the temperature of the coal gradually increases, exposing pores and fissures on the surface of the coal that can react in this oxidising atmosphere, as shown in Figure 1.7.

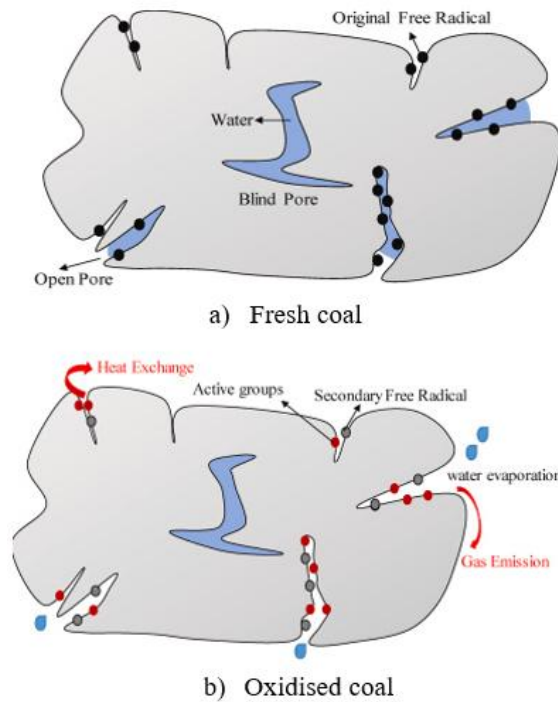


Figure 1.7. The main heat generation and dissipation pathways for coal particles [47]

Generally, when the temperature reaches 50 °C, the main oxygen adsorption method switches from physical to chemical adsorption, while the aliphatic hydrocarbon side chains begin to break down and oxidise, thereby producing oxygen-containing functional groups and gaseous hydrocarbon products.

The C-O and hydroperoxide groups increased in content during spontaneous combustion dormancy, whereas the carbonyl and carboxyl groups continued to decrease in content. The main gaseous products appearing during the latent state are CO, CO₂, CH₄, and C₂H₆, indicators used to predict such a phenomenon.

In the case of biomass, the microbial process mentioned above involves the respiration of plant cells, as well as the growth and respiration of microorganisms, fungi, and bacteria that colonise the biomass materials. As can be seen in Figure 1.8, the chemical process, notably, occurs mainly above 75 °C, driven by heat generated by microbial activities below 70-80 °C [48,56].

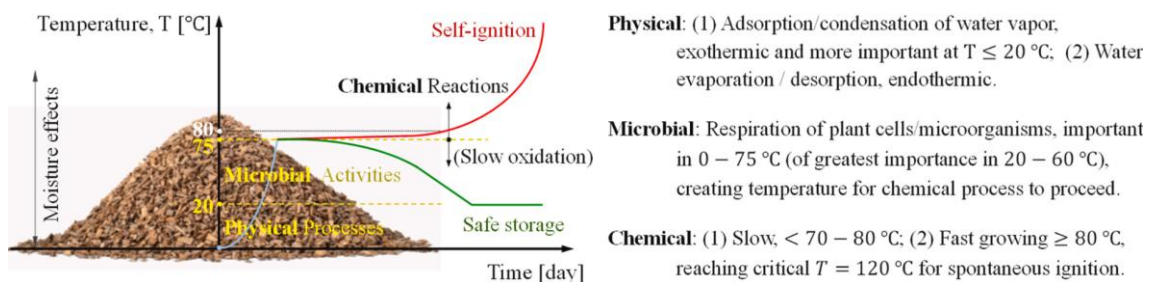


Figure 1.8. Physical, microbial and chemical processes (biomass self-heating) [48]

In general terms, and according to Figure 1.8, as well as the scheme given by Meijer et al. (2004) [57], following moisture loss, the next step is biological oxidation, accompanied by the release of CO₂ and volatile organic species, such as acids and aldehydes [58,59]. Microorganisms must be present in significant numbers; however, this is not always the case. This is why many mathematical models omit this stage (the simplest being the Frank-Kamenskii and Semenov models). Then, the thermal oxidation of the biomass begins with the release of CO, and finally, if the critical temperature is reached and no preventive measures are taken, the temperature increases, leading to ignition.

In addition to these phenomena, numerous factors affect self-heating, such as temperature, oxygen concentration, relative humidity, wind speed, biomass type, chemical composition, initial moisture, size, and porosity, making the prediction of this phenomenon particularly complex owing to the variables involved.

The self-ignition risk of solid fuels under storage or handling conditions is commonly assessed by determining the self-ignition temperature (SIT) according to EN ISO 15188 [60]. This standard describes an isothermal method that allows for the evaluation of a substance's tendency to self-heat and ignite without the application of an external ignition source. The test involves placing a defined quantity of the sample in a controlled-temperature oven and monitoring it over time to determine the lowest ambient temperature at which self-ignition occurs under specific conditions. From the results obtained with both sample volumes, the critical auto-ignition temperature for arbitrary volumes can be extrapolated using the Semenov or Frank-Kamenetskii theory, as previously cited, by applying the logarithmic relationship between the volume to be analysed and the critical temperature.

1.3.1.1. Frank Kamenetskii Method

Frank Kamenetskii's method for evaluating spontaneous ignition or self-combustion is based on finding a stationary solution of the energy equation for an infinite flat plate of an exothermic material [61]. Frank Kamenetskii's model uses a dimensionless parameter that represents heat generation, called the Damkohler number (δ), represented in Equation 1.1.

$$\delta = \frac{E_a}{R T_{FK}} \frac{\rho A Q r^2}{\lambda T_{FK}} \exp \frac{-E_a}{R T_{FK}} \quad 1.1$$

Where r denotes the radius or characteristic length of the powder sample, Q signifies the high heating value (HHV), A stands for the pre-exponential factor, R represents the universal gas constant, T_{FK} denotes the spontaneous ignition temperature, ρ is the bulk density, λ signifies the thermal conductivity and E_a represents the activation energy.

Subsequently, it must be compared with its critical number (δ_c), which depends on the geometry [62]. Spontaneous ignition or self-combustion occurs when $\delta > \delta_c$. The values of δ_c for different geometries are listed in Table 1.4.

Table 1.4. δ_c as a function of the Bi number for diverse geometries [63]

Body	δ_c
Infinite plane slab	0.878
Infinite cylinder	2.000
Infinite square rod	1.700
Sphere	3.322
Equicylinder	2.764
Cube	2.519

However, Frank Kamenetskii's theory is only valid under certain assumptions [64,65]:

- A single zero-order exothermic reaction generates heat as a function of temperature alone. In addition, there is no depletion or consumption of reagents owing to the heat generation reaction.
- The activation energy is sufficiently high to hold that $\varepsilon = \frac{R T_a}{E_a} \ll 1$, where ε is the reduced ambient temperature and T_a is the ambient temperature.
- Conduction explains that the transfer of heat within the body and the convective and radiative heat transfer between the body surface and the environment is sufficient for the body surface temperature to be maintained at approximately the temperature of the surrounding air. A high heat transfer between the body and environment implies that the Biot number approaches infinity ($Bi = \frac{h r}{\lambda} \rightarrow \infty$), where h is the effective heat transfer coefficient and r is the characteristic length of the body. If the Biot number is finite, it is necessary to adjust the critical Damkohler number.

1.3.1.2. Semenov Method

The Semenov self-combustion or thermal ignition model is a stationary model that considers that the internal temperature of the body is uniform, and that the generation of heat reaches equilibrium with the loss of heat to the environment. In practice, this situation applies to a state in which the number of Biot is very small and in which there is a sudden change in temperature on the surface outside the environment. Heat is exchanged between the body and the fluid at a constant temperature (T_a) surrounding the body. For a self-heating body of arbitrary geometry, a stationary energy balance is developed using Equation 1.2, assuming constant physical properties [66], where T is the absolute temperature and k is the thermal conductivity (assumed constant).

$$k\nabla^2 T + Q\rho A \exp\left(\frac{-E_a}{RT}\right) = 0 \quad 1.2$$

On the other hand, Newton's law describes the heat transfer of a body with respect to its surroundings; therefore, the boundary condition is reflected in Equation 1.3, where n is the coordinate directed outwards (normal to the surface).

$$k \frac{dT}{dn} + h(T - T_a) = 0 \quad 1.3$$

These equations can be partially supplemented by the usual Frank-Kamenetskii's (F-K) parameters that provide approximations for $\varepsilon \ll 1$ and θ , if it is not a high value. These variables are defined as the excess of reduced temperature and the reduced ambient temperature, respectively, and are developed as shown in Equation 1.4 and Equation 1.5.

$$\theta = \frac{T - T_a}{R \frac{T_a^2}{E_a}} \quad 1.4$$

$$\varepsilon = \frac{R T_a}{E_a} \quad 1.5$$

After substituting the new variables, the energy equation and boundary condition are reunited with the following expressions (Equations 1.6 and 1.7, respectively):

$$\nabla^2 \theta + \frac{Q\rho A \exp\left(\frac{-E_a}{RT_a}\right)}{kRT_a^2} \exp \theta = 0 \quad 1.6$$

$$\frac{d\theta}{dn} + h\theta = 0 \quad 1.7$$

Because the excess Frank-Kamenetskii's temperature is uniform over the volume of a body, V , the energy equation can be integrated over the boundary condition along the surface of the body, S . The Semenov number (Equation 1.8) is defined as the solution given by these simplifications.

$$Se = \frac{VQ\rho AE \exp\left(\frac{-E_a}{RT_a}\right)}{hSRT_a^2} = \theta \exp(-\theta) \quad 1.8$$

The static state criterion for the critical condition, given a uniform internal temperature, is satisfied when the excess dimensionless temperature, θ , equals unity. The critical Semenov number is $Se_{cr} = e^{-1} \approx 0.3679$. Therefore, any ambient temperature that exceeds the critical Semenov value is considered unstable and represents supercritical conditions for the body [67].

1.3.2. ATEX Characterisation

Characterising the flammability behaviour of solid fuels is a fundamental step in effective industrial risk management. This is mainly because characterisation allows the classification of materials according to their intrinsic hazards and provides the critical parameters necessary for the design and implementation of preventive and protective measures in facilities where these materials are handled, stored, or processed.

1.3.2.1. Ignition Sensitivity

The objective of this test group is to evaluate ignition sensitivity by various ignition sources and boundary conditions, represented in order in Figure 1.9 a), b), c) and d). Within this group, the following tests were performed:



Figure 1.9: a) Severity test apparatus (20 litres sphere), b) minimum ignition energy test apparatus (Hartmann tube), c) minimum ignition temperature of dust layer test apparatus and d) minimum ignition temperature of dust cloud test apparatus (G-G furnace) [68]

Minimum Ignition Temperature of Dust Layer and Minimum Ignition Temperature of Dust Cloud

The first test determines the minimum temperature at which a layer of dust of 5 mm height ignites on contact with a hot surface instantaneously or over a specified period [43]. The second determines the minimum temperature at which a dust cloud ignites. Moreover, according to the ATEX 137 directive, there is a relationship between the two. The hot surfaces of electrical devices must not exceed 2/3 of the minimum ignition temperature of dust cloud [43], and their temperature must be at least 75 K lower than the minimum ignition temperature of dust layer (if dust deposits do not exceed 5 mm in height).

Minimum Ignition Energy

Determines the minimum electrical energy in the form of an arc spark required for the sample to ignite at the time of its suspension into the modified Hartmann tube [43]. According to the thermal theory of electric spark ignition by Lewis and von Elbe (1961) [69], instants after discharge, the electric spark generates a very small volume of hot gas. In the first moments, the temperature inside the core increases, but as the ignition volume increases, due to the heat flow towards the environment, the temperature inside the core decreases.

Moreover, according to several authors, various factors, such as the inductance of the electrical discharge circuit [42,70,71], turbulence [42], dust particle size [72], temperature [42] and moisture content influence the minimum ignition energy among other ignition sensitivity and explosion severity parameters.

Lower Explosive Limit

Determines the minimum concentration of the sample (g/m^3) that is explosive when a detonation of 2 kJ is applied in the form of chemical igniters (saturated with a mixture of zirconium and other elements) [73]. As with all other parameters, depends on the intrinsic characteristics of the dust, e.g. moisture and ash content or PSD, according to Mevlevioğlu, U. (2019) [74].

1.3.2.2. Explosion Severity

The purpose of this group of tests is to evaluate the severity of the explosion of the powdery sample. Within this group, the following four tests are performed, which are carried out on the 20-liter sphere, represented in Figure 1.9 a), as well as the lower explosive limit test in the previous point:

Maximum Pressure

Determines the maximum achievable pressure applied [75] to a confined dust cloud when an energy of 10 kJ is applied in the form of an exothermic chemical reaction using zirconium ignitors [76]. The final maximum value is determined by the maximum corrected deflagration value over a given concentration range. For example, in research by Büschgens et al. (2017) [77], different concentrations of sugar were examined. The results show that there is a trend, the higher the concentration, the higher the pressure. Furthermore, it is reported that the highest overpressure was close to 7 bar at 1,000 g/m³, calling this point the optimum concentration [77].

Maximum Rate of Pressure Rise

Determines the maximum ratio of pressure with respect to time under the same operating conditions as for the maximum pressure [78]. According to Ramirez et al. (2009) [79], this parameter is the derivative with respect to the time of the P-t curve plotted. This parameter is commonly used in venting and explosion suppression. Abbasi et al. (2007) [80] stated that the maximum rate of pressure rise is influenced by compartment design as well as compartment size, temperature, pressure, ignition source and turbulence, among others.

Therefore, it is common to see some disparities between the results obtained in different compartments. According to Eckhoff et al. (1978) [81], the 1 m³ sphere and Hartman tube show some decrease in the parameter due to the lag between dust dispersion and heightened ignition. One of the reasons given is that the intensity of the dust dispersion decreases, and therefore, the turbulence applied to the dust cloud also triggers the reduction in flame speed.

Deflagration Index

The intensity or severity of an explosion depends directly on the maximum value of dP/dt and the dimensions of the sphere through the K_{ST} [78] parameter [82–84]. This parameter obtains the status of relevance because the design of explosion safety measures is closely dependent on it. For example, it can be decisive for explosion suppression, venting, etc., and even in certain situations, the theoretical knowledge of this parameter can be effective.

On the other hand, research by Kumar et al. (1992) [85] showed that turbulence caused an increase in the K_{ST} value from 180 bar×m/s under turbulent conditions to 70 bar×m/s under ambient conditions.

Limiting Oxygen Concentration

Determines the minimum concentration of oxygen [86] in an explosive atmosphere capable of exploding a dust cloud. According to Mittal et al. (2013) [87], the data reported in their research on the oxygen concentration limit in coals differ according to particle size and composition and according to Kim et al. (2016) [88] in the case of biomass.

Defining the flammable characteristics properly requires conducting numerous tests which can be challenging. Consequently, many researchers have developed techniques to estimate these parameters from different tests [89,90] to streamline the procedure. For example, thermogravimetric analysis (TGA) has been shown to be highly beneficial because of the valuable data it provides [91–93], the minimal sample amount needed for testing, and the high reproducibility of the results.

1.3.2.3. Ignition Susceptibility

Apart from these tests, there are several additional tests to evaluate other properties. Among these parameters, the BZ Burning Class Number, Maciejasz index, Emission Temperature of Flammable Volatiles and Thermogravimetric Analysis stand out. These are of particular relevance when evaluating mechanisms other than those mentioned above, such as the evolution of combustion and flame propagation mechanisms, exothermic oxidation kinetics at low temperatures, and the decomposition and emission of flammable volatiles.

The first of these, the **BZ Burning Class Number** (BZ) test [94], assesses the behaviour of a powdery sample in terms of combustion and flame propagation, characterising them from BZ 1 to BZ 6. Leksin et al. (2019) [95] in their study on quasi-steady-state behaviour for combustion of dust, presents a new classification (Table 1.5), introducing a new safety factor to characterise the combustion and flame behaviour under these particular conditions.

This new classification was developed in order to evaluate dust behaviour in fluid beds, because traditional BZ ratings were insufficient for it, where materials can exhibit different and often more severe combustion characteristics than in their settled state.

The BVZqs system uses four levels (I-IV) rather than six, with each level representing increasing severity of fire behaviour, according to Figure 1.10. The critical dividing line in the classification occurs between BVZqs II and III, indicating the threshold at which additional safety measures become mandatory. Levels I and II represent contained fire scenarios with no spreading, whereas levels III and IV indicate continuous fire conditions that pose significantly greater risks in industrial settings.

Table 1.5. Comparison between the BVZqs and BZ values [95]

BZ	BVZqs	Explanation
1	I	No fire behaviour.
2		
3		
4	II	Local fire behaviour of the fluidized bed or jet flame in the presence of an ignition source.
5		
6	III	Continuous fire behaviour with open flame (torch fire).
5		
6	IV	Continuous fire behaviour over the entire length or rapid combustion with flame propagation.
6		

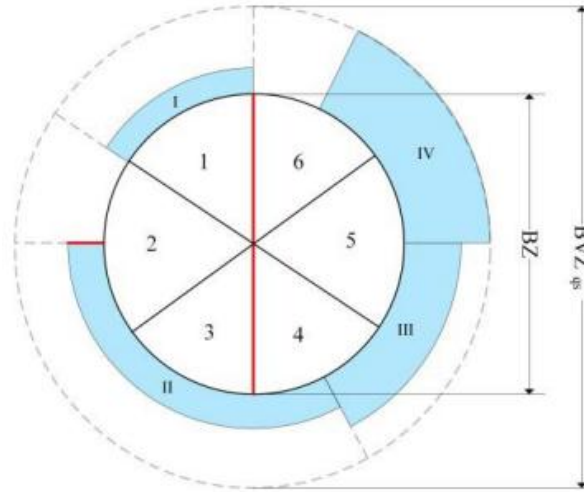


Figure 1.10. Comparison of the BZ and BVZqs [95]

The **Maciejasz Index (MI)** [96] evaluates the behaviour of combustible dust when attacked with hydrogen peroxide. This index has units of min^{-1} and is calculated as $MI = \frac{100}{t}$ being t the minutes needed for the sample to reach 65 K above ambient temperature, thus determining its risk of autoignition ($MI > 10$). García Torrent et al. (2016) [93] tested various biomasses to determine their response to hydrogen peroxide attack, obtaining only one positive result. This positive result was observed in the sewage sludge sample, with a MI value of 25. That is, the sample took 4 minutes to reach 65 K above ambient temperature.

Finally, the **Emission Temperature of Flammable Volatiles** (VTE) [96] consists of analysing the possible thermal degradation of organic matter, generating volatiles capable of being ignited. According to Larrad Moreno (2016) [97], the test consists of heating a portion of the sample at increasing temperatures by applying an ignition source consisting of an incandescent resistor.

If the sample emits flammable vapours, these would be more sensitive to ignition than the sample itself and could ignite at reduced temperatures (even lower than the minimum ignition temperatures in a dust cloud). This is because gas-dust-air hybrid mixtures are more sensitive to ignition than separate gas-air or dust-air mixtures.

This statement is corroborated by García Torrent et al. (2016) [93], where it is observed that the VTE values are lower in all the samples tested than the values of the minimum ignition temperature of dust cloud.

Finally, thermogravimetry or thermogravimetric analysis (TGA) [98] is a technique in which the mass of a substance is measured as a function of either temperature or time while the substance is subjected to a temperature- and atmosphere-controlled program. Mass loss can be categorised as volatile components, such as absorbed moisture, major thermal degradation processes, and oxidation of carbonaceous residues, as will be detailed in later chapters.

1.4.EXPLOSION FUNDAMENTALS

An explosion is a thermodynamic process in which energy is released quickly, strongly, and in the form of an exothermic chemical reaction, although explosions in which the release is in the form of a physical reaction (e.g. steam boiler explosion) should also be considered [99]. Chemical explosions cause a rapid and pronounced increase in temperature and pressure in a localised area. Consequently, a blast wave is generated, which propagates spherically through the surrounding medium. Broadly speaking, explosions fall into two main categories: detonations and deflagrations, as shown in Figure 1.11, depending on the reaction rate.

Confinement of the material can significantly alter the process. Because there is no outlet, the gases generated by combustion increase the pressure, which in turn increases the combustion rate [100]. When this combustion becomes self-sustaining but remains subsonic, it is classified as deflagration. This phenomenon can be initiated by various phenomena, such as flames, sparks, impacts, or friction, and is characterised by rapid and violent combustion, although always at speeds lower than the speed of sound [101].

However, detonation involves the propagation of a shock wave through an explosive material at supersonic speeds, typically between 1,500 and 9,000 m/s [102]. This process can be initiated directly by a detonator, or it can evolve from deflagration when the pressure and rate of combustion increase to exceed the speed of sound.

When detonation occurs, it generates an incandescent zone of explosive gases that rapidly expands, producing a shock front that propagates from the initiation point [103]. At any fixed distance from the explosive, the shock wave is characterised by an instantaneous increase in pressure followed by a decay until it returns to ambient pressure.

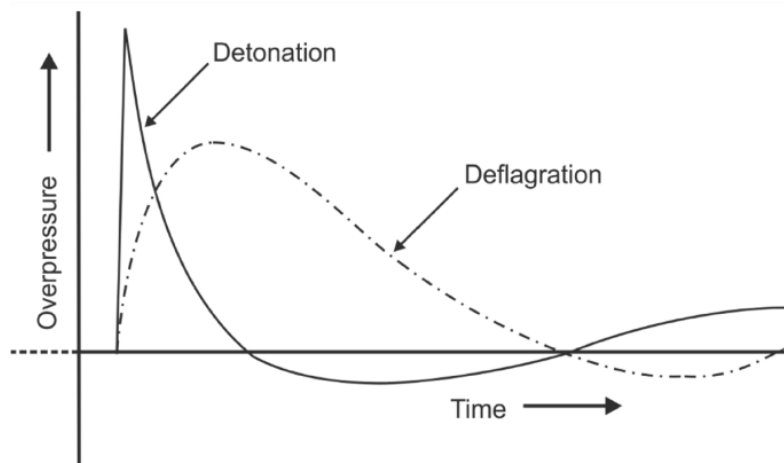


Figure 1.11: Comparison between detonation and deflagration [104]

1.4.1. Detonation

The pressure-time profile of a detonation is characterised by a sudden increase in pressure followed by an exponential decrease, transitioning to a negative pressure or suction phase, as shown in Figure 1.12. Explosion protection standards for facades and glazing often use explosive detonation as a stage for shunting charges. The key parameters are the maximum overpressure and impulse of the blast wave, which represent the total effect of the blast force during the exposure time [105].

The incident pressure, also known as the lateral pressure, instantly reaches a certain point in space at the time of arrival (t_A), reaching its maximum value (P_{S0}). From that point onwards, the pressure decreased exponentially. The area under the pressure-time curve represents the specific impulse. In general, only the positive specific impulse is considered to be responsible for structural deformation because the negative specific impulse is usually neglected owing to its relatively small magnitude.

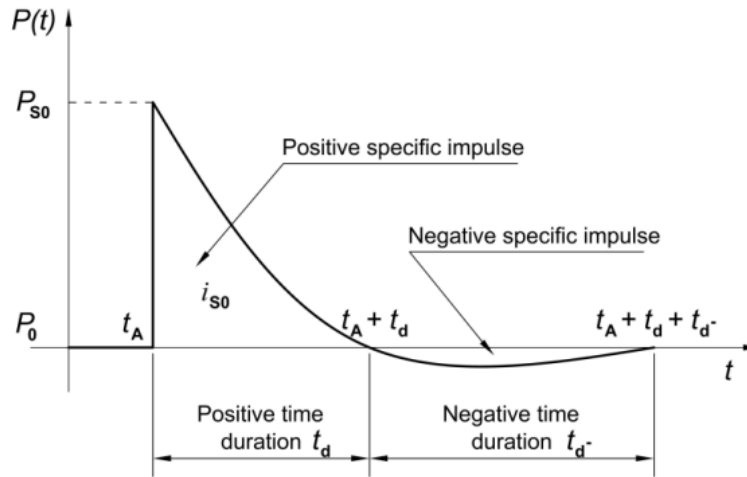


Figure 1.12: Blast wave pressure-time history [105]

The simplest way to represent a blast wave in free air is described by the modified Friedlander's wave equation, as shown in Equation 1.9.

$$P(t) = P_0 + P_{S0} \times \left(1 - \frac{t}{t_d}\right) \times e^{-\frac{b \times t}{t_d}} \quad 1.9$$

where P_0 is the atmospheric pressure, P_{S0} is the maximum overpressure of the incident wave, b is the coefficient of wave decay, t is the time and t_d is the duration of the positive phase of the pressure.

The shock wave is further characterised by its positive impulse i_s , which represents the total force per unit area applied to a structure due to an explosion and can be calculated by integrating the pressure-time curve, as described in Equation 1.10 [106].

$$i_s = \int_{t_A}^{t_A+t_0} P_s(t) dt = P_{s0} \times t_0 \left(\frac{1}{b} - \frac{1 - e^{-b}}{b^2} \right) \quad 1.10$$

1.4.2. Deflagration

In the case of deflagrations, a slower pressure increase is observed. These are typical in reactions of combustible dust, gases and mixtures of combustible liquids and air. Compared with detonations, deflagrations typically have lower peak overpressures but considerably longer positive pressure phases, resulting in significantly larger thrusts.

Deflagration is the most common mode of flame propagation and is characterised by a less severe wave propagating at subsonic velocity relative to the unburned gas immediately ahead of the flame. In this type of blast wave, the heat produced by a chemical reaction in any reaction zone is transported ahead of the reaction zone, where the mixture is preheated for the reaction, with the expansion of the products of combustion at elevated temperatures creating a flow field ahead of the flame. In deflagrations, the representative parameters to be considered are the flame speed and explosion pressure, the composition of the cloud originating and the concentration, as well as the geometrical condition inside the cloud.

Initially, the combustion rate or flame propagation is laminar, and the overpressure does not have a high value. However, the increase in turbulence, being a repercussion of the advance of the explosion, causes a higher burning velocity and, obviously, a more turbulent deflagration, as shown in Figure 1.13. This increase in turbulence is mainly due to the interaction between the processes and structures. Therefore, according to Bakke et al. (1992) [107], deflagration requires confinement or obstruction to propagate at high velocities.

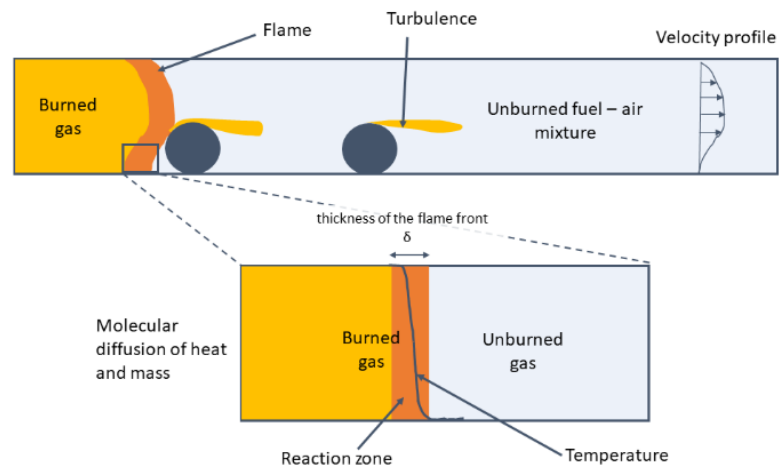


Figure 1.13: Laminar flame front in a premixed gas and introduction of turbulence in a channel owing to obstacles [107]

In addition to confinement and turbulence, several factors influence the deflagration pressure. These include temperature; higher ambient temperatures generally cause a more rapid rise in pressure and fuel/air ratio, and a mixture close to the stoichiometric ratio tends to generate higher pressures as complete combustion occurs.

1.4.3. TNT Equivalent

Studies on explosive effects can be based on an analysis and comparison with 2,4,6-trinitrotoluene (TNT) as a reference explosive.

TNT equivalent is based on mathematical relationships, as shown in Equation 1.11, which correlates the effects produced by specific masses of alternative explosives with those generated by TNT under controlled conditions [108,109]. Where E_{TNT} represents the TNT equivalent, W_{TNT} is the mass of TNT causing the equivalent, positive pressure impulse at the same distance as the mass W_{EXP} of the material in question, I is the impulse, and Z is the reduced distance from the explosive. This characterisation includes fundamental parameters such as overpressure, specific impulse, arrival time, positive phase duration and shock wave velocity.

$$TNT_{equivalent} = E_{TNT} = \left(\frac{W_{EXP}}{W_{TNT}} \right)_I = \left(\frac{Z_{EXP}}{Z_{TNT}} \right)^3_{P_{max} = constant} \quad 1.11$$

The predominant methodology used to determine these equivalences is based on the analysis of shock waves using blast tests in open air, which allows correlations to be established mainly through pressure and impulses. Temporal parameters, such as arrival time and positive phase duration, are used less frequently in these analyses.

Variations in the determination of the TNT equivalent depend significantly on experimental factors such as the configuration of the confinement, the method of initiation, the geometry of the charge and the arrangement of the explosive elements. Although a comparison with TNT charges under identical conditions would ideally be sought, the usual practice uses standardised reference values according to UFC 3-340-02 [110], thus facilitating comparability between different explosive systems.

The analytical process requires contrasting experimental results with established reference values, applying higher-order polynomial adjustments that incorporate logarithmic transformations to characterise the various parameters of the blast wave, according to Equation 1.12.

$$P = e^{(A+B \times (\ln Z) + C \times (\ln Z)^2 + D \times (\ln Z)^3 + E \times (\ln Z)^4 + F \times (\ln Z)^5 + G \times (\ln Z)^6)} \times 10^{-3} \quad 1.12$$

Where Z represents the scale distance, defined in detail at the next section, and A , B , C , D , E , F and G are the simplified Kingery air blast coefficients and are listed in Table 1.6.

Table 1.6. Simplified Kingery Air Blast Coefficients for Blast Overpressure [111]

Z (m/kg ^{1/3})	A (-)	B (-)	C (-)	D (-)	E (-)	F (-)	G (-)
0.2 – 2.9	7.2106	-2.1069	-0.3229	0.1117	0.0685	0	0
2.9 – 23.8	7.5938	-3.0523	0.40977	0.0261	-0.01267	0	0
23.8 – 198.5	6.0536	-1.4066	0	0	0	0	0

The characterisation of the positive wave parameters, both incident and reflected, for hemispherical configurations of TNT on the surface is graphically shown as a function of the scaled distance, following the criteria established in the 2008 UFC, as shown in Figure 1.14.

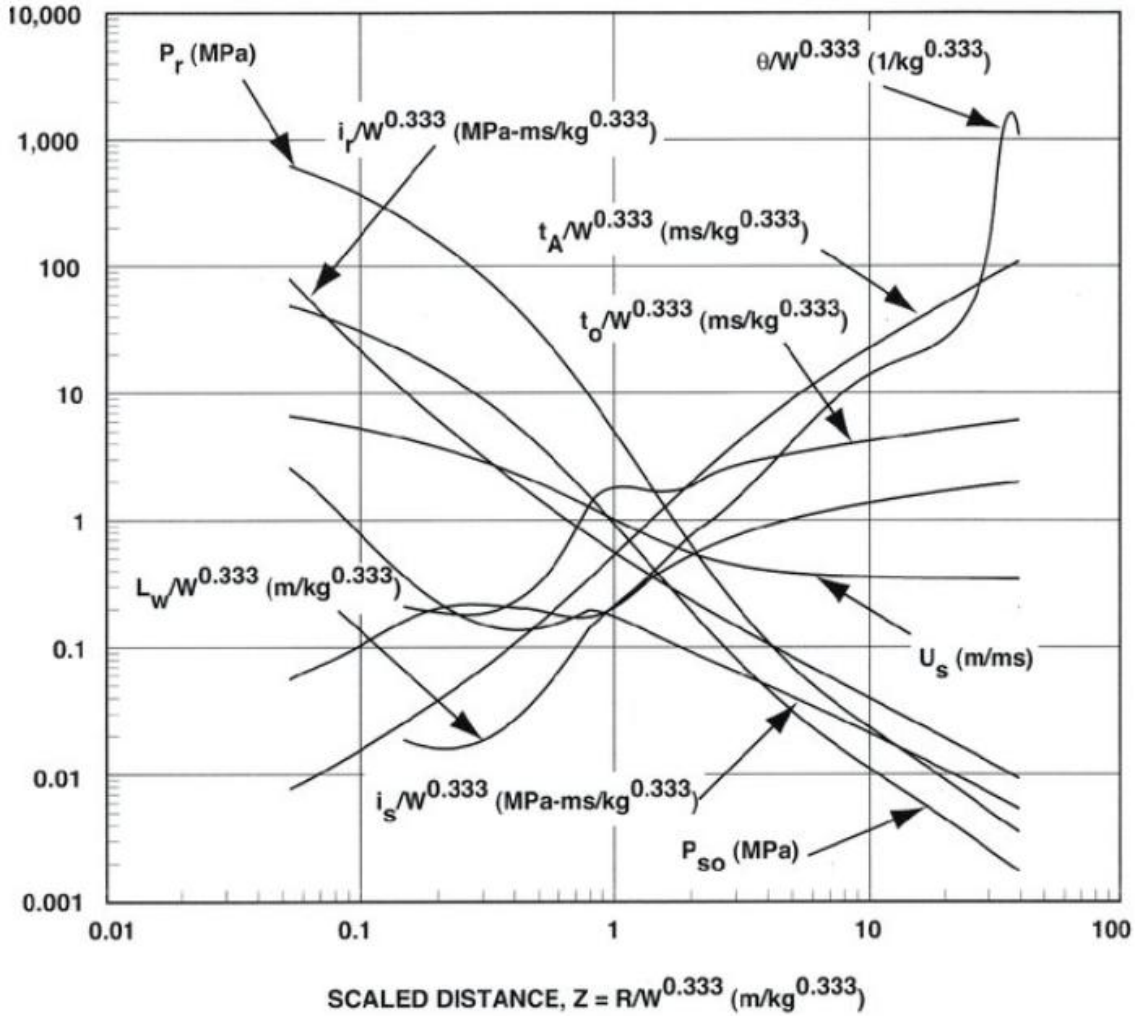


Figure 1.14: Blast-wave parameters according to [112]

1.4.3.1. Scaled Distances

Kleine et al. (2007) [113], in their study of laboratory-scale shock wave phenomena, highlighted how reducing the size of the explosive charge to the order of milligrams could eliminate most of the difficulties associated with large-scale experiments. This demonstrates the extent to which small-scale assays can produce appropriately scaled results that replicate large-scale or even full-scale explosions.

After World War I, Hopkinson (1915) [114] and Cranz (1926) [115] independently developed what is now known as the most widely used scaling law, also called the "cube root" scaling law, as seen in Equation 1.13. This law states that shock waves produced by two explosives of similar geometry and of the same material, but of different sizes, will generate the same maximum pressures when measured at equivalent scaled distances (Z).

$$Z = \frac{d}{W^{\frac{1}{3}}} \quad 1.13$$

Where d is the distance from the point of detonation and W is the mass of the explosive. This principle can be illustrated by an example: if a target at distance d of the centre of an explosive charge W is subject to a shock wave with maximum overpressure P , duration t_d and momentum i . The Hopkinson-Cranz scaling law states that a target positioned at a k_d distance from a k^3W mass explosive charge will be exposed to the same maximum overpressure P , but with a kt_d duration and a ki impulse, as can be seen in Figure 1.15.

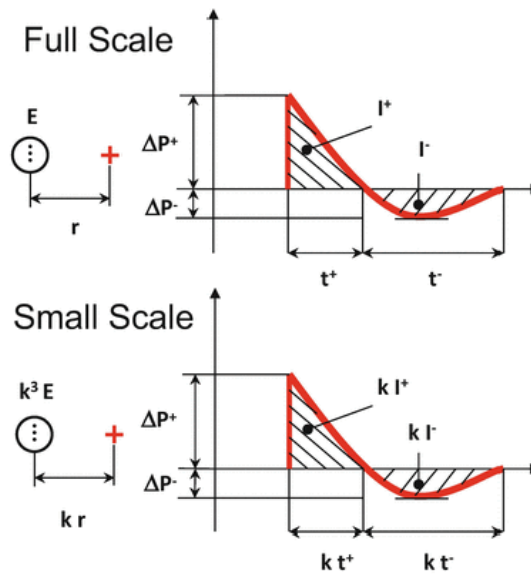


Figure 1.15: Hopkinson-Cranz wave scaling [116]

1.4.3.2. TNT Equivalent Assessment Methods

According to what has been presented by various authors, there are several empirical or theoretical methods to evaluate the TNT equivalent, among which three empirical methods (ballistic mortar, cylinder and air blast methods) [109] and three theoretical methods (Berthelot, Cooper and based on heat of detonation methods) are presented below [109,110,117].

Ballistic Mortar

The method consists of quantifying the amount of explosive sample required by a ballistic mortar to reach the same height it reaches when 10 g of TNT is used.

Cylinder

In this method, high-speed photography is used to quantify the radial velocity of the explosion of a metal cylinder filled with explosives, thereby measuring the detonation

velocity and the effects of the explosive on the metal cylinder. Once this quantification is obtained, the results obtained are compared with respect to TNT.

Air blast

The experimental method consists of detonating the charges in open air by quantifying the incident pressure, as well as the impulse, at various distances from the explosion, and finally, comparing these data with those resulting from the TNT.

Berthelot

Berthelot's model consists of determining the TNT equivalent using the chemical composition of the explosive under study, as shown in Equation 1.14.

$$TNT_{equivalent} = 840 \times \Delta n \times \frac{-\Delta H_R^0}{MW_{expl}} \quad 1.14$$

Where Δn represents the number of moles of gas released/number of moles of the explosive, ΔH_R^0 represents the standard detonation reaction heat and MW_{expl} the molecular mass of the explosive.

Cooper

Cooper's model is based on the square of the detonation velocities of explosives, a ratio expressed in Equation 1.15, where D is the detonation velocity in m/s for both the explosive (D_{exp}) and the TNT (D_{TNT}).

$$TNT_{equivalence} = \frac{D_{exp}^2}{D_{TNT}^2} \quad 1.15$$

Based on heat of detonation

This model is proposed using Equation 1.16, where the heat of detonation of both explosives (H_{exp}^d and H_{TNT}^d) is related to the amount of effective charge (W_E) and that of the explosive to be quantified (W_{exp}).

$$W_E = \frac{H_{exp}^d \times W_{exp}}{H_{TNT}^d} \quad 1.16$$

1.4.4. Computational Simulations

One technique for studying the effects of explosions is to use the finite element method. Improvements in computational capacity and finite element codes have led to an increasing amount of work using this methodology. The finite element method aims to obtain approximate numerical solutions in a discretised continuum medium in elements interconnected by nodes. The equations of motion that characterise the physical response to the problem are defined employing a variational or weak formulation of the equations of motion and the construction of an approximate solution based on nodal coordinates and shape functions of the elements [118,119].

Time-integrated algorithms are used to solve the equations. There are two main techniques for integrating differential equations expressing the dynamical problem into time: implicit and explicit methods. In implicit methods, the system state at the next time step (x^{n+1}) is obtained using the current state (x^n), current state derivative ($\dot{x}^n$) and the dynamical equation at time t^{n+1} are known. However, these methods are unconditionally stable; therefore, their passage of time is not limited. In the explicit methods, known x^n and $\dot{x}^n$ and the dynamical equation at time t^n , x^{n+1} is obtained. These methods are conditionally stable; therefore, the passage of time must be limited by the Courant condition [118,119]. This can be interpreted as requiring that the maximum numerical rate of transmission of information may in no case be less than the physical rate; otherwise, the integration may become unstable.

Implicit integration methods

The main characteristic of implicit methods is that they are unconditionally stable; therefore, the passage of time can be large, but they have a higher number of operations per cycle than explicit methods. There are several implicit methods of integration over time, among which those of the β -Newmark family stand out, such as the trapezoidal method and the Hilber-Hughes-Taylor method (HHT- α) [120].

The first of these, thus represents the approximations of the displacement field and velocity. The second, the HHT- α method, although it uses the same displacement and velocity fields used in the Newmark method, the treatment of the dynamic equilibrium equation is different.

Explicit integration methods

The essential characteristic of explicit methods is that the integration interval is so short that contiguous nodes of the mesh do not have time to communicate with each other during an interval. This is formalised as the Courant-Friedrich-Lewy condition [121], which guarantees the stability of the integration, as shown in Equation 1.17.

$$\Delta t_{crit} = \frac{h}{c} \quad 1.17$$

Where Δt_{crit} is the time it takes for the wave to travel through an element, h is the minimum dimension of the element and c is the wave propagation velocity. Thus, the critical time is the time required for a wave to travel through an element. Imposing this maximum time step decouples the equations from the motion of the nodes such that they can be solved individually in each integration interval.

On the other hand, the finite volume method (FVM) is a discretisation method for the approximation of partial differential equations or a system that expresses the convergence or balancing of one or several variables. Similar to the finite element method, a mesh is constructed consisting of a partition of the domain where the special variable is expressed. The elements of the mesh are referred to as control volumes. The integration of the PDE at each control volume results in an equilibrium equation. Subsequently, the set of equilibrium equations is discretised with respect to a set of discrete unknowns. The main issue is the discretisation of the flows at the boundaries of each control volume [122,123].

1.4.4.1. Viper::Blast

One of the CFD software capable to simulate the detonation of various TNT charges is Viper::Blast [124], which can simulate different explosions, as shown in Figure 1.16 and Figure 1.17. Viper::Blast is a finite-volume CFD code using the Advection Upstream Splitting Method (AUSMDV) numerical scheme [125].

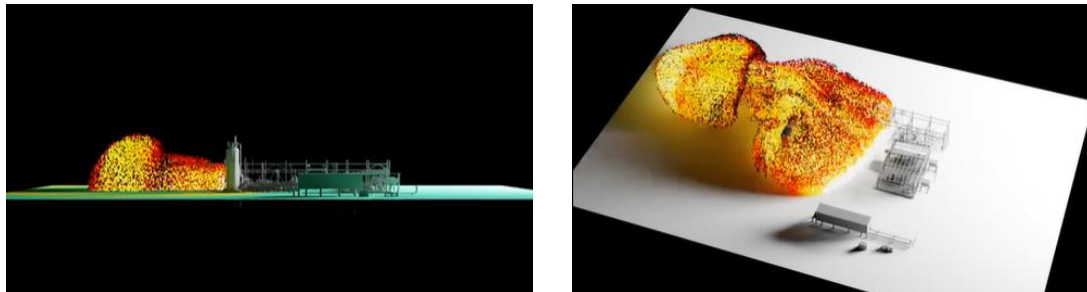


Figure 1.16: Simulation of vapour cloud explosion (VCE) [124]

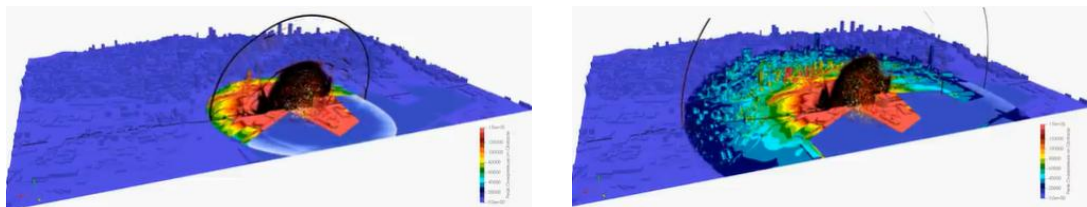


Figure 1.17: Simulation of the explosion that occurred in Beirut (2,750 T of ammonium nitrate) [124]

The main advantage of Viper::Blast is that the simulation times are reduced because it uses hardware acceleration and runs on a graphics processing unit (GPU) [124]. Explosion scenarios can be simulated in Viper::Blast using one of the two methods:

- The first is to directly release energy into an ideal gas domain by specifying the mass of the charge, its geometry, the density of the explosive, and the energy of the detonation [126,127].
- The other method that can be used is the specification of the parameters of the Jones-Wilkins-Lee equation of state (JWL) for the explosive [128–130].

Specifically, the second is widely used in simulations, whose objective is to define the behaviour of the detonation and expansion of the explosive in relation to its pressure-volume energy. The JWL governs the pressure behaviour of detonation gases as a function of the relative volume (V) and internal energy (E), as shown in Equation 1.18.

$$P = A \left(1 - \frac{\omega}{R_1 V} \right) e^{-R_1 V} + B \left(1 - \frac{\omega}{R_2 V} \right) e^{-R_2 V} + \frac{\omega E}{V} \quad 1.18$$

where A , B , R_1 , R_2 and ω are constants to be determined experimentally, with the cylinder test being the most common methodology [131] (see Table 1.7 for examples of different explosives). While $V = \frac{\rho}{\rho_0}$ it is the ratio between the current and initial density. On the other hand, E is the internal energy per unit volume calculated through Gurney energy [132] and E_0 is the total available energy.

Table 1.7. JWL Equation of state (EOS) parameters for various explosives [133]

Explosive	A (GPa)	B (GPa)	C (GPa)	R_1 (-)	R_2 (-)	E_0 (GPa)	ω (-)
Panelling	203.58	2.97	0.39	6.65	1.13	2.05	0.39
No glasses	266.80	3.44	0.24	7.04	1.16	1.73	0.39
Nagolita	207.79	2.91	0.43	5.91	1.08	2.29	0.40
Alnafo	135.76	1.35	0.66	5.46	0.70	3.38	0.32
A-U-50	216.04	1.84	0.15	7.16	0.87	1.56	0.34
A-U-100	231.80	3.41	0.10	6.76	1.07	1.58	0.36
Titan-6000-E1	209.69	3.51	0.52	5.76	1.29	2.39	0.39
Titan-6000-E6	365.29	2.70	0.23	5.00	0.89	3.04	0.23
Titan-6080-E4	140.65	2.44	0.28	6.00	1.09	1.69	0.38
Titan-6080-E3	115.80	1.24	0.15	5.07	0.53	2.01	0.38
Titan-6080-E12	385.82	5.05	0.33	5.49	1.17	3.27	0.25
Titan-6080-E7	557.60	5.35	0.45	6.10	1.07	4.09	0.24
Titan-6080-E9	849.56	16.68	0.45	6.85	1.66	3.38	0.42

Finally, Gurney's model [132,134] allows the estimation of the velocity imparted to a metal in contact with an explosive. The chemical energy available from the explosive after detonation and during the gas expansion phase is transformed into the kinetic energy of the metal and gases themselves. In other words, it is assumed that the specific energy of the explosive (chemical) is converted into kinetic energy, which is the Gurney energy.

1.5.AIM OF THE THESIS

The main objective of this thesis is to model the flammability and combustible properties of solid fuels to mitigate the existing risk in terms of industrial safety. This study introduces novel methodologies that correlate experimental thermal behaviour with predictive models. In addition, this study uniquely integrates experimental characterisation, numerical modelling, and computational fluid dynamics to create a more complete understanding of the combustion mechanisms of various solid fuels. To achieve this, three sub-objectives were established:

The first objective focuses on experimental characterisation using diverse thermogravimetric analysis and specific experimental tests to understand the thermal behaviour and determine the ignition sensitivity and explosion severity of various solid fuels. This first objective is essential for achieving precise quantitative values to improve the understanding of the physicochemical mechanisms inherent in the combustion of solid fuels.

Once the experimental values have been established, the second objective is to perform numerical modelling of the flammability of solid fuels using complementary approaches. First, the composition was characterised using the Fraser-Suzuki deconvolution method. Subsequently, the thermal reactivity and ‘runaway’ tendency were evaluated by developing a new parameter that correlates critical temperatures with the reactive tendencies obtained in thermogravimetric tests. Chemical kinetics were so studied by applying isoconversional methods (Friedman, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose). Finally, thermodynamics in the thermal degradation range are analysed, as well as different combustion indices.

In addition, within this objective, the development of numerical modelling methods for three experimental tests is contemplated: the minimum ignition temperature of dust layer (MIT_L), the minimum ignition temperature of dust cloud (MIT_C) and the explosion severity, quantified by obtaining three parameters: the maximum explosion pressure (P_{max}) or maximum overpressure, maximum explosion rate $(dP/dt)_{max}$ and deflagration index (K_{ST}).

Finally, the third objective involves computational modelling of the experimental test to categorise the severity of dust explosions by computational fluid dynamics (CFD) through the Viper::Blast software.

This will allow a comparative analysis to be carried out between the experimental values, the numerically modelled results and the computationally derived results.

Chapter 2

Materials and Experimental Methods

2.1.MATERIALS

Ten samples were analysed in the present research and divided into two groups: seven of these samples were biomass and the remaining three were coal. Table 2.1 shows the identification, as well as the material and origin of these.

Table 2.1. Samples identification and origin

Material	Origin	Identification
Olive pulp	Portugal	BPA
Almond shell	Portugal	BCA
Olive leaf	Córdoba, Spain	BHO
Pellets	Gipuzkoa, Spain	BPM
Straw	Switzerland	BP
Soy	Huesca, Spain	BPS
Cork oak	Portugal	BPC
Charcoal	Extremadura, Spain	CV
Bituminous coal	Álava, Spain	CH
Anthracite	A Coruña, Spain	CA

As can be seen in Table 2.1, two different olive samples were analysed, as well as samples of almond shells, pellets, straw, soybeans and cork oak in the biomass group. On the other hand, in the group of coals, three variants were chosen in order to be able to study the maximum spectrum of the Van Krevelen diagram, as shown in Figure 2.1, and thus be able to analyse flammability and its direct relationship with the composition. All the samples were milled and sieved using a 1 mm light sieve.

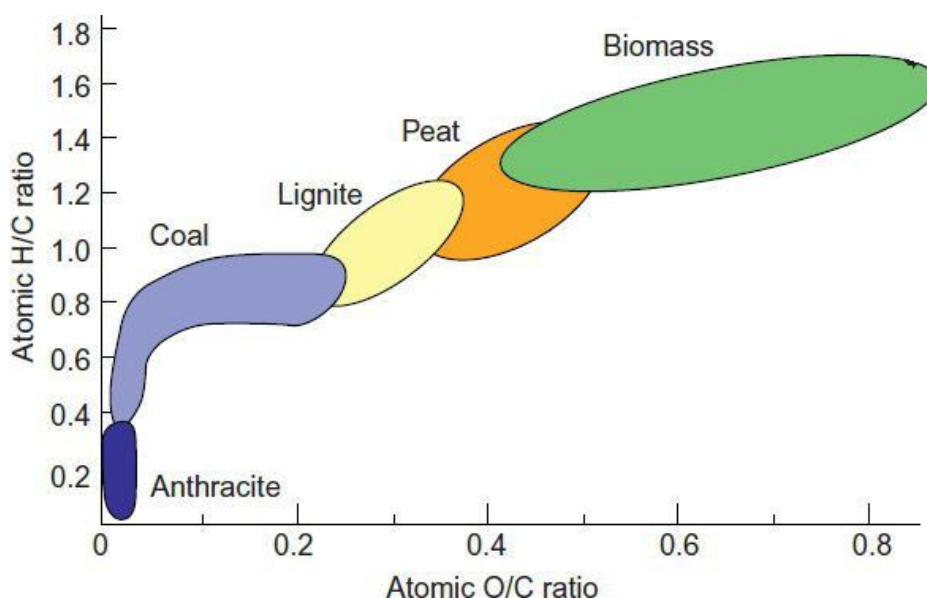


Figure 2.1. Van Krevelen diagram [135]

2.2. EXPERIMENTAL METHODS

The experimental work of this study was structured in two complementary aspects. On the one hand, a complete characterisation of the samples was carried out through the determination of physical properties, immediate analysis, and thermogravimetric analysis, which allowed a detailed profile of the materials studied to be established. In contrast, various ATEX (atmospheres explosives) parameters were evaluated, which are essential for understanding the associated risks and developing preventive measures in industrial environments.

2.2.1. Physical Properties

The physical properties were determined as follows: granulometry, bulk density and moisture content. Granulometric analysis was performed using a Malvern Mastersizer 2000 (Malvern Instruments Ltd. Worcestershire, UK) device. The device allows for the analysis of the particle size distribution of the samples in an interval between 60×10^{-9} and 2×10^{-3} m. To do this, it uses two light sources, the first of which is a helium-neon laser and the second is a solid-state light. Because of these two sources and the application of Mie's dispersion theory, the device can calculate the particle size distribution (PSD).

The software provides the curves of the particle distribution (see Figure 2.2) emphasising the following parameters: d_{10} , d_{50} , d_{90} (particle diameter where 10, 50 and 90% respectively, of the distribution has a smaller particle size), Sauter $d[3,2]$ and De Brouckere $d[4,3]$ parameters (mean diameters of the particle size based on area-weighted and volume-weighted, respectively) and SSA (mean the specific surface area). In addition, through these PSD parameters, the polydispersity index (σ_D) can be determined as $\frac{d_{90}-d_{10}}{d_{50}}$.

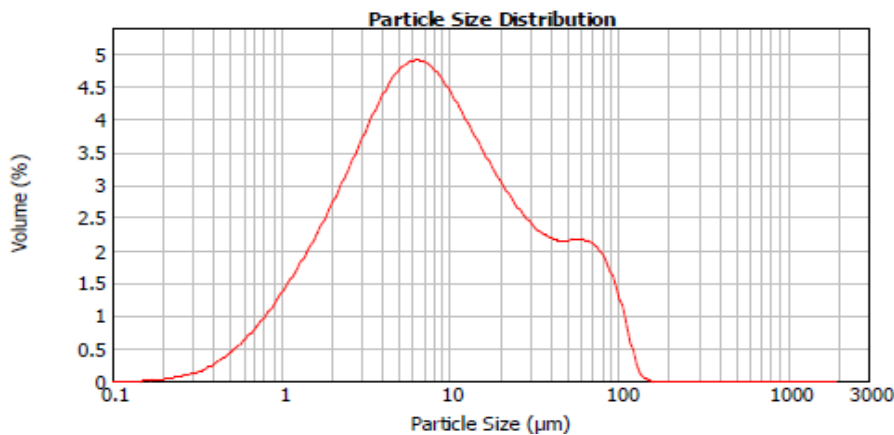


Figure 2.2. Particle size distribution example curve

The moisture content, represented by the amount of water present in the samples, covering both their surface and the inner pores, was measured using a Mettler Toledo HN43-S halogen analyser by applying a constant temperature of 105 °C until the weight loss measurement remained null. Each sample was subjected to three repetitions of the test, followed by the calculation of the standard deviation. The acceptance of the results was valid as long as the standard deviation did not exceed 15%. Once the results were validated, the mean values of the three tests were calculated.

On the other hand, a container of known volume was used to obtain the bulk density of the samples. The procedure consisted of initially weighing the empty container on an analytical balance and then filling it with uncompacted powder, maintaining a level surface, and eliminating air bubbles trapped in the container. Subsequently, the entire container was weighed with the powder, and this process was repeated three times to ensure the reproducibility of the results. Finally, this parameter was calculated as the ratio of the mass of the powder to the known volume of the container.

2.2.2. Proximate Analysis

Proximate analysis refers to the determination of the volatile matter, fixed carbon and ash content of samples. The analysis was performed according to the following regulations: UNE 32019-84 [136] for volatile content (*VM*) and UNE 32004-84 for ash content (*ASH*) [137]. The fixed carbon (*FC*) content was calculated as $100 - \text{Volatile matter} - \text{Ash content}$.

2.2.2.1. Volatile Matter

The volatile content was calculated as a percentage using Equation 2.1.

$$VM = \frac{m_2 - m_3}{m_2 - m_1} \times 100 - MS \quad 2.1$$

Where m_1 is the weight of the crucible with lid in grams, m_2 is the weight when m_1 it has been filled with the sample before heating in grams, m_3 is the weight of m_2 after heating in grams and *MS* is the moisture content in percentage. On the other hand, to obtain the value on a dry basis (d.b.), Equation 2.2 is applied.

$$VM_{d.b.} = \frac{100}{100 - MS} \times VM \quad 2.2$$

2.2.2.2. Ash

The ash content was calculated as a percentage using Equation 2.3.

$$ASH = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \quad 2.3$$

Where m_1 is the laboratory dish weight in grams, m_2 is the weight of m_1 when it has been filled with the sample before heating in grams and m_3 is the weight of m_2 after heating with the remaining sample (ash) in grams. On the other hand, to obtain the value on a dry basis, Equation 2.4 was applied.

$$ASH_{d.b.} = \frac{100}{100 - MS} \times ASH \quad 2.4$$

2.2.3. Thermogravimetry Analysis

Simultaneous thermal analysis (STA) refers to the joint use of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermogravimetric analysis focuses on the measurement of mass variations when the temperature changes or during isothermal processes. In the present research, to carry out these tests, Mettler Toledo TG/DSC T50 equipment was used, together with 70 μ L alumina crucibles. The tests were carried out in an air atmosphere at various constant heating rates ($\beta = 3, 5, 7, 10$ and 20 K/min) in a temperature range of 30 - 800 $^{\circ}\text{C}$. However, at the end of the 5 K/min test, an isothermal process at 800 $^{\circ}\text{C}$ in a pure oxygen atmosphere was incorporated to estimate the fixed carbon content. The sample amount used to perform these tests was 20 mg, with a margin of error of ± 2 mg.

Generally, the results of thermogravimetric tests are arranged in the form of three curves: the thermogravimetric curve (TG) and the first and second derived curves (DTG and DDTG, respectively). The first of these shows the loss of mass (mg or %) as a function of temperature increase ($^{\circ}\text{C}$) and, therefore, its derivatives will have units of mg -or- $\%/^{\circ}\text{C}$ and mg -or- $\%/^{\circ}\text{C}^2$, respectively. In addition, four identified events were observed during the test: event *I* represents the drying process, event *II* corresponds to the loss of intramolecular moisture, event *III* corresponds to the thermal degradation process, and event *IV* represents the oxidation of the carbonaceous residue of the sample, as shown in Figure 2.3.

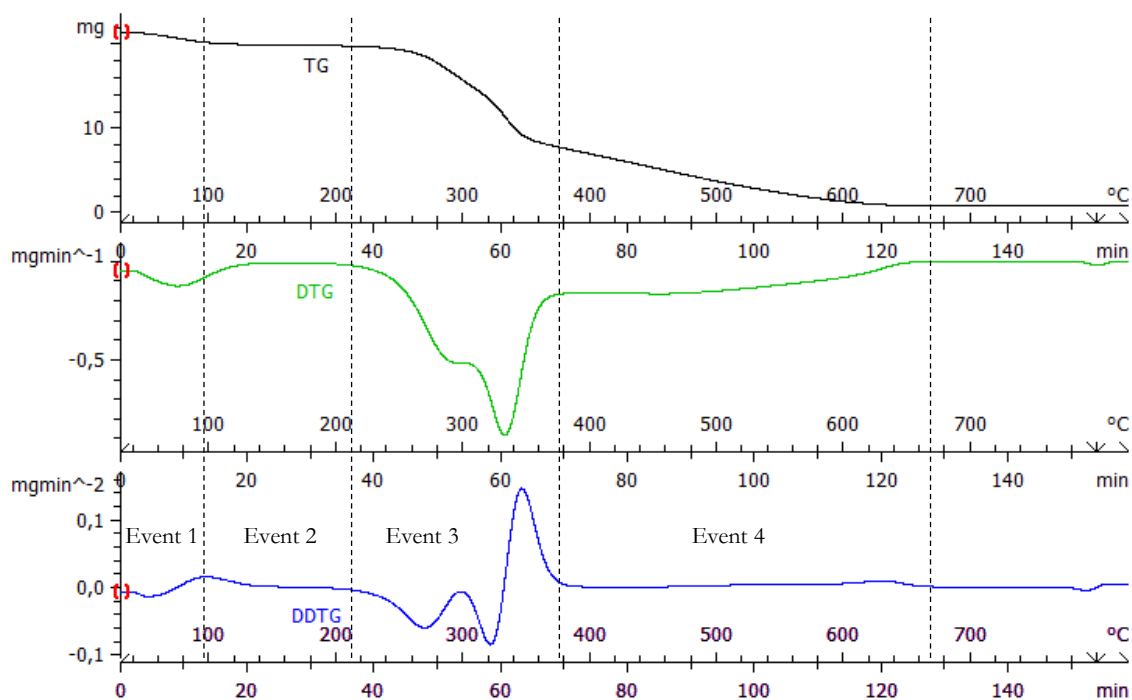


Figure 2.3. TG, DTG and DDTG curves

By analysing the TG-DTG curves at the thermal level in Figure 2.4, a series of points or characteristic temperatures can be observed.

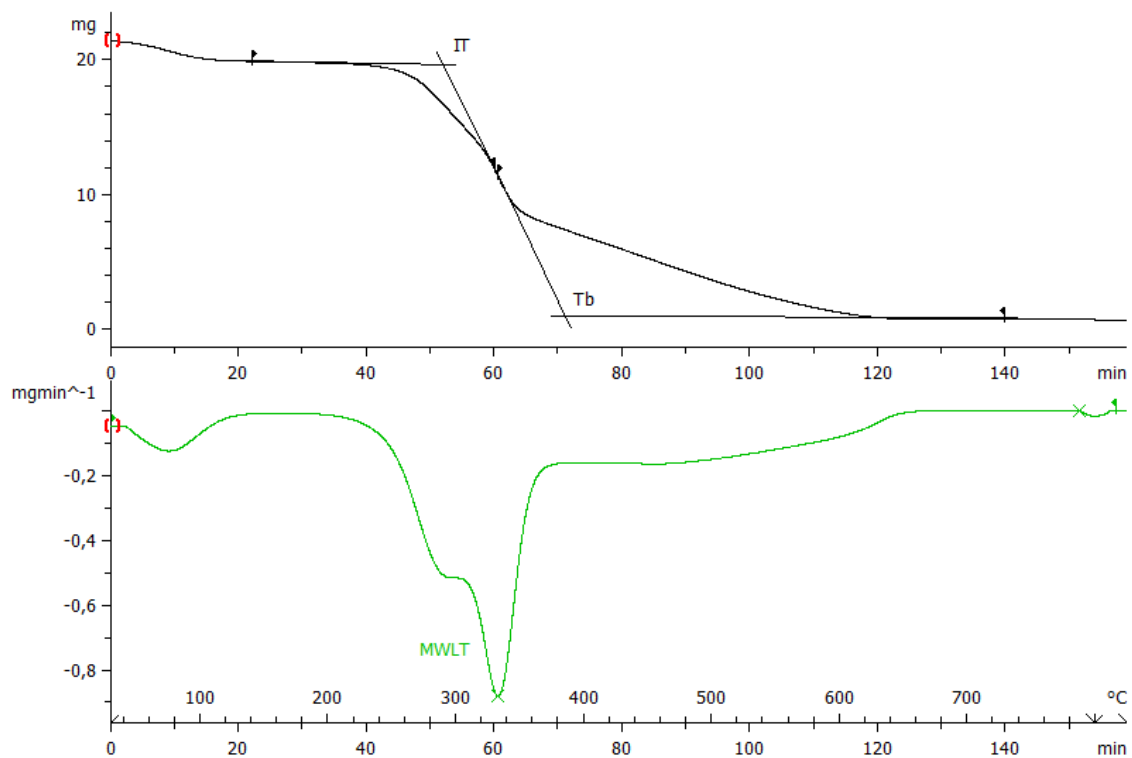


Figure 2.4. Characteristic TG-DTG points

Where IT represents the induction or onset temperature ($^{\circ}\text{C}$) calculated according to Castells et al. (2021) [138]. At this point, the reaction accelerates to such an extent that the mass loss decreases significantly. On the other hand, $MWLT$ represents the maximum weight loss temperature, determined as the temperature of the absolute minimum of the DTG curve ($^{\circ}\text{C}$) [138], therefore, the temperature at which the reaction rate reaches its maximum; and T_b ($^{\circ}\text{C}$) represents the burnout temperature, determined as the intersection between the tangent in the absolute minimum of the DTG curve referred to the TG curve and the tangent in the carbonaceous residue area [139].

On the other hand, analysing the three curves at the thermal and compositional level, that is, taking into account the devolatilisation of the three predominant macromolecules in biomass – hemicellulose, cellulose, and lignin – in Figure 2.5, various points and stripes can be observed.

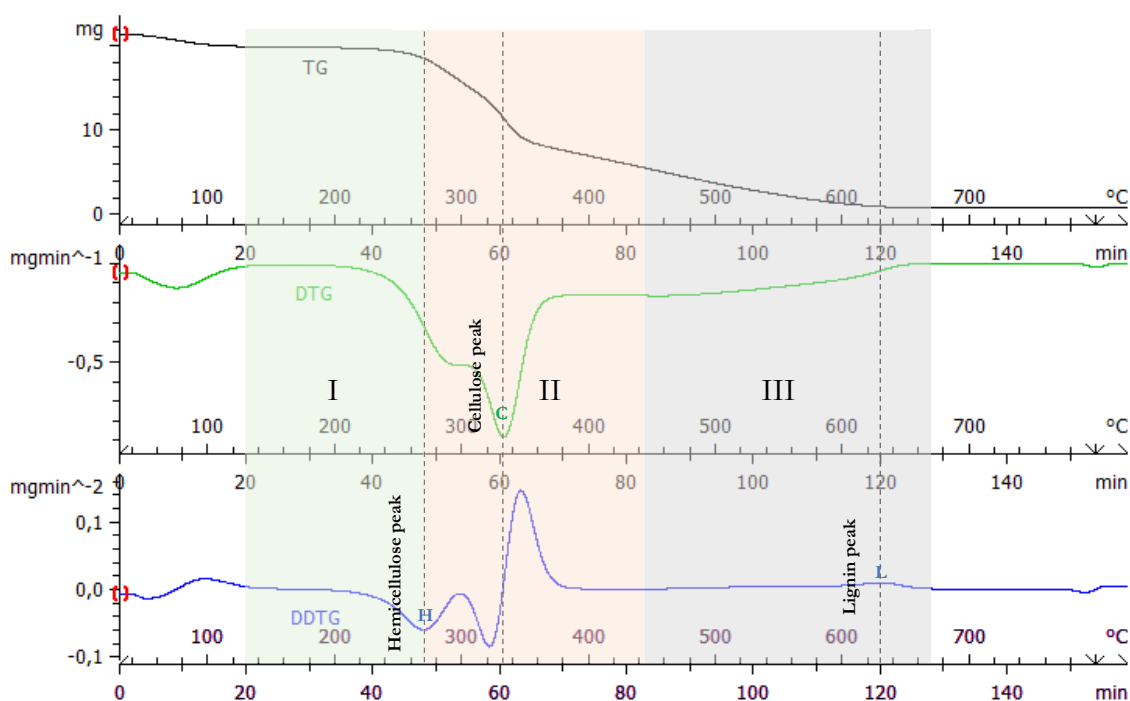


Figure 2.5. Thermal devolatilisation ranges and characteristic points

Three different stages can be observed. *I* corresponds to the range of the thermal decomposition of hemicellulose and lignin (mostly hemicellulose). The maximum devolatilisation temperature of hemicellulose is expressed as H in the DDTG curve. *II* corresponds to the thermal decomposition range of cellulose and lignin (mostly cellulose). The maximum cellulose devolatilisation temperature is expressed as C in the DTG curve. *III* corresponds to the thermal decomposition range of lignin and carbonaceous residue. The maximum devolatilisation temperature is expressed as L in the DDTG curve [140,141].

2.2.3.1. Proximate Analysis

Through thermogravimetric tests, it is possible to obtain approach values for moisture, volatile matter, fixed carbon, and ash content that are close to those presented experimentally. According to Papari et al. (2015) [142] and Dewayanto et al. (2015) [143], these values can be calculated as the mass percentages loss in three different stages, whose approximation is shown in Figure 2.6.

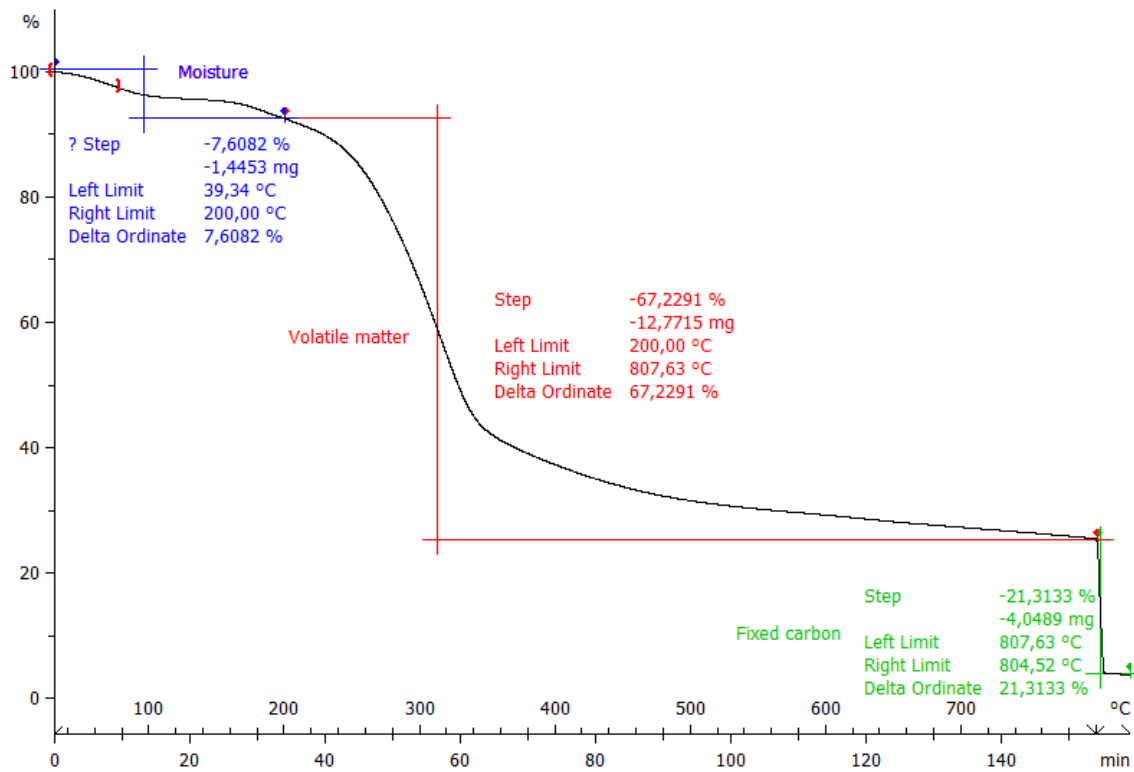


Figure 2.6. Proximate analysis by TGA approach

Figure 2.6 exposes the approach of moisture (up to 200 °C, temperature at which all intramolecular moisture has been lost- blue zone), volatile matter (before the sudden drop due to the injection of O₂ in the test- red zone), fixed carbon (until the end of the test- green zone), and ash content, which is calculated as $100 - MS - VM - FC$.

2.2.4. ATEX Parameters

2.2.4.1. Minimum Ignition Temperature of Dust Layer

The minimum ignition temperature of dust layer (MIT_L) determines the minimum temperature at which a powdery substance deposited on a hot surface ignites. The determination of this parameter is regulated under the European standard UNE-EN ISO/IEC 80079-20-2:2016 [43], and the test device is observed in Figure 2.7.



Figure 2.7. Minimum ignition temperature of dust layer apparatus

The device consists of a heated dish and a metal ring where the sample is to be deposited. This heated tray must be metallic with a working area not less than 20 cm in diameter and 2 cm in thickness. In addition, it must be electrically heated, and the temperature must be controlled.

However, layers of dust must be formed without compression. Once dust is deposited on the metal ring, it must be removed. This must have an internal nominal diameter of 10 cm, and, in this case, the research was carried out with a dust layer thickness of $5 \text{ mm} \pm 0.1 \text{ mm}$ under ambient conditions.

In the test method, ignition is considered when a visible flame or combustion occurs, a temperature of 450°C is exceeded, or a temperature increase of 250 K above the temperature of the pan is quantified, with 400°C being the upper-limit temperature of the pan to be tested. Once the temperature at which the powdery sample does not ignite in the range of 5 K in 30 min has been determined, tests should be carried out at 60 and 120 min.

2.2.4.2. Minimum Ignition Temperature of Dust Cloud

The minimum ignition temperature of dust cloud determines the minimum temperature at which a powdery cloud ignites. The determination of this parameter is regulated under the European standard UNE-EN ISO/IEC 80079-20-2:2016 [43] the test device can be seen in Figure 2.8.

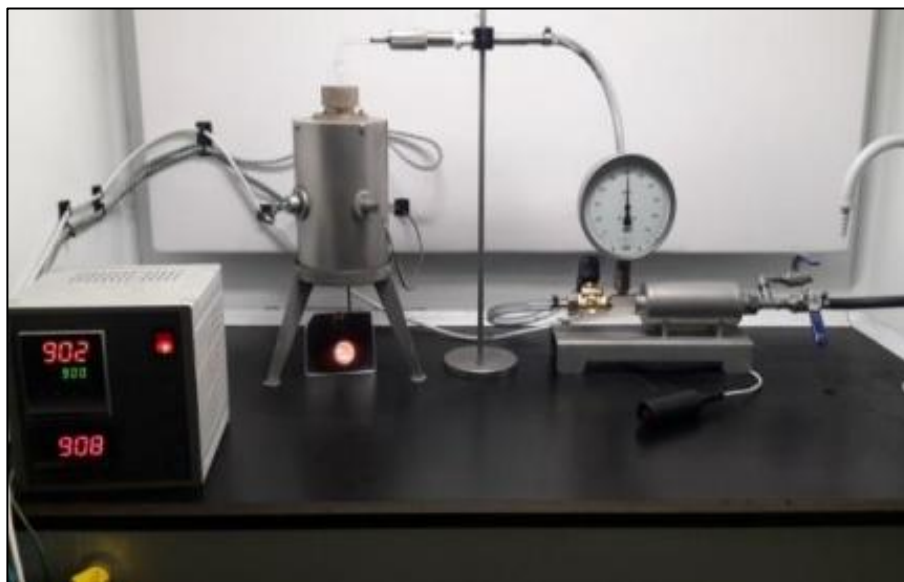


Figure 2.8. Minimum ignition temperature of dust cloud apparatus [144]

The device consists of a vertical furnace (Godbert Greenwald furnace) capable of reaching 800 °C, where swelling is visually detected. In addition, the entire furnace is composed of the dust dispersion system, including the 500 mL air reservoir and temperature control unit.

On the other hand, regarding the test procedure, the amount of dust to be tested should be within the range of 0.05 – 0.5 g, although typically the quantities to be tested are 0.1, 0.2 and 0.3 g. In addition, the dust dispersion pressure should vary between 10 and 50 kPa, although typically the pressures to be tested are 10, 20, 30 and 50 kPa.

In the absence of prior information, the test will start at 500 °C, with an amount of 0.3 g and an air pressure of 30 kPa. In the case of no ignition, the temperature must be increased in steps of 50 K until it reaches 600 °C, although there is no prohibition for testing above this temperature. Once ignition is observed, ten checks should be carried out throughout the aforementioned range and the temperature should be reduced by 20 K to 300 °C. If the minimum ignition temperature is below 300 °C, the pitch will not be at 20 K, but at 10 K.

2.2.4.3. Explosion Severity

The explosion severity of dust is determined by three parameters: maximum explosion pressure (P_{max}), maximum explosion rate $(dP/dt)_{max}$, and deflagration index (K_{ST}).

The maximum explosion pressure is the maximum overpressure produced during explosions of explosive atmospheres within the explosive range of combustible dust in a closed vessel. The test procedure is governed by the following standards: UNE-EN 14034-1:2005+A1:2011 [75] and UNE-EN 14034-2:2006+A1:2011[78].

The dust is dispersed through the sample holder into the sphere, and at the moment when the dust is in suspension, detonation is caused by two igniters of a zirconium mixture of 5 kJ each. Once the explosion of the combustible dust ($P_{ex} \geq 0.5$ bar) occurs, the software provides the P-t curve, where the values of the maximum explosion pressure and the maximum value of its derivative are collected, as well as the direct calculation of the deflagration index (K_{ST}), as will be seen in later chapters. The 20-litre sphere vessel is shown in Figure 2.9.



Figure 2.9. 20 litres sphere apparatus [68]

Once the representative parameters are obtained and, under the classification established in Table 2.2, the severity of the explosion is categorised.

Table 2.2. Combustible dust explosion classification [78]

Explosion Class	K_{ST}	Characteristics
St 0	0	No explosion
St 1	$0 > K_{ST} \leq 200$	Weak explosion
St 2	$200 > K_{ST} \leq 300$	Strong explosion
St 3	> 300	Very strong explosion

2.2.4.4. BZ Burning Class Number

The behaviour of a combustible substance to combustion and flame propagation can be quantified through the BZ Burning Class Number through the board method, following the UNE EN 17077:2018 standard [94]. The BZ Burning Class Number varies between 1 and 6, according to Table 2.3.

Table 2.3. BZ Burning Class Number possible results [94]

Test Result		BZ Burning Class Number
No ignition		1
Brief ignition, rapid extinction	No propagation	2
Localized combustion or glowing with practically no spreading or only local propagation	of combustion	3
Glowing or smouldering (without sparks or flames) or slow decomposition without flames	Full propagation of	4
Quiet combustion with flame or sparks	combustion through the	5
Very rapid combustion with flame or very rapid decomposition	whole dust train	6

The experimental procedure of the test consists of depositing a certain amount of the sample on an insulating surface and causing it to ignite. In addition, there must be a constant airflow of 0.2-0.4 m/s in the direction of reaction propagation. The method consists of performing the test on a clean, flat and non-combustible insulating plate placed in a laboratory fume hood.

A mould 20 ± 2 mm wide, 10 ± 1 mm high, and at least 40 mm long was used to form a triangular dust train. Once the triangular dust train was deposited, ignition was performed. This ignition could result from electrical heating, which reached a temperature of approximately 1,000 °C, or from an open flame from a burner (operated with butane, propane, natural gas, etc.). The source of ignition chosen was the open flame of the burner.

Chapter 3

Numerical Methods

3.1.COMPOSITION ANALYSIS

The compositional analysis of the samples was developed using numerical methods, encompassing ultimate analysis (carbon-C, hydrogen-H, oxygen-O) from the experimental data of the proximate analysis (*MS*, *FC*, *VM*, and *ASH*) and, specifically for lignocellulosic samples, the content of its three main polymers (hemicellulose, cellulose, and lignin) by Fraser-Suzuki.

3.1.1. Ultimate Analysis

Ultimate analysis was performed based on the model developed by Ghugare et al. (2017) [145] which used the results of the proximate analysis of the 830 samples. In that study, neuronal networks were used to predict the elemental composition (%C, %H, and %O) of biomass. However, its usefulness in predicting the ultimate analysis of coal was also analysed. This analysis was conducted on the premise that coals tend to have proximate and ultimate analysis values outside the biomass range, particularly for fixed carbon (*FC*) and carbon content (%C). In addition, the decomposition mechanisms are different owing to a higher degree of aromatisation, differences in molecular structure, and different mineral matter content and composition, among other factors.

The established models are called the "GP-Model". Specifically, "GP-Model-I" is used to predict the percentage of carbon by mass, "GP-Model-II" to predict the percentage of hydrogen by mass and "GP-Model-III" to predict the percentage of oxygen by mass. Additionally, in these models, the normalised percentage by mass (on a dry basis) of fixed carbon ($\hat{x}_1$), volatile matter ($\hat{x}_2$) and ash ($\hat{x}_3$) influences, as shown in Table 3.1.

Table 3.1. Ultimate analysis equations approach [145]

GP Models	
I	$C = 35.255 \times (0.1834 + 1.271 \times \hat{x}_1 + 0.3891 \times \hat{x}_2 - 0.2873 \times \hat{x}_2^3 \hat{x}_3) + 57.605$
II	$H = 5.45 \times \frac{-\hat{x}_1 - \hat{x}_3}{2.409 + \hat{x}_2} + 3.062425$
III	$O = 24.84 \times (0.2451 + 1.495 \times \hat{x}_2 + 0.3608 \times \hat{x}_3 + 0.8407 \times \hat{x}_1^3) + 27.19$
$\hat{x}_1$	$\frac{2 \times FC - 94.64}{84.56}$
$\hat{x}_2$	$\frac{2 \times VM - 102.13}{87.33}$
$\hat{x}_3$	$\frac{2 \times ASH - 56.2}{56}$

3.2.THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) was the fundamental experimental technique used in this study. From the data obtained from the TG curve and its derivative (DTG), several analytical methods were implemented to characterise the composition, reactivity, kinetic behaviour, thermodynamic parameters, and various combustion indices.

3.2.1. Fraser-Suzuki Analysis

The Fraser-Suzuki method for estimating the hemicellulose, cellulose and lignin content of lignocellulosic biomasses consists of applying deconvolution to the DTG curve and calculating the area under the curve of each component. The expression for its calculation is shown in Equation 3.1 [146].

$$y = \sum_{i=1}^n h_i \times \exp \left[-\frac{\ln 2}{s_i^2} \ln \left(1 + 2s_i \frac{T - p_i}{w_i} \right)^2 \right] \quad 3.1$$

Where p represents the mean value of the i th curve, w is the width of the i th curve, h is the height of the i th curve with respect to the total curve, s is the asymmetry factor of the i th curve, and T is the absolute temperature, as shown in Figure 3.1.

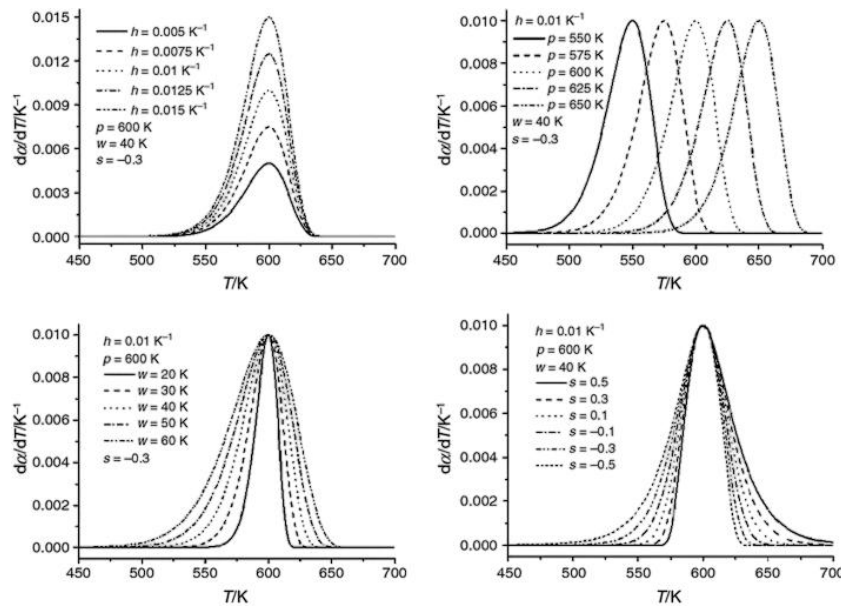


Figure 3.1. Parametric representation of the Fraser-Suzuki function [147]

In addition, n represents the number of assumed components to be analysed. Although typically $n = 3$, including in this research, owing to hemicellulose, cellulose, and lignin, in various studies involving samples that produce carbonaceous residue or char at the end of the reaction, it can be modified to $n = 4$ to account for the latter component.

3.2.2. Reactivity Analysis

The trend towards the reactivity of solid fuels was evaluated using two methods. The first of them, according to Janković et al. (2020) [92], uses five thermogravimetric tests at different heating rates ($\beta = 3, 5, 7, 10$ and 20 K/min) in air atmosphere. In this method the so-called "self-heating coefficient", is calculated considering the volatile matter content, differential analysis of the TG curve (DTG) and the reference temperatures of the critical points of these curves for each heating ratio: start peak (as T_{CRC}), inflexion and end peak (as $MWLT$).

The second method was developed as part of this study and is called the RB Index or Advanced Thermal Reactivity Index, which evaluates the tendency to reactivity by means of the critical temperature determined by the Frank-Kamenetskii thermal explosion theory, the critical temperature (T_{CRC}) evaluated as the first maximum of the DTG- runaway temperature [148]- curve and the reactivity parameter evaluated taking into account the peaks of the DTG curve according to El-Sayed et al. (2024) [149], all using a heating ratio of 5 K/min.

3.2.2.1. Thermogravimetric Index of Spontaneous Ignition

According to the above and Jankovic et al. (2020) [92], by means of the volatile matter (VM) content, the differential analysis of the TG curve (DTG) and the reference temperatures of the critical points of these curves can be defined two parameters: microscopic devolatilisation rate (ψ) and self-heating coefficient ($coef$), according to Equation 3.2 and Equation 3.3, respectively.

$$\psi = \frac{VM \times \beta_{j,i}}{T_{ref,i}} \quad 3.2$$

$$coef = \frac{DTG_i \times T_{ref,i}}{VM \times \beta_{j,i}} \quad 3.3$$

When plotting the self-heating coefficient ($coef$) vs. the reference temperatures ($T_{ref,i}$) for the three critical points, a linear relationship is obtained. The slope of this linear regression multiplied by the microscopic devolatilisation rate (ψ) represents the thermogravimetric index of spontaneous ignition (TG_{spi}), as defined in Equation 3.4, and classified according to Table 3.2.

$$TG_{spi} = slope \times \psi \quad 3.4$$

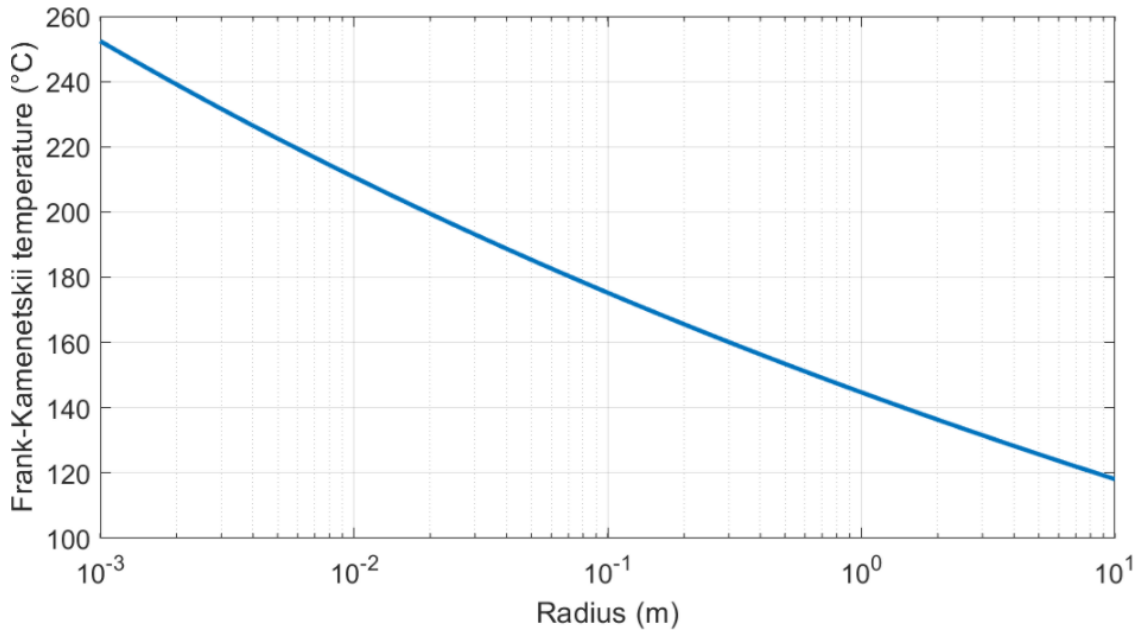
Table 3.2. Spontaneous ignition classification by TG_{spi} [92]

TG_{spi}	Class
< 0.02	Non-reactive
0.02 – 0.03	Low reactive
0.03 – 0.05	Reactive
> 0.05	High reactive

3.2.2.2. Advanced Thermal Reactivity Index

According to the above-mentioned, this parameter integrates the analysis of the investigation of the Frank-Kamenetskii thermal explosion, as well as the first derivative of the thermogravimetric curve.

The Frank-Kamenetskii critical temperature ($T_{FK}(r)$) was obtained by solving the equation (Equation 1.1) for each sample and different deposition radii (0.0025, 0.1, 0.5 and 1 m), assuming a cube as the geometric volume and, therefore, a δ of 2.519, as shown in Figure 3.2.

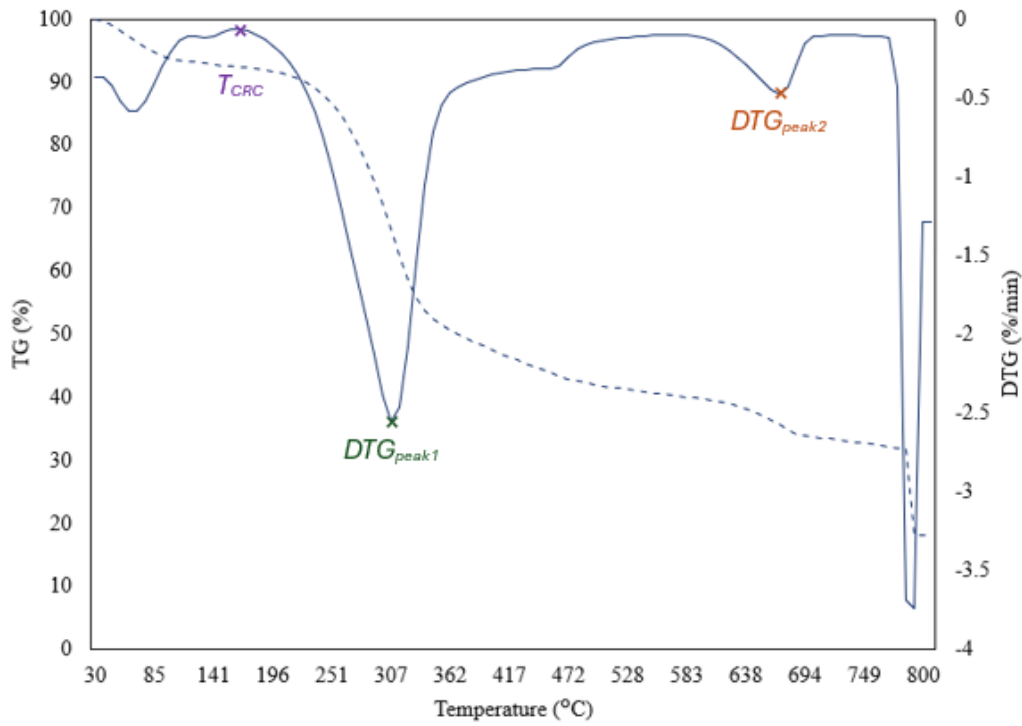
**Figure 3.2.** Frank-Kamenetskii temperature vs deposit radius curve

On the other hand, the critical temperature (T_{CRC}) was obtained by considering the first maximum of the DTG curve. This critical temperature according to Zhang et al. (2020) [148] is classified as shown in Table 3.3.

Table 3.3. Risk established through the critical temperature

Temperature	Risk
< 140 °C	High
140 – 160 °C	Medium
> 160 °C	Low

In addition, considering the relative minimums and the absolute of the DTG curve, as well as their temperatures, it was possible to quantify the reactivity (R_m). Figure 3.3 shows the evaluated critical temperature (T_{CRC}) and reactivity points.

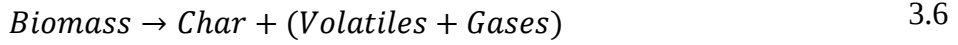
**Figure 3.3.** Critical temperature (T_{CRC}) and DTG peaks

Thus, the advanced thermal reactivity index was calculated using Equation 3.5. The term in the numerator is the quantification of the reactivity, and in the denominator, the critical temperatures.

$$RB\ Index\ (r)\ \left[\frac{\%}{min \times ^\circ C^3}\right] = \frac{100 \times \sum_i^n \frac{DTG_{peak_i}}{DTG_{peak\ temperature_i}}}{T_{FK}(r) \times T_{CRC}} \quad 3.5$$

3.2.3. Kinetic Analysis

According to Márquez-Montesino et al. (2021) [150], the thermal decomposition of biomass can be expressed by the reaction shown in Equation 3.6.



The kinetic expression that describes this process is as follows:

$$\frac{d\alpha}{dt} = Ae^{\left(-\frac{E_a}{RT}\right)} f(\alpha) \quad 3.7$$

Where t is time, $Ae^{\left(-\frac{E_a}{RT}\right)}$ is the kinetic rate constant given by the Arrhenius equation, $f(\alpha)$ is the dependent function of the reaction mechanism, and α is the normalised conversion, expressed as $\frac{m_i - m_t}{m_i - m_f}$.

In contrast, A represents the pre-exponential factor in s^{-1} , E_a is the activation energy in J/mol , R is the constant of ideal gases ($8.314 \text{ J/mol}\times\text{K}$), and T is the absolute temperature in K . In addition, m_i represents the initial mass in mg , m_f the final mass in mg at maximum temperature and m_t the mass in mg at the time t of the process. Considering that the heating rate is defined as $\beta = \frac{dT}{dt}$, Equation 3.7 can be rewritten as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} f(\alpha) \quad 3.8$$

Several non-isothermal methods based on thermogravimetry have been reported in the literature [151–153]. Divided into two large groups: model-based kinetics and model-free kinetics or isoconversional methods. The main difference between the two is that the former uses adjustment models and one of them is chosen when the best statistical behaviour is found, and the second, the isoconversional methods, use several TGA curves with different heating rates to calculate the kinetic parameters at the same conversion value and thus obtain the energy of activation.

Therefore, owing to the accuracy of the isoconversional methods, kinetic analysis was performed using three isoconversional methods (Friedman, Kissinger-Akahira-Sunose, and Flynn-Wall-Ozawa) at three different heating rates (5, 10, and 20 K/min).

The determination of the activation energy is crucial for understanding the thermal decomposition behaviour of samples, as it represents the minimum energy barrier necessary for various reactions to take place. In addition, it also provides insights into the reaction mechanisms and thermal stability of the material. A high activation energy indicates that the reaction requires more energy to initiate, suggesting greater thermal stability, whereas a lower value indicates that the reaction occurs more easily at lower temperatures.

3.2.3.1. Friedman Method

Friedman's method is characterized by being a differential method that assumes that the reaction model remains constant, therefore, degradation depends on the rate of mass loss [154]. Taking logarithms on both sides, Equation 3.8 yields the expression developed by Friedman:

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln(Af(\alpha)) - \frac{E_a}{RT} \quad 3.9$$

Plotting $\ln\left(\beta \frac{d\alpha}{dT}\right)$ versus $1/T$ for each α , yields a straight line whose slope is proportional to the activation energy.

3.2.3.2. Kissinger-Akahira-Sunose Method

The Kissinger-Akahira-Sunose method is based on the Coats-Redfern approximation (non-isoconversional method) and results in Equation 3.10 [155].

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(x)}\right) - \frac{E_a}{RT} \quad 3.10$$

Where $g(x)$ is the integral form of the reaction model. The activation energy can be obtained by plotting $\ln\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ for a given conversion value α , where the slope is equal to $-\frac{E_a}{R}$.

3.2.3.3. Flynn-Wall-Ozawa Method

The Flynn-Wall-Ozawa method [156,157] is based on Doyle's approximation of the temperature integral [158], $p(x)$, where this is $\ln p(x) = -2.315 - 0.4567x$ and x means $\frac{E_a}{RT}$.

$$\ln(\beta) = \ln\left(\frac{0.0048 E_a}{R g(\alpha)}\right) - 1.0516 \frac{E_a}{RT} \quad 3.11$$

The determination of activation energy can be achieved through the measurement of temperatures corresponding to the α fixed values, using tests conducted with diverse β values. The activation energy can be obtained by plotting $\ln(\beta)$ against $\frac{1}{T}$ for a given conversion value α , where the slope is equal to $\frac{-1.052 E_a}{R}$.

3.2.4. Thermodynamic Analysis

The thermodynamic parameters (ΔH , ΔG and ΔS) as well as the pre-exponential factor (A), as a kinetic parameter, were calculated by kinetic analysis developed from thermogravimetric tests following the expressions represented in Table 3.4. The reaction order cannot be obtained by isoconversional methods, as it requires assuming a model type; therefore, in this study, an order one reaction was assumed, as defined in Ali (2018) [159].

Table 3.4. Thermodynamic parameters and their expressions [146]

Thermodynamic Parameters	Expressions	
Pre-exponential factor, A (1/s)	$\frac{\beta \times E_{\alpha} \times \exp\left(\frac{E_{\alpha}}{R \times MWLT}\right)}{R \times MWLT^2}$	3.12
Enthalpy, ΔH (kJ/mol)	$E_{\alpha} - R \times T$	3.13
Gibbs free energy, ΔG (kJ/mol)	$E_{\alpha} + R \times MWLT \times \ln \frac{K_B \times MWLT}{h \times A}$	3.14
Entropy, ΔS (kJ/mol×K)	$\frac{\Delta H - \Delta G}{MWLT}$	3.15

Where K_B represents the Boltzmann constant with a value of 1.381×10^{-23} J/K, h is Planck's constant with a value of 6.626×10^{-34} J×s, T is the absolute temperature in Kelvin (K), and $MWLT$ is the peak temperature observed in the DTG curve in Kelvin (K).

These parameters provide information on the nature and spontaneity of the thermal decomposition process. Enthalpy indicates the amount of heat absorbed or released during the reaction, and positive values indicate endothermic processes requiring energy input. The Gibbs free energy is related to the spontaneity of the reaction: negative values indicate a spontaneous process, whereas positive values indicate a non-spontaneous reaction requiring external energy input.

Furthermore, entropy reflects the degree of disorder or randomness in the system, with positive values representing an increase in molecular disorder during decomposition. Moreover, the pre-exponential factor represents the frequency of molecular collisions and the probability of molecular interactions leading to a reaction.

3.2.5. Combustion Indices Analysis

The characterisation of the combustion behaviour was determined using the parameters outlined in Table 3.4.

Table 3.5. Combustion indices and their expressions [160,161]

Combustion Indices	Expressions	
Combustibility Index, CI (-)	$\frac{VM}{FC}$	3.16
Ignition index, D_i (%/min ³)	$\frac{-R_p}{t_i \times t_p}$	3.17
Burnout index, D_b (%/min ⁴)	$\frac{-R_p}{\Delta t_{1/2} \times t_i \times t_b}$	3.18
Comprehensive combustion index, S (% ² /min ² ×°C ³)	$\frac{R_p \times R_v}{IT^2 \times T_b}$	3.19
Flammability index, C (%/min×°C ²)	$\frac{-R_p}{IT^2}$	3.20
Combustion index, H_f (°C×min ² /%)	$T_p \times \ln \frac{\Delta t_{1/2}}{-R_p}$	3.21
Combustion stability index, D_w (%/min×°C ²)	$\frac{-R_p}{IT \times T_p}$	3.22

Where R_p is the maximum rate of weight loss (%/min), R_v is the average rate of mass loss (%/min), IT is the induction temperature (K), T_b is the burnout temperature (K), taken as the point immediately preceding the cessation of the reaction when the rate of weight loss is 1%/min, T_p is the peak temperature (K), t_p is the peak time (min), t_i is the induction temperature time (min), $\Delta t_{1/2}$ is the time to reach half the maximum burning speed (min), and t_b is the burnout temperature time (min).

On the one hand, the ignition index (D_i) [162] provides information on the ignition resistance of the sample and thus the reactivity of the sample, while the burnout index (D_b) [163] provides information on the difficulty of achieving complete combustion. Moreover, based on the comprehensive combustion index (S) [164], the higher this parameter, the higher the combustion efficiency. Similarly, the flammability index (C) [160] indicates the stability of fuel combustion and ignition.

On the other hand, the combustion index (H_f) [161] provides information on the energy rate involved in the combustion process. Finally, the combustion stability index (D_w) [165] provides information on the combustion stability between the ignition and burnout periods.

3.3. ATEX PARAMETERS

ATEX parameters are fundamental indicators for risk assessment in potentially explosive atmospheres where combustible dust is handled. These parameters allow, for the most part, the characterisation of the critical conditions under which a powdery material can initiate an ignition process and the quantification of the potential consequences of a potential explosion. In this study, several ATEX parameters were determined experimentally and theoretically.

3.3.1. Minimum Ignition Temperature of Dust Layer

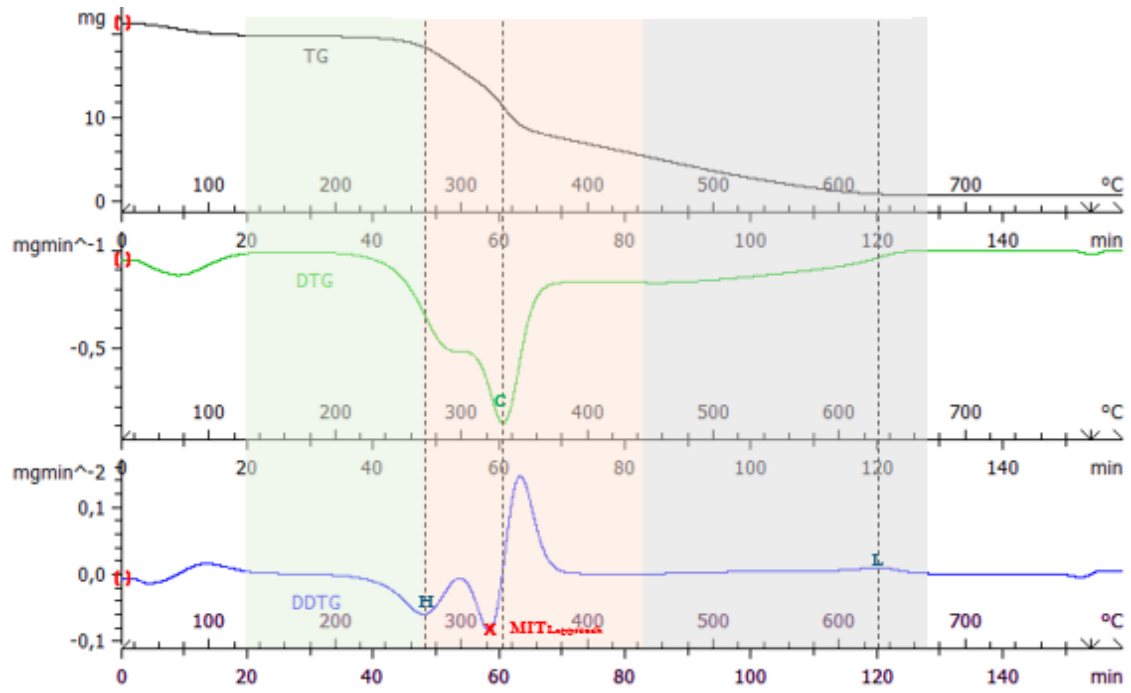
3.3.1.1. Thermogravimetric Approach

Numerous researchers have investigated the configuration of thermocouples in the minimum ignition temperature test of the dust layer [166]; however, only a few have developed numerical or computational methodologies to quantify this parameter [167–169].

According to Paredes et al. (2024) [170], it is possible to establish a correlation between the minimum ignition temperature of dust layer (MIT_L) and characteristic temperatures of the main biomass polymers (hemicellulose, cellulose, and lignin) obtained by thermogravimetric analysis.

The basis of this correlation lies in the thermal degradation range of different polymers. The importance of these decomposition ranges lies in the products generated during decomposition. On the one hand, hemicellulose releases mainly CO_2 , acting as an inhibitor of the ignition process. In contrast, cellulose and lignin generate flammable volatiles (CH_4 and CO respectively), which promote ignition.

Therefore, it is proposed that the temperature marking the transition between the end of the maximum devolatilisation of hemicellulose and the beginning of the devolatilisation of cellulose can serve as an approximation of the minimum ignition temperature in the layer. This transition point ($MIT_{L_{\text{approach}}}$) is identified by differential analysis of the thermogravimetric curves, namely by applying the second derivative to the TG curve (DDTG), as the local or absolute minimum preceding the absolute maximum value, according to Figure 3.4, and calculated by Equation 3.23 from the data obtained at various heating rates ($\beta = 3, 5$ and 7 K/min).

Figure 3.4. $MIT_{Lapproach}$

Thus, the approximation by thermogravimetry was obtained according to Equation 3.23.

$$MIT_{Lapproach} = \frac{\sum_{\beta=(3, 5, 7)|_{k \times min-1}} MIT_{Lapproach_{\beta}}}{length(\beta)} \quad 3.23$$

3.3.2. Minimum Ignition Temperature of Dust Cloud

3.3.2.1. Frank-Kamenetskii & Semenov Approach

To estimate the minimum ignition temperature in a dust cloud, two theoretical models were used: the Frank-Kamenetskii and Semenov models. To do this, using the modification considered by Chen et al. (2022) [171] as a starting point, considering the geometry of the Godbert-Greenwald furnace as well as the various concentrations to be tested, an estimate of the minimum ignition temperature of dust cloud was obtained.

Once the estimate has been obtained, the parameters (a - e , exposed in Equation 3.30) obtained are adjusted considering the intrinsic characteristics of the samples, such as the polydispersity index, proximate analysis, and particle size.

The equation that describes the Frank-Kamenetskii model is Equation 3.24:

$$\delta_{cr} = \frac{a_0^2 \times Q \times E_a \times k(T) \times conc}{k_{eff}(T) \times R \times T^2 \times (\rho - conc)} \quad 3.24$$

Where: a_0 is the furnace radius (m), Q is the calorific value (J/kg), E_a is the activation energy (J/mol), and k is the reaction rate calculated as:

$$k(T) = A \times conc \times \exp\left(-\frac{E_a}{R \times T}\right) \quad 3.25$$

A is the pre-exponential factor (s^{-1}), $conc$ is the dust concentration (kg/m^3), k_{eff} is the effective thermal conductivity ($W/m \times K$), R is the ideal gas constant ($8,314 J/mol \times K$), T is the absolute temperature (K), ρ is the density of the material (kg/m^3) and δ_{cr} is the critical Frank-Kamenetskii value (3.331).

The effective thermal conductivity was calculated using the Maxwell-Eucken model:

$$k_{eff}(T) = \frac{k_{air}(T) \times (2 \times k_{air}(T) + k_p - 2 \times \varphi \times (k_{air}(T) - k_p))}{2 \times k_{air}(T) + k_p + \varphi \times (k_{air}(T) - k_p)} \quad 3.26$$

Where k_{air} is the thermal conductivity of air ($W/m \times K$), k_p is the thermal conductivity of the particles ($W/m \times K$), and φ is the volumetric fraction of the particles (set at $20 g/m^3$).

The thermal conductivity of air was considered to be temperature-dependent:

$$k_{air}(T) = 0.024 + 7.58 \times 10^{-5} \times (T - 273.15) - 1.9 \times 10^{-8} \times (T - 273.15)^2 \quad 3.27$$

On the other hand, Semenov's model was calculated using the following expression:

$$\varphi_{cr} = \frac{V \times Q \times E_a \times r}{h \times S \times R \times T^2} \quad 3.28$$

Where V is the volume of the particle (m^3), S is the surface area of the particle (m^2), h is the total heat transfer coefficient ($\text{W}/\text{m}^2 \times \text{K}$) and φ_{cr} is the Semenov critical value ($1/e \approx 0.368$) as previously pointed out in Chapter 1.

The total heat transfer coefficient was calculated as the sum of the convection and radiation heat transfer coefficients. The convection heat transfer coefficient was estimated using the Nusselt correlation for natural convection around a sphere, as follows:

$$Nu = 2 + \frac{0.589 \times Ra^{\frac{1}{4}}}{h \times S \times R \times \left(1 + \left(\frac{0.469}{Pr}\right)^{\frac{9}{16}}\right)^{\frac{4}{9}}} \quad 3.29$$

Where Ra is Rayleigh's number and Pr is Prandtl's number. The radiation heat transfer coefficient (h_{rad}) was calculated as follows:

$$h_{rad} = \varepsilon \times \sigma \times \frac{(T^4 - T_{amb}^4)}{T - T_{amb}} \quad 3.30$$

Where ε is the emissivity of the particle (assumed as 0.95 according to Copelli et al. (2019) [76], σ is the Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W}/\text{m}^2 \times \text{K}^4$) and T_{amb} is the ambient temperature (which can be assumed to be constant at a value of 298 K)

To improve the prediction accuracy, an adjustment factor based on the physical and chemical properties of the samples was introduced. The simplex search method of Lagarias et al. (1998) [172] was chosen to minimise the error.

$$\psi = a \times \log(\sigma_D - 0.8) + b \times \sqrt{\frac{VM}{FC}} + c \times (ASH + MS)^{0.05} + d \times \sqrt{d_{50}} + e \quad 3.31$$

Where σ_D is the polydispersity index, VM is the volatile matter content (%), FC is the fixed carbon content (%), ASH is the ash content (%), MS is the moisture content (%), d_{50} is the mean particle size (m) and a to e are the adjustment parameters.

Finally, the minimum ignition temperature of dust cloud was calculated as shown in Equation 3.32:

$$MIT_C = T_{Frank-Kamenetskii} T_{Semenov} \times \psi \quad 3.32$$

3.3.3. Severity

The severity of a dust explosion is a critical parameter for assessing the destructive potential of these phenomena and, among other uses, for adequately dimensioning protection systems. The complete characterisation of explosion severity requires the determination of several interrelated parameters that describe both the magnitude of the generated overpressure and the kinetics of the process. In this study, analytical methodologies based on different thermodynamic and combustion principles were implemented to estimate these parameters from the physicochemical characteristics of the samples. The procedure followed for the determination of the maximum overpressure, maximum rate of pressure increase, and deflagration index is detailed below.

3.3.3.1. Overpressure

To numerically determine the overpressure achieved by the samples in the explosion severity test, the TNT equivalent was developed, a methodology based on the principles of thermodynamics and combustion chemistry. This methodology [88] uses the elemental composition (percentages of *C*, *H*, and *O*) and high heating value of each sample as the input data. In addition, to evaluate the hazardousness of the samples, the calculation of the oxygen balance and its categorisation were determined [173], governed by Equation 3.33, and the ranges that lead to the risk classification are listed in Table 3.6.

$$OB (\%) = \frac{-1600 \times (2X + \frac{Y}{2} - Z)}{MW} \quad 3.33$$

Where n_C , n_H , and n_O correspond to the moles of carbon, hydrogen, and oxygen, respectively, and MW corresponds to the molecular mass of the compound.

Table 3.6. Hazard rank estimation through oxygen balance [173]

<i>Oxygen-Balance</i>	<i>Hazard Rank</i>
More positive than +160	Low
+160 to +80	Medium
+80 to -120	High
-120 to -240	Medium
More negative than -240	Low

The analysis process began with the determination of the normalised molecular formula for each sample. To do this, the mass percentages of *C*, *H*, and *O* were converted to moles, assuming a calculation base of 100 g of sample:

$$n_c = \left(\frac{\%C}{100} \right) \times \left(\frac{100}{12} \right) \quad 3.34$$

$$n_H = \left(\frac{\%H}{100} \right) \times \left(\frac{100}{1} \right) \quad 3.35$$

$$n_O = \left(\frac{\%O}{100} \right) \times \left(\frac{100}{16} \right) \quad 3.36$$

Then, these moles must be normalised to obtain the molecular formula of type $C_xH_yO_z$:

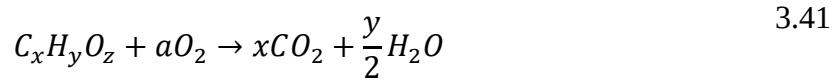
$$\text{minMol} = \min(n_c, n_H, n_O) \quad 3.37$$

$$x = \frac{n_c}{\text{minMol}} \quad 3.38$$

$$y = \frac{n_H}{\text{minMol}} \quad 3.39$$

$$z = \frac{n_O}{\text{minMol}} \quad 3.40$$

Using the established molecular formula, the coefficients of the balanced combustion equation were calculated:



Where the coefficient a of oxygen is determined by $[n_{O_2}/n_{fuel}]$:

$$a = \frac{2x + 0.5y - z}{2} \quad 3.42$$

From this balanced equation, several key stoichiometric calculations were performed:

- Stoichiometric oxygen mass for complete combustion of 1 mol of fuel (m_{O_2}) as $a \times 32$.
- Mass of 1 mol of fuel (m_{comb}) as $12 \times x + y + 16 \times z$.

- Stoichiometric concentration in air is as follows: $\frac{m_{comb} \times C_{O_2air}}{m_{O_2}}$. Where C_{O_2air} is the concentration of oxygen in the air (274.24 g O₂/m³ air).
- Stoichiometric mass-oxygen-fuel (Ψ_o) ratio as $\frac{m_{O_2}}{m_{comb}}$.

However, the energy analysis of combustion focuses on the calculation of ΔH_o and $\Delta H_{o,vol}$, where HHV is the highest calorific value calculated according to Estiati et al. (2016) [174] for each sample [MJ/kg].

$$\Delta H_o = \frac{HHV}{\Psi_o} \quad 3.43$$

$$\Delta H_{o,vol} = \Delta H_o \times C_{O_2air} \quad 3.44$$

To estimate the explosive parameters, the equivalent mass of TNT (m_{TNT}) was calculated for each sample, as follows:

$$m_{TNT} = \frac{\Delta H_{o,vol} \times V_{air} \times \eta_{exoxy}}{E_{TNT}} \quad 3.45$$

Where E_{TNT} is the explosive energy of TNT (4,686 kJ/kg), V_{air} is the volume of air in the test apparatus (0.02 m³) and η_{exoxy} is the oxidation yield in combustion (7% assumption).

The evaluation of the peak pressure generated by a possible explosion was carried out using two methods based on the scaled distance, but with different expressions to calculate the overpressure. The first method is based on the scaled distance, where r is the distance from the centre of the explosion (0.62 m) in the 1 m³ sphere, according to [88].

$$Z = r \times \sqrt[3]{m_{TNT}} \quad 3.46$$

The scaled overpressure is calculated as follows:

$$P_s = \frac{1616 \times \left(1 + \left(\frac{Z}{4.5}\right)^2\right)}{\sqrt{1 + \left(\frac{Z}{0.048}\right)^2} \times \sqrt{1 + \left(\frac{Z}{0.32}\right)^2} \times \sqrt{1 + \left(\frac{Z}{1.35}\right)^2}} \quad 3.47$$

And the peak overpressure, being P_a the atmospheric pressure (1.013 bar), where:

$$P = P_s \times P_a \quad 3.48$$

If the explosion is not planar,

$$P_{np} = \frac{P}{2} \quad 3.49$$

The second method calculates the overpressure according to Salvado et al. (2017) [175]:

$$Z_o = r_o \times \sqrt[3]{m_{TNT}} \quad 3.50$$

Where r_o is the radius of the 20-litre sphere used to determine this parameter by counting the length of the ignitor (0.139 m). Finally, the equation used for the calculation of the overpressure was:

$$P_o = \frac{5.924}{Z_o} + \frac{2.941}{Z_o^2} + \frac{3.259}{Z_o^3} + \frac{0.210}{Z_o^4} + \frac{0.037}{Z_o^5} \quad 3.51$$

3.3.3.2. Maximum rate of explosion pressure rise- $(dP/dt)_{\max}$ - and Deflagration index- K_{ST}

The maximum rate of explosion pressure and deflagration index are key parameters for characterising the kinetics of dust explosions and are decisive for the design of protective systems, such as venting and suppression devices. For their theoretical determination, several mathematical models have been developed that attempt to describe the dynamics of flame propagation in a confined space. In this study, two complementary approaches were implemented: the adiabatic model of Bradley and Mitcheson [176–180] and the isothermal model of Nagy, Conn, and Verakis [181–183], whose fundamentals and equations are detailed below.

3.3.3.2.1. Bradley and Mitcheson's Adiabatic Model

The Bradley-Mitcheson (BM) model is based on a series of assumptions that allow the propagation of dust flames in confined spaces to be analysed. These assumptions include the uniform dispersion of combustible dust in a spherical vessel; ignition in the centre of the container, considered as zero time; rigid, adiabatic, and impermeable vessel walls; constant heat capacity ratios for mixtures; equal molar masses for burnt and unburnt mixtures; applicability of the ideal gas state equation for both burnt and unburned mixtures; description of the flame propagation process as a thin flame with a laminar

combustion rate; and the linear relationship of Lewis and Von Elbe model (*LvE*) between the fraction of burned mass and the instantaneous pressure.

The method begins with the mass balance in the unburned mixture, expressed as:

$$\frac{dm_u}{dt} = -4\pi r_b^2 \rho_u S_u \quad 3.52$$

where m_u is the mass of the unburned mixture, r_b is the radius, ρ_u is the density of the unburned mixture, and S_u is the laminar combustion rate. This expression indicates that the mass of the unburned mixture was depleted by the flow of the unburned mixture through the flame surface.

An expression is sought for the unburned mass in terms of pressure. This requires expressions that link the amounts of burnt and unburned mass, pressure of the mixture, and radius of the spherical vessel. These variables are obtained from the total mass balance in the dust cloud, the fractional pressure rise ratio of *LvE* and the mass specification of the initial fuel powder mixture:

$$\frac{m_u}{m_i} = 1 - \frac{m_b}{m_i} = 1 - f; \quad 3.53$$

$$f = \frac{m_b}{m_i} = \frac{P - P_0}{P_{ex} - P_0} \quad 3.54$$

$$m_i = \frac{4\pi}{3} r_w^3 \rho_i \quad 3.55$$

Where m_i is the initial mass, m_b is the burnt mass, f is the fraction of burnt mass, P is the instantaneous pressure, P_0 is the initial pressure, P_{ex} is the burst pressure, r_w is the radius of the vessel and ρ_i is the initial density.

These equations are combined to provide an expression for the unburned mass in the container for any value of the burned mass fraction f :

$$m_u = \frac{4\pi}{3} r_w^3 \rho_i \left[1 - \left(\frac{P - P_0}{P_{ex} - P_0} \right) \right] \quad 3.56$$

Substituting the expression for the unburned mass into the mass balance and solving for the pressure derivative, the following differential equation is obtained:

$$\frac{dP}{dt} = \left(\frac{3S_u}{r_w}\right) \left(\frac{\rho_u}{\rho_i}\right) (P_{ex} - P_0) \left(\frac{r_b}{r_w}\right)^2 \quad 3.57$$

An expression is required for the square of the radius ratio. Using the geometric relationships for a sphere, the following equation can be written:

$$\frac{m_u}{m_i} = 1 - f = \frac{\rho_u}{\rho_i} \left[1 - \left(\frac{r_b}{r_w}\right)^3 \right] \quad 3.58$$

This expression is solved for the ratio of the radii. Two substitutions are then made: the adiabatic compression relation is invoked for the density relation, $P\rho_u^{-\gamma_u} = \text{constant}$, where γ_u is the unburnt gas (or dust/air mixture) heat capacity ratio and the fractional pressure relation of *LvE*:

$$\left(\frac{r_b}{r_w}\right)^3 = 1 - \left(\frac{\rho_i}{\rho_u}\right) (1 - f) = 1 - \left(\frac{P}{P_0}\right)^{1/\gamma_u} \left[1 - \left(\frac{P_0}{P}\right)^{\frac{1}{\gamma_u}} \left(\frac{P - P_0}{P_{ex} - P_0}\right) \right] \quad 3.59$$

Equation 3.59 is substituted into Equation 3.57 to obtain the desired result:

$$\frac{dP}{dt} = \left(\frac{3S_u}{r_w}\right) (P_{ex} - P_0) \left(\frac{P}{P_0}\right)^{1/\gamma_u} \left[1 - \left(\frac{P_0}{P}\right)^{\frac{1}{\gamma_u}} \left(\frac{P - P_0}{P_{ex} - P_0}\right) \right] \quad 3.60$$

This is an ordinary nonlinear differential equation that must satisfy both the initial condition, $P(t = 0) = P_0$, and the final condition, $P(t = t_{P_{ex}}) = P_{ex}$, where $t_{P_{ex}}$ is the symbol for the time to the maximum pressure.

The BM model exhibited a good fit to the experimental data for the methane-air system. An important final feature of this model is that the pressure increases without a limit of up to $P(t = t_{P_{ex}}) = P_{ex}$, and the maximum rate of pressure increase occurs at $t = t_{P_{ex}}$. This is not under typical empirical data, where the rate of pressure increase reaches a maximum and then decreases as the pressure approaches P_{ex} .

An expression for K_{ST} can be derived from the adiabatic model. Recognising that the maximum rate of pressure increase occurs when $P = P_{ex}$:

$$\left(\frac{dP}{dt}\right)_{max} = \left(\frac{3S_u}{r_w}\right) (P_{ex} - P_0) \left(\frac{P_{ex}}{P_0}\right)^{1/\gamma_u} \quad 3.61$$

Substituting the expression for the volume of a sphere, $V^{\frac{1}{3}} = \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} r_w$, the final expression for K_{ST} can be obtained.

3.3.3.2.2. Nagy, Conn and Verakis Isothermal Model

The Bradley-Mitcheson (BM) adiabatic model introduces a nonlinear term owing to adiabatic compression restriction, which significantly hinders the integration of the pressure history. Nagy, Conn, and Verakis developed a similar adiabatic model and faced the same problem. They found that, by assuming isothermal compression rather than adiabatic compression, it was possible to obtain a closed-form solution.

The isothermal compression approximation assumes that the temperature of the unflared gas remains constant at its initial mixing temperature, whereas the temperature of the flared gas is equal to the temperature of the flame. Although not explicitly mentioned in its derivation, it is evident that the temperature of the flared gas must be assigned to the value of the isochoric combustion temperature.

The Nagy-Conn-Verakis (NCV) model presented here assumes spherical geometry, the ideal gas state equation, and equal molar masses for the burnt and unflared gas mixtures. A second distinguishing feature of the isothermal NCV model is that it does not require a mathematical LvE relationship that links the fractional pressure increase to the fraction of the mass burned. Instead, the isothermal assumption naturally leads to an algebraic expression that links pressure changes to changes in the burned volume fraction.

The derivation begins with a balance between the number of moles in the mixture and the substitution of the equation of state of the ideal gas, where n is the number of moles of species i , T represents temperature, R_g represents the universal gas constant, P represents pressure, and V represents volume. On the other hand, the subscripts b , 0 , w , and u are related to the burnt mixture, initial, total vessel volume, and unburnt mixture, respectively.

$$n_i = n_u + n_b \rightarrow \frac{P_0 V_w}{R_g T_u} = \frac{P V_u}{R_g T_u} + \frac{P V_b}{R_g T_b} \quad 3.62$$

Grouping similar terms, recognising that $\frac{T_b}{T_u} = \frac{P_{ex}}{P_0}$, and solving for the fraction of volume burned, $\frac{V_b}{V_w}$, it obtained:

$$\frac{V_b}{V_w} = \left(\frac{r_b}{r_w}\right)^3 = \frac{1 - \frac{P_0}{P}}{1 - \frac{P_0}{P_{ex}}} \quad 3.63$$

The next step was to derive an expression for the rate of change in the pressure with time, where M represents the molar mass of the species. Starting with mass balances for burnt and unburnt mixtures:

$$\frac{dm_u}{dt} = \frac{M}{R_g T_u} \times \frac{d(PV_u)}{dt} \rightarrow \frac{R_g T_u}{M} \times \frac{dm_u}{dt} = V_u \times \frac{dP}{dt} + P \times \frac{dV_u}{dt} \quad 3.64$$

$$\frac{dm_b}{dt} = \frac{M}{R_g T_b} \times \frac{d(PV_b)}{dt} \rightarrow \frac{R_g T_b}{M} \times \frac{dm_b}{dt} = V_b \times \frac{dP}{dt} + P \times \frac{dV_b}{dt} \quad 3.65$$

Noting that $\frac{dm_u}{dt} = -\frac{dm_b}{dt}$ and $\frac{dV_u}{dt} = -\frac{dV_b}{dt}$, Equation 3.64 and Equation 3.65 can be added together to obtain an expression for the rate of change of pressure to time, where A_b represents the surface area of the spherical flame, serving as the interface between the burnt and unburnt mixture:

$$V_w \times \frac{dP}{dt} = \frac{R_g}{M} (T_b - T_u) \frac{dm_b}{dt} = \rho_u S_u A_b \left(\frac{R_g}{M} \right) (T_b - T_u) \quad 3.66$$

Applying the equation of state of the ideal gas for the unburned density ρ_u , substituting the ratio of the fraction of volume burned (Equation 3.63) and simplifying the geometric identities, the following result is obtained:

$$\frac{dP}{dt} = \beta P^{\frac{1}{3}} (P - P_0)^{\frac{2}{3}}; \beta = 3 \left(\frac{P_{ex}}{P_0} \right)^{\frac{2}{3}} \left[\left(\frac{P_{ex}}{P_0} \right) - 1 \right]^{\frac{1}{3}} \left(\frac{S_u}{r_w} \right) \quad 3.67$$

The mathematical behaviour of the pressure increase is similar to that of the BM model; it is predicted that the pressure rate will increase monotonically with the maximum rate at $P = P_{ex}$. The value of K_{ST} is given by the expression:

$$K_{ST}(NCV) = \left(\frac{dP}{dt} \right)_{max} V^{\frac{1}{3}} = (36\pi)^{\frac{1}{3}} \left(\frac{P_{ex}}{P_0} \right) (P_{ex} - P_0) S_u \quad 3.68$$

Chapter 4

Computational Fluid Dynamic Method

4.1.MODEL

The experimental model was based on the test for the determination of the parameters referring to the characterisation of the severity of the explosion. To do this, the standard 20-litre sphere is used, the scheme of which is shown in Figure 4.1 and has a radius of $\sqrt{\frac{0.015}{\pi}}$ meters.

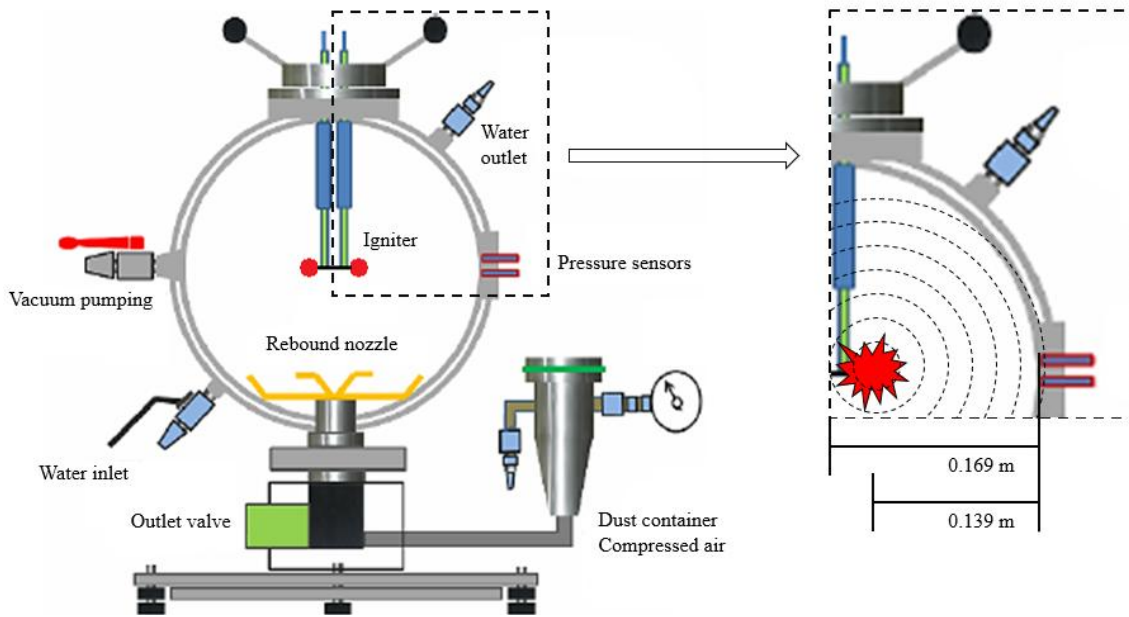


Figure 4.1. Experimental 20-litre sphere scheme

For the computational modelling, it is hypothesised that the explosion does not occur in the centre of the sphere but at a shorter distance, 0.139 m, which corresponds to the real distance between the igniter and the pressure sensors

The modelling was carried out using the Viper::Blast software, which, as mentioned in Chapter 1, is a tool specialised in the simulation of detonations of various explosives, among other purposes. This software implements a CFD approach from finite volumes using the Advection Upstream Splitting Method (AUSMDV) numerical scheme [125].

Viper's selection of this method responds to its ability to eliminate numerical dissipation in the vector division of Van Leer flow into contact discontinuities, providing:

- Accurate resolution of stationary and mobile contact discontinuities.
- Conservation of enthalpy in stationary flows.
- Algorithmic simplicity and adaptability to general conservation laws.
- Solution to the "carbuncle" phenomenon employing specialised shock solutions.
- Implementation of entropy solutions to prevent failures at the sonic point.

However, the computational simulation was based on the methodology of the equivalent mass TNT for each sample under study expressed in Section 3.3.3.1.

The optimisation of the computational model required a mesh sensitivity analysis with two cell sizes: 0.0009 and 0.001 m, selecting 0.0009 m as the computational limit. This is because, according to several authors [184–187], the sensitivity analysis of the mesh size represents a critical parameter when comparing the computational and experimental results. For example, Montazeri et al. (2013) [188], in their CFD simulation of wind-induced pressure coefficients on buildings with and without balconies, analysed three different mesh sizes and stated that the smallest mesh size is the one with the lowest error compared to experimental data.

The Viper::Blast computational environment allows the development of models in different dimensions (1D-3D). In this study, the first one-dimensional approximation was made for its subsequent inclusion in the three-dimensional model. Figure 4.2 shows the schematic of the analysed model, which represents a hemispherical free-air surface explosion with the pressure sensor located at 0.139 m.

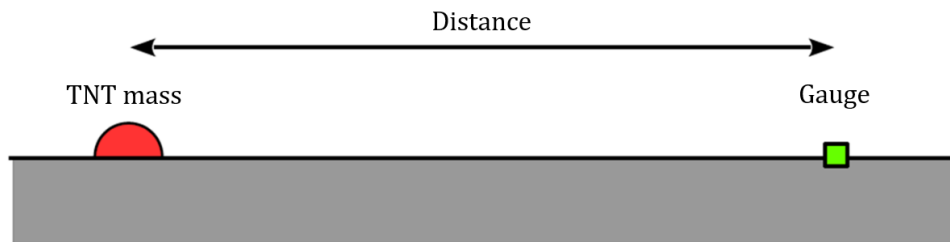


Figure 4.2. Freefield surface burst with pressure gauge

Moreover, the software requires the specifications listed in Table 4.1. The parameter "radius" is established to be very close to but less than the distance between the TNT load and the location of the pressure sensor according to the recommendations of the manual to ensure that the wave exceeds the point of analysis [124]. The use of a one-dimensional domain combined with a two- or three-dimensional domain makes it possible to perform much finer meshing in the initial stage of detonation, resulting in better results. Subsequently, the simulation continues in the extended domain, where further meshing is allowed.

On the other hand, the parameter "mass" according to the Viper::Blast specifications must be double the value of the equivalent mass TNT obtained for each sample. This specification arises because the wave is to be transformed into a three-dimensional hemispherical simulation and therefore half of the detonated sphere will be used. Therefore, it is necessary to use twice the charge for this type of simulation. However, if a detonation were to be performed in air and then transformed into a 3D domain, it would not be necessary to double the charge size.

Table 4.1. 1D setup

Domain definition	
Radius	0.139 m
Cellsize	0.0009 – 0.001 m
Charge definition	
Composition	TNT
Mass	- kg
Density	1,600 kg/m ³
Energy	4.52×10^6 J/kg
Atmosphere	
Pressure	101,325 Pa
Temperature	288 K
Solver options	
CFL	0.5
Method	AUSMDV

After the execution of the one-dimensional model, the results are transferred to the 3D computational domain, as observed in Figure 4.3, where the parameters of the setup differ from those exposed for the one-dimensional domain (see Table 4.1). In this case, because it is a hemispherical surface, the computational domain is defined by the following three-dimensional vector $[d]$:

$$[d] = \begin{bmatrix} X, Y, Z \\ \text{Minimum} \\ \text{Maximum} \end{bmatrix} (m) = \begin{bmatrix} X & Y & Z \\ -0.2 & -0.2 & 0.0 \\ 0.2 & 0.2 & 0.2 \end{bmatrix} (m)$$

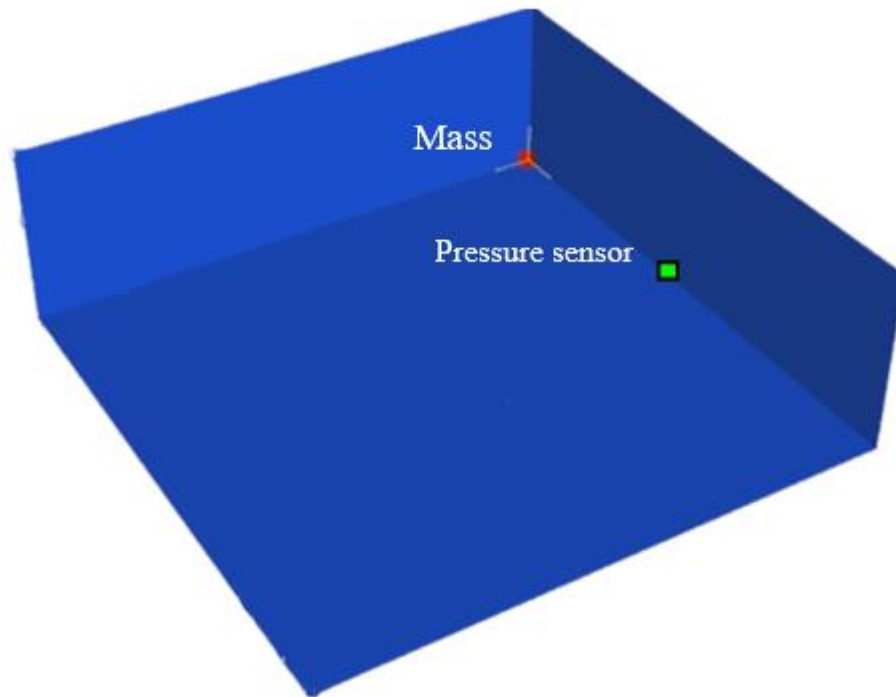


Figure 4.3. 3D computational environment

However, in the three-dimensional model, the Courant-Friedrichs-Lewy (CFL) stability parameter used was 0.5, instead of 0.4, which is used in the one-dimensional model, following Viper's specific recommendations for three-dimensional simulations, ensuring the numerical stability of the model while maintaining the accuracy of the results.

Once the computational environment has been created in its entirety, the objective is to obtain the value of the overpressure obtained by the wave at the determined distance, which is compared with its hypothetical counterpart in the standard 20-litre sphere.

Chapter 5

Results

5.1. Physical Properties

Table 5.1 shows the main parameters obtained from the particle size distribution (PSD) tests, as well as those obtained from the calculation of the polydispersity index and bulk density of each sample.

On the one hand, it can be observed that although the samples have been ground and sieved through a 1 mm light sieve, several samples, generally lignocellulosic ones, obtain higher d_{90} values at the light of the sieve. This is due to the shape of the biomass; while coals have a more spherical grain shape, lignocellulosic biomass tends to have an elongated shape due to its fibrous nature [189].

The polydispersity index (σ_D) for the biomass shows a wide range of values, from 1.39 for BPS to 7.38 for BP, reflecting the diversity in structure and composition. As for the coals, CV and CH (2.81 and 2.59, respectively) present intermediate values, while anthracite, CA (6.48), presents the highest value, indicating a very wide particle size distribution, being coherent due to the extremely low values of d_{10} and d_{50} .

Regarding the specific surface area (SSA), an inverse relationship with particle size was observed. Biomass generally presented lower values, with a minimum value of $0.015 \text{ m}^2/\text{g}$ for BPS and a maximum value of $0.235 \text{ m}^2/\text{g}$ for BP. Regarding the coal samples, CV and CH present intermediate values (0.10 and $0.08 \text{ m}^2/\text{g}$) while the anthracite sample (CA) presents the highest value ($1.60 \text{ m}^2/\text{g}$), being consistent with a very small particle size in the same way as stated in the previous paragraph with the polydispersity index.

Sauter ($d[3,2]$) and De Brouckere ($d[4,3]$) mean diameters were analysed. The $d[3,2]$, more sensitive to fine particles, shows values in the range of $3.75 \text{ }\mu\text{m}$ for CA to $409.37 \text{ }\mu\text{m}$ for BPS, while the $d[4,3]$, more sensitive to large particles, presents a wider range, from $17.47 \text{ }\mu\text{m}$ for CA to $822.75 \text{ }\mu\text{m}$ for BPS. For both parameters, biomass generally presents higher values compared to coals: for $d[3,2]$, BPS, BPA and BHO stand out ($409.37 \text{ }\mu\text{m}$, $238.20 \text{ }\mu\text{m}$ and $188.33 \text{ }\mu\text{m}$, respectively), while for $d[4,3]$, BPS, BPC and BCA ($822.75 \text{ }\mu\text{m}$, $654.34 \text{ }\mu\text{m}$ and $607.10 \text{ }\mu\text{m}$, respectively).

The bulk density values of the samples reveal that, while most of the biomass present low densities, such as BPM (176.92 kg/m^3) and BP (234.07 kg/m^3), the coals show higher values, with CH and CV reaching 678.20 kg/m^3 and 651.74 kg/m^3 , respectively. This trend is attributed to the more porous structure of the biomass. However, BPS stands out with an exceptionally high density of 708.89 kg/m^3 , surpassing even the coals.

Table 5.1. Physical parameters

Sample	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	σ_D (-)	SSA (m^2/g)	$d[3,2]$ (μm)	$d[4,3]$ (μm)	<i>Bulk density</i> (kg/m^3)
BPA	141.49	509.50	1,190.13	2.06	0.025	238.20	596.36	376.94
BCA	69.23	534.24	1,260.72	2.23	0.042	143.33	607.10	451.30
BHO	188.44	518.60	1,167.03	1.89	0.032	188.33	604.00	376.30
BPM	51.88	167.51	653.89	3.59	0.061	97.73	272.77	176.92
BP	9.59	135.31	1,008.83	7.38	0.235	25.48	318.05	234.07
BPS	338.21	769.14	1,409.92	1.39	0.015	409.37	822.75	708.89
BPC	123.35	594.87	1,259.05	1.91	0.033	180.41	654.34	426.28
CV	23.71	341.19	982.18	2.81	0.10	61.89	430.62	651.74
CH	40.80	320.43	870.68	2.59	0.08	79.39	397.68	678.20
CA	1.58	7.69	51.37	6.48	1.60	3.75	17.47	599.83

5.2. Proximate Analysis

The results of the proximate analysis are presented in Table 5.2, including moisture content (*MS*), volatile matter (*VM*), fixed carbon (*FC*), and ash (*ASH*).

On the one hand, the biomass presented moisture contents between 5.04% (BPA) and 10.20% (BPC), which is typical for materials of biological origin, as well as charcoal with a similar content (7.18%). On the other hand, the remaining coals, bituminous coal and anthracite (CH and CA, respectively), had significantly lower moisture contents (1.86% and 0.53%).

As for the volatile matter (*VM*) and fixed carbon (*FC*) contents, the lignocellulosic samples showed a high volatile matter content, with values between 59% and 80.3% (BPC and BPA, respectively), while their fixed carbon contents were relatively low, between 12.5% and 20.6% (BP and BCA, respectively). In contrast, the coals showed lower volatile matter content (25.7% and 39.1% for CV and CH, respectively) as well as higher fixed carbon content (CV: 35.3%; CH: 53.5%). On the other hand, the anthracite (CA) sample was characterised by the lowest volatile matter content (11.2%) and the highest fixed carbon content (80%).

The ash content (*ASH*) shows a wide range of values. On the one hand, biomass showed a minimum value of 1% (BPM) up to a maximum of 18.7% (BP). On the other hand, charcoal was distinguished by the highest ash content of all samples (31.8%). In contrast, the CH and CA samples showed values within the biomass range.

Table 5.2. Proximate analysis results

Sample	<i>MS</i> (%)	<i>VM</i> (%)	<i>FC</i> (%)	<i>ASH</i> (%)
BPA	5.04	80.3	13.1	1.6
BCA	7.45	68.0	20.6	3.9
BHO	6.22	63.3	16.6	14.0
BPM	7.92	77.6	13.5	1.0
BP	6.87	61.9	12.5	18.7
BPS	7.35	70.5	15.2	6.9
BPC	10.20	59.0	19.5	11.3
CV	7.18	25.7	35.3	31.8
CH	1.86	39.1	53.3	5.7
CA	0.53	11.2	80.0	8.3

5.3.Composition Analysis

5.3.1. Elemental Analysis

Table 5.3 shows the elemental analysis values of the samples as well as the H/C and O/C ratio values.

In the case of biomass, carbon content ranges from 36.74% (BP) to 45.79% (BPA), hydrogen content ranges from 5.44% (BP) to 6.26% (BPM), and oxygen content ranges from 27.82% (BP) to 38.59% (BPA). The $H/C \times 10$ ratios for the biomass are in a narrow range from 1.32 to 1.48, while the O/C ratios vary from 0.70 to 0.84.

However, the coals exhibited a significantly different elemental composition. The carbon content increased from charcoal (CV, 44.35%) to anthracite (CA, 89.09%), whereas the hydrogen and oxygen contents decreased significantly. This is reflected in much lower $H/C \times 10$ and O/C ratios for the coals, with values ranging from 0.79 to 0.33 for $H/C \times 10$ and from 0.28 to 0.03 for O/C .

Table 5.3. Ultimate analysis results

Sample	C (%)	H (%)	O (%)	$H/C \times 10$ (-)	O/C (-)
BPA	45.79	6.17	38.59	1.35	0.84
BCA	45.20	5.97	34.70	1.32	0.77
BHO	40.20	5.56	31.09	1.39	0.77
BPM	44.52	6.26	36.46	1.41	0.82
BP	36.74	5.44	27.82	1.48	0.76
BPS	42.04	5.96	33.90	1.42	0.81
BPC	41.04	5.71	28.70	1.39	0.70
CV	44.35	3.52	12.42	0.79	0.28
CH	66.70	4.74	15.99	0.71	0.24
CA	89.09	2.82	2.61	0.33	0.03

5.4. Thermogravimetric Analysis

5.4.1. Curves Flammability Points

Thermogravimetric analysis was carried out for each sample in an air atmosphere at different heating rates. The mean values are reported in Table 5.4.

By analysing the thermogravimetric (TG) curve, two key parameters were determined: IT and T_b . For biomass, IT values ranged from a minimum of 236.77 °C (BPC) to a maximum of 305.04 °C (BP), while T_b values ranged from 357.71 °C (BPM) to 434.59 °C (BPA). Generally, higher temperatures are observed for coals than for biomass. Charcoal (CV) showed IT values of 278.43 °C and T_b values of 398.13 °C. The bituminous coal (CH) sample exhibited even higher temperatures (IT : 408.20 °C and T_b : 545.50 °C), whereas anthracite was distinguished by its highest temperatures (IT : 575.45 °C and T_b : > 800.00 °C). It has to be noted that it was not possible to precisely determine the burnout temperature of anthracite, because the upper limit of the test temperature range was 800 °C.

For the first derivative of the TG curve (DTG), the key parameter was the maximum weight loss temperature ($MWLT$). The mean value for biomass ranges from 304.86 °C (BPS) to 350.92 °C (BPM). For the coals, a clear increasing trend was observed compared to the biomass. The CV sample presented a value of 303.32 °C, while CH and CA presented significantly higher values (474.59 °C and 722.46 °C, respectively).

Analysing the second derivative of the TG curve (DDTG), three key parameters have been reported: the temperature of maximum decomposition of hemicellulose (H -Peak), cellulose (C -Peak), and lignin (L -Peak). These peaks were not considered for coals because they are not lignocellulosic samples. The mean temperature of maximum hemicellulose decomposition ranged from 210.24 °C (BPS) to 288.13 °C (BPM). The mean temperature for cellulose ranged from 304.86 °C (BPS) to 350.92 °C (BPM) and for lignin, showing the highest values, from 422.94 °C (BPA) to 483.94 °C (BP). For the BCA sample, the lignin peak (NAP) was not appreciable.

Table 5.4. TGA results

Sample	Heating rate (K/min)	TG (°C)		DTG (°C)		DDTG (°C)	
		<i>IT</i>	<i>T_b</i>	<i>MWLT</i>	<i>H-Peak</i>	<i>C-Peak</i>	<i>L-Peak</i>
BPA	Average	279.20	434.59	341.92	247.57	341.92	422.94
BCA	Average	258.28	363.76	317.05	254.14	317.05	NAP
BHO	Average	249.78	404.85	331.05	233.79	331.05	428.02
BPM	Average	298.60	357.71	350.92	288.13	350.92	441.89
BP	Average	305.04	379.79	310.32	278.23	310.32	483.94
BPS	Average	260.07	371.20	304.86	210.24	304.86	463.67
BPC	Average	236.77	370.95	346.74	256.86	346.74	427.54
CV	Average	278.43	398.13	303.32	-	-	-
CH	Average	408.20	545.50	474.59	-	-	-
CA	Average	575.45	> 800.00	722.46	-	-	-

* NAP: Not Appreciable Peak

5.4.2. Proximate Analysis

The results of the proximate analysis carried out by thermogravimetric analysis (TGA) and their comparison with the experimental data are presented in Table 5.5, and the TGA graphs showing the content of each parameter are reported in Appendix 2. The values obtained by both methods and the associated error for each parameter are included in Table 5.5, where the highest discrepancies between both methods are highlighted in red.

For moisture (*MS*), the values obtained by TG tended to be slightly higher than the experimental values for most biomass, with errors ranging from 3.57% (BHO) to 0.06% (BPC). The coals show better agreement, with smaller errors: 0.77% for CV, 0.30% for CH and 0.05% for CA.

For volatile matter (*VM*), samples such as BCA and BP showed good agreement with errors of 0.81% and 1.74%, respectively, while others such as BPS and CA showed more significant discrepancies with errors of 6.23% and 9.78%, respectively.

Fixed carbon (*FC*) shows considerable variation between the methods. While some samples, such as BCA and BP, show relatively low errors (0.70% and 0.90%), others, such as BHO and CH, show significant discrepancies (6.87% and 44.55%, respectively).

For ash content (*ASH*), most samples showed good agreement between TG and experimental methods, with errors generally below 2%. However, among the biomass samples, BPC showed the highest discrepancy with an error of 4.42 %. Nevertheless, this error is negligible when compared with the CH sample, with a notable discrepancy of 48.14%. It is important to highlight the particular case of CH, which shows significant discrepancies in the fixed carbon and ash values.

Table 5.5. Proximate analysis modelling: TG approach results

Sample	MS TG (%)	MS Exp (%)	Error (%)	VM TG (%)	VM Exp (%)	Error (%)	FC TG (%)	FC Exp (%)	Error (%)	Ash TG (%)	Ash Exp (%)	Error (%)
BPA	6.71	5.04	1.67	76.41	80.28	3.87	15.80	13.12	2.68	1.08	1.56	0.48
BCA	7.64	7.45	0.19	67.20	68.01	0.81	21.30	20.60	0.70	3.86	3.94	0.08
BHO	9.79	6.22	3.57	68.17	63.28	4.89	9.68	16.55	6.87	12.36	13.95	1.59
BPM	8.49	7.92	0.57	76.19	77.62	1.43	16.15	13.45	2.70	-0.83	1.02	1.85
BP	8.36	6.87	1.49	60.16	61.90	1.74	13.39	12.48	0.90	18.09	18.74	0.65
BPS	10.12	7.35	2.77	64.24	70.47	6.23	20.30	15.24	5.05	5.35	6.94	1.59
BPC	10.14	10.20	0.06	55.01	58.99	3.98	19.13	19.51	0.39	15.72	11.30	4.42
CV	6.41	7.18	0.77	26.68	25.72	0.96	35.67	35.28	0.39	31.24	31.81	0.58
CH	2.16	1.86	0.30	35.22	39.11	3.89	8.77	53.32	44.55	53.85	5.71	48.14
CA	0.48	0.53	0.05	1.38	11.17	9.78	87.99	79.98	8.01	10.15	8.32	1.83
Average	-	-	1.14	-	-	3.76	-	-	7.22	-	-	6.12

5.4.3. Fraser-Suzuki Analysis

The compositional values of the lignocellulosic samples according to the Fraser-Suzuki analysis are shown in Table 5.6, together with the coefficient of determination (R^2).

Olive samples (BPA and BHO) stood out for having the highest lignin content (56.07% and 55.51%, respectively) and the lowest cellulose content (16.41% and 19.13%, respectively). These samples also contained relatively high percentages of hemicellulose (27.52% and 25.36%, respectively). In contrast, BPC showed the highest cellulose content (51.12%) and one of the lowest lignin content (33.12%).

BP followed a similar trend, with a high cellulose content (47.83%) and low lignin content (33.64%). BPM presented the most balanced distribution among the three components, with the highest percentage of hemicellulose (32.80%), and similar amounts of cellulose (34.96%) and lignin (32.24%). BPS and BCA showed intermediate profiles, with BPS having the lowest hemicellulose content (12.83%) but considerable amounts of cellulose (44.00%) and lignin (43.17%).

Table 5.6. Fraser-Suzuki deconvolution results

Sample	<i>Hemicellulose</i> (%)	<i>Cellulose</i> (%)	<i>Lignin</i> (%)	R^2
BPA	27.52	16.41	56.07	0.988
BCA	21.00	39.61	39.39	0.993
BHO	25.36	19.13	55.51	0.933
BPM	32.80	34.96	32.24	0.985
BP	18.53	47.83	33.64	0.975
BPS	12.83	44.00	43.17	0.980
BPC	15.76	51.12	33.12	0.975

5.4.4. Reactivity Analysis

5.4.4.1. Thermogravimetric Index of Spontaneous Ignition

According to the categorisation in Table 3.2, the classification of the spontaneous combustion tendency of the samples is presented in Table 5.7 and Appendix 4.

Analysing the lignocellulosic samples, only BPM obtained a reactive classification with a TG_{spi} of 0.0344, with the sample having the highest *slope* value (0.0173) and the second behind BPA comparing the value of Ψ (BPA: 2.0419 and BPM: 1.9900). BPA, BCA and BP are classified as low reactive with TG_{spi} values between 0.0194 (BPA) and 0.0276 (BP), while BHO, BPS and BPC, despite being lignocellulosic samples, are classified as non-reactive with TG_{spi} below 0.02.

In contrast, all coals were classified as non-reactive, with significantly lower TG_{spi} values, ranging from 0.00001 (CA) to 0.0078 (CH). Anthracite (CA) showed the lowest Ψ value (0.0191), indicating an extremely high resistance to spontaneous combustion.

Table 5.7. TG_{spi} results

Sample	Ψ Mean (-)	Slope (-)	TG_{spi} (%/min $\times$ °C)	Classification
BPA	2.0419	0.0095	0.0194	Low reactive
BCA	1.9167	0.0130	0.0249	Low reactive
BHO	1.6253	0.0082	0.0133	Non-reactive
BPM	1.9900	0.0173	0.0344	Reactive
BP	1.8035	0.0153	0.0276	Low reactive
BPS	1.9198	0.0085	0.0163	Non-reactive
BPC	1.5084	0.0114	0.0172	Non-reactive
CV	0.7232	0.0100	0.0072	Non-reactive
CH	0.7634	0.0102	0.0078	Non-reactive
CA	0.0191	0.0006	0.00001	Non-reactive

5.4.4.2. Advanced Thermal Reactivity Index

According to the values obtained and presented in Table 5.8, the analysis of the thermal reactivity of the samples revealed significant variations in the critical parameters. The critical temperature (T_{CRC}), determined from the first maximum of the DTG curve (without considering the peak of moisture loss), ranges from 120.27 °C (BHO) to 394.40 °C (CA).

The reactivity, quantified in $\%/min \times ^\circ C$, showed a range from 0.00001 for CA to 1.37 for BPM. Biomass exhibited notably higher reactivity values (0.88-1.37 $\%/min \times ^\circ C$) than coals (0.00001-0.32 $\%/min \times ^\circ C$), indicating higher susceptibility to rapid thermal decomposition.

The Frank-Kamenetskii critical temperatures ($F-K$) demonstrate a strong dependence on the deposit radius, consistent with the thermal explosion theory. For all samples, a non-linear decrease in the $F-K$ temperature was observed with increasing deposit radius.

The RB Index, which integrates the reactivity and critical temperatures, provides a comprehensive assessment of the propensity for self-ignition. The RB Index values (see Table 5.9) vary by several orders of magnitude between samples, from 7.75×10^{-9} for CA to 1.26×10^{-3} ($\%/min \times ^\circ C^3$) for BCA, both at a 1 m radius.

Among the biomass, BCA presented the highest RB Index at all analysed radii, indicating a particularly high susceptibility to self-ignition. In contrast, BPC and BPA showed the lowest RB indices among the biomass, suggesting a higher relative stability. The coals exhibited lower RB indices than the biomass, with CA showing exceptionally high thermal stability.

For all samples, the index increased significantly with increasing deposit radius, which is consistent with the higher risk of self-ignition in larger deposits. This effect is particularly pronounced in samples such as BCA, where the RB Index increases by more than an order of magnitude when going from a 2.5 mm to a 1 m radius.

Table 5.8. RB Index results

Sample	T_{CRC} (°C)	Reactivity (%/min × °C)	<i>F-K Temperature</i> r = 2.5 mm (°C)	<i>F-K Temperature</i> r = 0.1 m (°C)	<i>F-K Temperature</i> r = 0.5 m (°C)	<i>F-K Temperature</i> r = 1 m (°C)
BPA	139.51	1.11	235.02	175.20	153.36	144.64
BCA	126.62	1.15	88.92	33.76	14.71	7.26
BHO	120.27	0.88	140.64	94.13	76.99	70.14
BPM	140.31	1.37	307.82	221.40	191.38	179.63
BP	160.20	0.98	142.56	94.03	76.27	69.19
BPS	160.70	1.32	201.62	124.37	98.15	87.96
BPC	171.15	1.18	225.06	166.83	145.53	137.03
CV	167.42	0.32	189.20	117.49	92.84	83.22
CH	167.56	0.31	315.30	228.11	197.79	185.91
CA	394.40	0.00	544.80	437.31	386.34	366.72

Table 5.9. RB Index results

Sample	RB Index (2.5 mm) (%/min $\times$ °C ³)	RB Index (0.1 m) (%/min $\times$ °C ³)	RB Index (0.5 m) (%/min $\times$ °C ³)	RB Index (1 m) (%/min $\times$ °C ³)	Classification
BPA	3.40×10^{-5}	4.56×10^{-5}	5.20×10^{-5}	5.52×10^{-5}	High reactive
BCA	1.02×10^{-4}	2.70×10^{-4}	6.20×10^{-4}	1.26×10^{-3}	Reactive
BHO	5.22×10^{-5}	7.79×10^{-5}	9.53×10^{-5}	1.05×10^{-4}	Low reactive
BPM	3.16×10^{-5}	4.40×10^{-5}	5.09×10^{-5}	5.42×10^{-5}	Non-reactive
BP	4.28×10^{-5}	6.49×10^{-5}	8.01×10^{-5}	8.82×10^{-5}	
BPS	4.06×10^{-5}	6.58×10^{-5}	8.34×10^{-5}	9.31×10^{-5}	
BPC	3.07×10^{-5}	4.14×10^{-5}	4.74×10^{-5}	5.04×10^{-5}	
CV	1.00×10^{-5}	1.61×10^{-5}	2.04×10^{-5}	2.28×10^{-5}	
CH	5.78×10^{-6}	8.00×10^{-6}	9.22×10^{-6}	9.81×10^{-6}	
CA	7.75×10^{-9}	9.65×10^{-9}	1.09×10^{-6}	1.15×10^{-8}	

5.4.5. Kinetic Analysis

Table 5.10 shows the values of the kinetic analysis of both groups of samples, where the mean values of the activation energy (E_a) and the pre-exponential factor (A), obtained by different methods, are shown. Furthermore, the E_a and A vs. α curves are presented in Appendix 5.

For the biomass, the results of the application of three isoconversional methods are presented: Friedmann (differential method), Kissinger-Akahira-Sunose, and Flynn-Wall-Ozawa (KAS and FWO, respectively, integral methods). The BPA sample exhibited the highest E_a among the biomass samples, with values ranging from 239.78 to 252.44 kJ/mol, followed by BPC with a range of 236.79 to 246.76 kJ/mol. In contrast, BCA and BPS had the lowest E_a values, ranging from 129.36 to 158.07 kJ/mol and 157.41 to 163.72 kJ/mol, respectively. On the other hand, the BP sample is distinguished by exhibiting the highest A values, on the order of 10^{32} to 10^{34} s⁻¹, while BPS shows the lowest values, on the order of 10^{15} to 10^{16} s⁻¹.

For the coals, owing to their particular thermal degradation, the kinetic parameters were obtained using the n th-order kinetic method based on a single dynamic measurement, implemented in STARE software [190]. The E_a values obtained were 161.88 kJ/mol for charcoal (CV), 216.98 kJ/mol for bituminous coal (CH), and 258.00 kJ/mol for anthracite (CA), which were 1.17×10^{17} s⁻¹, 9.95×10^{17} s⁻¹, and 5.23×10^{14} s⁻¹ for pre-exponential factor results, respectively.

Table 5.10. Kinetic results

Sample	E_a (kJ/mol)			A (s ⁻¹)		
	Friedman	KAS	FWO	Friedman	KAS	FWO
BPA	252.44	242.07	239.78	5.13×10 ²⁷	1.25×10 ²³	5.46×10 ²²
BCA	158.07	129.36	131.92	5.70×10 ²²	9.36×10 ¹⁶	8.54×10 ¹⁶
BHO	215.38	207.33	206.74	1.59×10 ²⁷	1.46×10 ²⁴	4.28×10 ²³
BPM	214.55	213.29	212.32	1.03×10 ¹⁸	7.94×10 ¹⁷	6.34×10 ¹⁷
BP	182.67	199.84	199.48	1.12 ×10 ³⁴	1.44×10 ³³	1.93×10 ³²
BPS	163.72	157.41	158.71	2.80×10 ¹⁶	8.21×10 ¹⁵	9.57×10 ¹⁵
BPC	246.76	239.19	236.79	1.15×10 ²³	1.05×10 ²³	3.99×10 ²²

Sample	E_a (kJ/mol)		A (s ⁻¹)
	<i>STARe n-order kinetic method</i>		
CV	161.88		1.17×10 ¹⁷
CH	216.98		9.95×10 ¹⁷
CA	258.00		5.23×10 ¹⁴

5.4.6. Thermodynamic Analysis

The results are presented in Table 5.11 and Appendix 5, showing the values of activation enthalpy (ΔH), activation Gibbs free energy (ΔG), and activation entropy (ΔS) calculated from the kinetic data obtained.

Analysing the results for the lignocellulosic samples, it was observed that the enthalpy (ΔH) showed a similar trend to the activation energy (E_a) previously analysed. BPA and BPC presented the highest ΔH values, ranging between 234.82 and 247.48 kJ/mol for BPA and between 231.83 and 241.80 kJ/mol for BPC. In contrast, BCA and BPS showed the lowest values, ranging from 126.36 to 158.07 kJ/mol and 152.45 to 158.77 kJ/mol, respectively.

The Gibbs free energy (ΔG) followed a similar pattern to that of ΔH but with generally lower values. BPA showed the highest ΔG range (202.56–209.59 kJ/mol), followed by BPC (202.82–208.17 kJ/mol). BCA has the lowest ΔG values (134.28 to 155.01 kJ/mol). Entropy (ΔS) shows positive values for most of the biomass samples, with a maximum of 0.061 kJ/mol $\times$ K for BPA (Friedman method). The BPS and BCA show some negative values or are very close to zero.

For the coal samples, the values were calculated using the nth-order kinetic model, as discussed above. CV showed ΔH of 159.36 kJ/mol and ΔG of 151.12 kJ/mol, with a positive ΔS of 0.027 kJ/mol $\times$ K. CH shows higher values, with ΔH of 213.03 kJ/mol, ΔG of 197.24 kJ/mol, and ΔS of 0.033 kJ/mol $\times$ K. CA shows the highest ΔH among the carbon samples with 251.99 kJ/mol, a ΔG of 248.75 kJ/mol, and the lowest ΔS of 0.004 kJ/mol $\times$ K.

Table 5.11. Thermodynamic Parameters results

Sample	ΔH			ΔG			ΔS		
	(kJ/mol)			(kJ/mol)			(kJ/mol×K)		
	Friedman	KAS	FWO	Friedman	KAS	FWO	Friedman	KAS	FWO
BPA	247.48	234.82	237.12	209.59	203.83	202.56	0.061	0.053	0.052
BCA	153.11	124.87	126.73	155.01	141.62	134.28	-0.003	-0.014	-0.012
BHO	210.42	202.38	201.79	173.56	170.01	170.41	0.060	0.053	0.051
BPM	209.59	208.33	207.36	190.68	189.98	189.44	0.030	0.029	0.028
BP	177.71	194.89	194.52	164.22	176.78	176.49	0.023	0.031	0.030
BPS	158.77	152.45	153.75	155.70	152.77	153.31	0.004	-0.0003	0.0006
BPC	241.80	234.23	231.83	208.17	204.13	202.82	0.054	0.048	0.046

Sample	ΔH			ΔG			ΔS		
	(kJ/mol)			(kJ/mol)			(kJ/mol×K)		
From STARe n-order kinetic values									
CV	159.36			151.12			0.027		
CH	213.03			197.24			0.033		
CA	251.99			248.75			0.004		

5.4.7. Combustion Indices Analysis

Table 5.12 presents the mean values of the combustion indices calculated for all samples.

The combustibility index (CI) for biomass ranges from 3.02 (BPC) to 6.12 (BPA), while coals show considerably lower values: 0.73 for CV and CH, and 0.14 for CA.

The ignition index (Di) for biomass varied from 6.63×10^{-3} to $1.35 \times 10^{-2} \text{ %/min}^3$, with BPM presenting the highest value. For coals, CV and CH show values of 2.90×10^{-3} and $2.29 \times 10^{-3} \text{ %/min}^3$, respectively, while CA exhibits a remarkably low value of $1.17 \times 10^{-4} \text{ %/min}^3$.

The burnout index (D_b) followed a similar pattern, with biomass values in the range of 4.41×10^{-4} to $8.74 \times 10^{-4} \text{ %/min}^4$. Coals show values of 1.45×10^{-4} , 9.73×10^{-5} , and $2.83 \times 10^{-6} \text{ %/min}^4$ for CV, CH and CA, respectively.

The comprehensive combustion index (S) for biomass is in the range of 9.51×10^{-8} to $2.14 \times 10^{-7} \text{ %}^2/\text{min}^2 \times \text{°C}^3$, with BPM showing the highest value. The coals exhibit values of 1.57×10^{-8} , 1.31×10^{-8} , and $7.02 \times 10^{-11} \text{ %}^2/\text{min}^2 \times \text{°C}^3$ for CV, CH and CA, respectively.

The flammability index (C) and combustion stability index (D_w) followed similar trends. For biomass, C varies from 4.03×10^{-5} to $7.25 \times 10^{-5} \text{ %/min} \times \text{°C}^2$, and D_w from 3.17×10^{-5} to $6.14 \times 10^{-5} \text{ %/min} \times \text{°C}^2$. Coals showed lower values for both indices, with CA presenting the lowest values (C : $6.02 \times 10^{-7} \text{ %/min} \times \text{°C}^2$, D_w : $4.68 \times 10^{-7} \text{ %/min} \times \text{°C}^2$).

The combustion index (Hf) shows an inverse trend, with values for biomass in the range of 1,074.65 to 1,344.28 $\text{°C} \times \text{min}^2/\text{°}$. Coals show higher values of 1,397.85, 2,331.63, and 3,894.25 $\text{°C} \times \text{min}^2/\text{°}$ for CV, CH, and CA, respectively.

Table 5.12. Combustion indices results

Sample	CI	D_i (%/min ³)	D_b (%/min ⁴)	S (%/min ² ×°C ³)	C (%/min×°C ²)	H_f (°C×min ² /%)	D_w (%/min×°C ²)
BPA	6.12	9.82×10 ⁻³	5.84×10 ⁻⁴	1.44×10 ⁻⁷	5.21×10 ⁻⁵	1,297.45	4.26×10 ⁻⁵
BCA	3.30	1.30×10 ⁻²	8.74×10 ⁻⁴	2.04×10 ⁻⁷	6.58×10 ⁻⁵	1,187.32	5.42×10 ⁻⁵
BHO	3.82	6.63×10 ⁻³	5.17×10 ⁻⁴	1.24×10 ⁻⁷	4.41×10 ⁻⁵	1,230.46	3.37×10 ⁻⁵
BPM	5.77	1.35×10 ⁻²	7.22×10 ⁻⁴	2.14×10 ⁻⁷	7.25×10 ⁻⁵	1,354.93	6.14×10 ⁻⁵
BP	4.96	1.19×10 ⁻²	7.23×10 ⁻⁴	1.67×10 ⁻⁷	5.83×10 ⁻⁵	1,183.43	4.93×10 ⁻⁵
BPS	4.62	1.11×10 ⁻²	7.76×10 ⁻⁴	1.83×10 ⁻⁷	6.13×10 ⁻⁵	1,074.65	4.83×10 ⁻⁵
BPC	3.02	7.55×10 ⁻³	4.41×10 ⁻⁴	9.51×10 ⁻⁸	4.03×10 ⁻⁵	1,344.28	3.17×10 ⁻⁵
CV	0.73	2.90×10 ⁻³	1.45×10 ⁻⁴	1.57×10 ⁻⁸	1.39×10 ⁻⁵	1,397.85	1.27×10 ⁻⁵
CH	0.73	2.29×10 ⁻³	9.73×10 ⁻⁵	1.31×10 ⁻⁸	1.31×10 ⁻⁵	2,331.63	1.13×10 ⁻⁵
CA	0.14	1.17×10 ⁻⁴	2.83×10 ⁻⁶	7.02×10 ⁻¹¹	6.02×10 ⁻⁷	3,894.25	4.68×10 ⁻⁷

5.5. ATEX Parameters

5.5.1. Minimum Ignition Temperature of Dust Layer

A comparative analysis between the MIT_L experimental values and those obtained using the thermogravimetric analysis (TGA) approach is presented in Table 5.13 and Appendix 6. The results showed a close correlation between both methods for most of the biomass samples studied.

For biomass, the experimentally obtained MIT_L values ranged from 270 °C (BPS) to 340 °C (BPM). The values calculated using the TGA approach showed a similar range, from 275.83 °C (BPS) to 334.32 °C (BPM).

The difference between the experimental and calculated values was expressed as a percentage error. The lowest error was observed for the BHO sample (0.45%), followed by the BPA (0.56%) and BCA (0.60%) samples. The BP and BPM samples exhibit slightly higher errors of 1.14% and 1.67%, respectively. BPS showed an error of 2.16%, whereas BPC showed the largest deviation with an error of 7.31%.

Furthermore, below the BPC, the CV sample shows a mean deviation, with an error of 4.11%. On the other hand, for the remaining coal samples, CH and CA, it was not possible to quantify the experimental value and, therefore, the error with the numerical method, as the upper-temperature limit of the experimental test is 400 °C. Nevertheless, both samples exhibited values above 400 °C using the numerical simulation method.

Table 5.13. Minimum ignition temperature of dust layer results

Sample	<i>Exp MIT_{LAYER}</i> (°C)	<i>TG Approach</i> (°C)	<i>TG error</i> (%)
BPA	320	318.21	0.56
BCA	290	288.26	0.60
BHO	310	311.41	0.45
BPM	340	334.32	1.67
BP	290	293.30	1.14
BPS	270	275.83	2.16
BPC	310	332.67	7.31
CV	290	278.08	4.11
CH	> 400	> 400	N.A.
CA	> 400	> 400	N.A.

* N.A. (Not Applicable)

5.5.2. Minimum Ignition Temperature of Dust Cloud

A comparative analysis between the experimental values obtained using MIT_C and those calculated using the Frank-Kamenetskii (F-K), Frank-Kamenetskii Adjusted (F-K adj), Semenov and Semenov Adjusted approaches is presented in Table 5.14. The results show significant variations between the methods for the different biomass and coal samples analysed.

For biomass, the experimental MIT_C values ranged from 400 °C (BHO and BPM) to 590 °C (BCA). As for the calculated values, the Frank-Kamenetskii approach provided a range between 312.8 °C (BHO) and 608.3 °C (BPC), whereas the Semenov method showed a range between 296.3 °C (BHO) and 574.8 °C (BPC).

The accuracy of the predictions, expressed as percentage error, showed considerable variations. The Frank-Kamenetskii approach showed errors ranging from 0.15% (BPS) to 42.07% (BCA). The Semenov method exhibited errors ranging from 1.04% (BP) to 48.39% (BCA).

It is particularly interesting to note that for some samples, such as BPM and BP, both predictive methods showed relatively low errors (F-K: 1.47% and 7.34%; Semenov: 7.28% and 1.04%, respectively). However, for other samples, such as BCA and BPC, both methods showed significant deviations above 30%.

For the CV and CH coal samples, the prediction methods showed better overall performance, with errors not exceeding 8.53% for the Semenov approach (CV) and 3.99% for F-K (CH). For the CA sample, because the experimental temperature exceeded 900 °C, it was not possible to establish a specific error, indicated as “N.A.” (Not Applicable).

It is noteworthy that the Semenov method tended to provide more accurate predictions than the F-K approach for some specific samples, particularly in the case of BP (1.04% vs. 7.34%) and CH (0.44% vs. 3.99%). However, this trend was not consistent for all samples analysed.

Table 5.14. Minimum ignition temperature of dust cloud results

Sample	<i>Exp</i> MIT_{CLOUD} (°C)	<i>F-K</i> Approach (°C)	<i>F-K adj</i> Approach (°C)	<i>F-K adj</i> Error (%)	<i>Semenov</i> Approach (°C)	<i>Semenov adj</i> Approach (°C)	<i>Semenov adj</i> Error (%)
BPA	440	318.48	470.4	6.91	305.80	451.7	2.66
BCA	590	169.60	341.8	42.07	151.12	304.5	48.39
BHO	400	206.47	312.8	21.80	195.58	296.3	25.93
BPM	400	411.87	394.1	1.47	448.43	429.1	7.28
BP	500	207.57	463.3	7.34	226.36	505.2	1.04
BPS	460	327.65	460.7	0.15	282.59	397.3	13.63
BPC	440	316.14	608.3	38.25	298.76	574.8	30.64
CV	620	293.66	599.5	3.31	277.79	567.1	8.53
CH	680	440.91	707.1	3.99	425.91	683.0	0.44
CA	> 900	> 900	> 900	N.A.	> 900	> 900	N.A.

5.5.3. Severity

The results of the oxygen balance, according to the classification given in Table 3.6, as well as the gross heat of complete combustion per unit mass of oxygen consumed and oxygen consumption energy per volume of air at the SATP condition for each sample are presented in Table 5.15.

The oxygen balance showed significant variations between the sample groups; however, in the biomass group, the variation was not significant, with values ranging from -146.70% (BPA) to -167.60% (BPC). On the other hand, the coal group showed substantially higher values, ranging from -222.23% (CV) to -272.46% (CA). This difference indicates that the coals are more oxygen-deficient than the biomass samples.

As for the gross heat of complete combustion per unit mass of oxygen consumed (ΔH_o), values ranged from 7.36 kJ/g (CV) to 13.53 kJ/g (BPA). In general, biomass samples showed higher ΔH_o values than coal samples. Among the biomass samples, BPA presented the highest value with 13.53 kJ/g, followed by BPM and BCA with 12.82 kJ/g and 12.78 kJ/g, respectively. In contrast, the coal samples showed lower values, with CV showing the lowest value at 7.36 kJ/g.

The oxygen consumption energy per unit volume of air ($\Delta H_{o,vol}$) exhibited a pattern similar to that of ΔH_o . BPA showed the highest value of 3,711.50 kJ/m³, while CV exhibited the lowest of 2,018.52 kJ/m³. Biomass samples consistently showed higher $\Delta H_{o,vol}$ values, generally above 3,000 kJ/m³, except for BP and BPC which exhibited values of 2,708.79 kJ/m³ and 2,908.45 kJ/m³, respectively. The coal samples showed comparatively lower values, ranging from 2,018.52 kJ/m³ (CV) to 2,985.75 kJ/m³ (CH).

Table 5.15. OB (%), ΔH_o and $\Delta H_{o,vol}$ results

Sample	OB (%)	Hazard Rank (-)	ΔH_o (kJ/g)	$\Delta H_{o,vol}$ (kJ/m ³)
BPA	-146.70	Medium	13.53	3,711.50
BCA	-155.64	Medium	12.78	3,506.08
BHO	-156.76	Medium	11.24	3,081.17
BPM	-151.81	Medium	12.82	3,516.21
BP	-162.39	Medium	9.88	2,708.79
BPS	-153.54	Medium	12.12	3,323.90
BPC	-167.60	Medium	10.61	2,908.45
CV	-222.23	Medium	7.36	2,018.52
CH	-228.49	Medium	10.89	2,985.75
CA	-272.46	Low	10.31	2,828.42

On the other hand, as shown in Table 5.16, the experimental results of the maximum overpressure obtained during the 20-litre sphere test were compared with the approximations obtained by three methods: TNT equivalent method (r), TNT equivalent method (r_o) and computational fluid dynamics with two different cell sizes (0.0009 and 0.001 m).

The test curves for each sample are presented in Appendix 7, where the maximum overpressures and $(dP/dt)_{max}$ values for each sample and concentration are presented.

The experimental values presented show maximum overpressure values in the range of 5.9 bar (CA) to 8.0 bar (BPS). The other samples exhibited intermediate values.

As can be seen, the TNT equivalent approach using the (r) method predicted systematically higher overpressure values than the TNT equivalent approach using the (r_o) method. For example, the r -approximation predicted an overpressure of 7.66 bar for BPA, while the r_o -approximation predicted 7.55 bar for the same sample. This trend was consistent across all samples, with the r -based calculations producing values approximately 3-8% higher than the r_o -based calculations. The difference between the two approaches is due to the different considerations of the shockwave propagation characteristics, assuming a different scaled distance expression.

The results obtained using computational fluid dynamics with the Viper::Blast software demonstrated clear sensitivity to the mesh. A finer mesh (0.0009 m) provided the most accurate results when compared to the experimental data. For example, in the case of BPA, the overpressure predictions were 7.74 and 7.67 bar for different cell sizes, respectively.

Furthermore, the values obtained with such a mesh showed better agreement with the experimental values for samples with higher overpressures. For example, the BPS sample, whose experimental overpressure reaches 8.00 bar, computationally with the finer mesh size amounts to 7.74 bar. However, some discrepancies were observed in the samples with lower experimental overpressures, such as CA, where the CFD prediction (6.38 bar) overestimated the experimental value (5.9 bar).

Therefore, the TNT (r_o) method shows the lowest mean absolute error (0.595 bar), followed by the TNT (r) method with 0.622 bar, and finally, the CFD method (0.689 bar).

On the other hand, since the TNT (r_o) method gave the best results in terms of overpressure, $(dP/dt)_{max}$ and K_{ST} were only analysed with this method and the computational one using Viper::Blast, as shown in Table 5.17, Table 5.18, Table 5.19 and Table 5.20.

As shown in Table 5.16, a comparative analysis between the maximum values of the experimental (see Appendix 7) and numerical $(dP/dt)_{max}$ values was performed. The laminar burning velocity for all models was obtained from the literature for similar samples; therefore, only the comparison of those samples for which this parameter was available is shown in these results.

According to the numerical estimations, the BM method exhibited large discrepancies when compared with the experimental values, producing errors ranging from 31.25% (CV) to 47.77% (BCA). For the BCA sample, the predicted value is 138.41 bar/s compared to an experimental value of 265 bar/s.

In contrast, the NCV method exhibited excellent modelling performance, with low errors between 3.63% for the CH sample and 14.42% for the BPM sample. This method was able to predict the experimental values with high accuracy, for example in the case of CH, with a predicted value of 243.53 bar/s compared to the experimental value of 235 bar/s, representing a deviation of only 3.63%.

Regarding the results of the values obtained by CFD, as shown in Table 5.17, it can be observed that the errors were generally larger than those previously mentioned.

The largest underestimation occurred in the CV sample, where the calculated value was 139.08 bar/s, representing a deviation of 44.36% compared to the experimental value of 250 bar/s. The best prediction using this method was achieved for BPM, with a calculated value of 204.19 bar/s, representing an error of 20.23%.

The application of the BM method resulted in even lower predictions, showing the highest systematic underestimation, with errors ranging from 34.15% for BPM to 54.07% for CV. In contrast, the NCV method showed much better performance in predicting the experimental values. The calculations showed better agreement, particularly for the CH and BCA samples, with errors of 7.77% and 9.45%, respectively. Both models were used from laminar combustion velocities found in the literature for the particular test conditions and sample, so only those that matched perfectly were used, leaving a total of five samples used.

As listed in Table 5.19, the experimental values of the deflagration index (K_{ST}) were compared with the numerical predictions obtained using two different calculation approaches. Once the calculation approach with the lowest overpressure error was determined, the remaining parameters were only calculated from this and not from the two used.

The BM method showed a clear tendency to underestimate the experimental values, producing errors between 21.35 - 34.43 bar×m/s (CV-BCA). For example, in the case of BCA, the method predicted 37.57 bar×m/s compared to the experimental value of 72 bar×m/s.

In contrast, the NCV method showed remarkably more accurate values, with errors between 4.10 - 10.51 bar×m/s (CA-BPM). This method showed high accuracy for several samples, e.g. CA, with a predicted value of 62.10 bar×m/s versus the experimental value of 58 bar×m/s.

Finally, according to the data collected as a result of the CFD modelling in Table 5.20, the application of the BM method resulted in low predictions, with absolute errors between 23.25 - 36.84 bar×m/s for BPM and CV, respectively.

The NCV method demonstrated superior performance in predicting the values, showing the best agreement for the CH and CA coal samples, with absolute errors between 2.17 - 5.83 bar×m/s. However, this method showed more significant deviations for certain samples, in particular CV, where the calculated value of 47.68 bar×m/s resulted in an absolute error of 20.32 bar×m/s compared to the experimental value.

Table 5.16. $P_{\max}$ results

Sample	<i>Exp</i> $P_{\max}$ (bar)	<i>TNT (r)</i> <i>Approach</i> (bar)	<i>TNT (r)</i> <i>Error</i> (bar)	<i>TNT (r_o)</i> <i>Approach</i> (bar)	<i>TNT (r_o)</i> <i>Error</i> (bar)	<i>CFD</i> (0.0009 m) <i>Approach</i> (bar)	<i>CFD</i> (0.001 m) <i>Approach</i> (bar)	<i>CFD</i> (0.0009 m) <i>Error</i> (bar)
BPA	6.5	7.66	1.15	7.55	1.04	7.74	7.67	1.24
BCA	6.7	7.46	0.75	7.32	0.62	7.27	6.84	0.57
BHO	6.6	7.05	0.44	6.84	0.23	6.51	6.11	0.09
BPM	7.4	7.47	0.06	7.33	0.06	7.38	7.31	0.02
BP	7.4	6.68	0.72	6.39	1.00	5.85	5.82	1.55
BPS	8	7.28	0.71	7.12	0.88	6.97	6.54	1.03
BPC	6.5	6.88	0.37	6.63	0.13	6.24	6.21	0.26
CV	6.4	5.97	0.42	5.51	0.89	4.49	4.45	1.91
CH	6.3	6.95	0.65	6.73	0.42	6.38	6.32	0.08
CA	5.9	6.80	0.89	6.54	0.63	6.04	5.67	0.14
Average	-	-	0.622	-	0.595	-	-	0.689

Table 5.17. $(dP/dt)_{\max}$ numerical results (r_o method)

Sample	<i>Exp</i> $(dP/dt)_{\max}$ (bar/s)	<i>Numerical</i> (<i>BM</i> r_o) $(dP/dt)_{\max}$ (bar/s)	<i>Numerical</i> (<i>BM</i> r_o) <i>Error</i> (%)	<i>Numerical</i> (<i>NCV</i> r_o) $(dP/dt)_{\max}$ (bar/s)	<i>Numerical</i> (<i>NCV</i> r_o) <i>Error</i> (%)
BCA	265	138.41	47.77	243.52	8.10
BPM	256	166.42	34.99	292.92	14.42
CV	250	171.87	31.25	278.82	11.52
CH	235	141.78	39.66	243.53	3.63
CA	214	134.29	37.24	228.79	6.91

Table 5.18. $(dP/dt)_{\max}$ CFD results

Sample	<i>Exp</i> $(dP/dt)_{\max}$ (bar/s)	<i>CFD</i> (<i>BM</i>) $(dP/dt)_{\max}$ (bar/s)	<i>CFD</i> (<i>BM</i>) <i>Error</i> (%)	<i>CFD</i> (<i>NCV</i>) $(dP/dt)_{\max}$ (bar/s)	<i>CFD</i> (<i>NCV</i>) <i>Error</i> (%)
BCA	265	136.64	48.43	239.94	9.45
BPM	256	168.56	34.15	297.25	16.13
CV	250	114.81	54.07	175.67	29.73
CH	235	128.12	45.48	216.73	7.77
CA	214	115.40	46.07	192.18	10.19

Table 5.19. K_{ST} numerical results (r_o method)

Sample	<i>Exp</i> K_{ST} (bar×m/s)	<i>Numerical</i> (<i>BM</i> r_o) K_{ST} (bar×m/s)	<i>Numerical</i> (<i>BM</i> r_o) <i>Error</i> (bar×m/s)	<i>Numerical</i> (<i>NCV</i> r_o) K_{ST} (bar×m/s)	<i>Numerical</i> (<i>NCV</i> r_o) <i>Error</i> (bar×m/s)
BCA	72	37.57	34.43	66.10	5.90
BPM	69	45.17	23.83	79.51	10.51
CV	68	46.65	21.35	75.68	7.68
CH	61	38.49	22.51	66.10	5.10
CA	58	36.45	21.55	62.10	4.10

Table 5.20. K_{ST} CFD results

Sample	<i>Exp</i> K_{ST} (bar×m/s)	<i>CFD</i> (<i>BM</i> 0.0009m) K_{ST} (bar×m/s)	<i>CFD</i> (<i>BM</i> 0.0009m) <i>Error</i> (bar×m/s)	<i>CFD</i> (<i>NCV</i> 0.0009m) K_{ST} (bar×m/s)	<i>CFD</i> (<i>NCV</i> 0.0009m) <i>Error</i> (bar×m/s)
BCA	72	37.09	34.91	65.13	6.87
BPM	69	45.75	23.25	80.69	11.69
CV	68	31.16	36.84	47.68	20.32
CH	61	34.78	26.22	58.83	2.17
CA	58	31.32	26.68	52.17	5.83

5.5.4. BZ Burning Class Number

The results of the experimental BZ Burning Class Number test are shown in Table 5.21, showing a clear distinction in combustion and flame spread behaviour between biomasses and coals, consistent with the review reported by Jenkins et al. (1998) [191].

The biomass obtained BZ values ranged from BZ 3 for the cork and soybean samples to BZ 5 for the olive pomace sample. The low values for soya and cork were due to their insulating properties. According to Şen et al. (2014) [192], these properties of cork can be attributed to the presence of suberin, a heat-resistant component.

However, for coal, a decreasing trend was observed from charcoal (BZ 3) to anthracite (BZ 1), with an intermediate value observed for bituminous coal (BZ 2). This degradation reflects fundamental differences in their molecular structure and degree of decarbonisation, as well as factors such as carbon content, volatile matter, oxygen content, aromatic structure, and porosity, which influence their behaviour during combustion.

Table 5.21. BZ Burning Class Number Results

Sample	<i>BZ Burning Class Number</i>
BPA	5
BCA	4
BHO	4
BPM	4
BP	4
BPS	3
BPC	3
CV	3
CH	2
CA	1

Chapter 6

Discussion

6.1. Physical Properties

The observed phenomenon of particles with d_{90} greater than 1 mm, particularly evident in samples such as BPA, BCA, and BHO, highlights the influence of the fibrous structure and its high aspect ratio on the retention of larger particles after grinding and sieving. This morphological characteristic of biomass results in the retention of larger particles, even after screening, owing to the anisotropic behaviour of the fibrous particles during screening. This is due to the fact that the fibres can pass through the mesh width in longitudinal orientation despite having a larger dimension than the nominal sieve aperture, which was already noted by Gil et al. (2014) and Guo et al. (2012) [193,194], finding that high aspect ratios and particle shape irregularities promote sieving inefficiencies. This aspect is crucial for flammability, as these elongated particles increase the surface area exposed to the oxidant compared to spherical particles of equivalent volume, which can accelerate flame propagation [195,196].

However, not only the morphology but also the full particle size distribution (PSD) curve strongly influences the flammability and explosiveness of dust because the finest particles contribute the most to these phenomena [196].

In contrast, coal samples, such as CV and CH, and BPM exhibit d_{90} values below 1 mm and more moderate size distributions, which could result in a more predictable combustion behaviour, as shown in Figure 6.1.

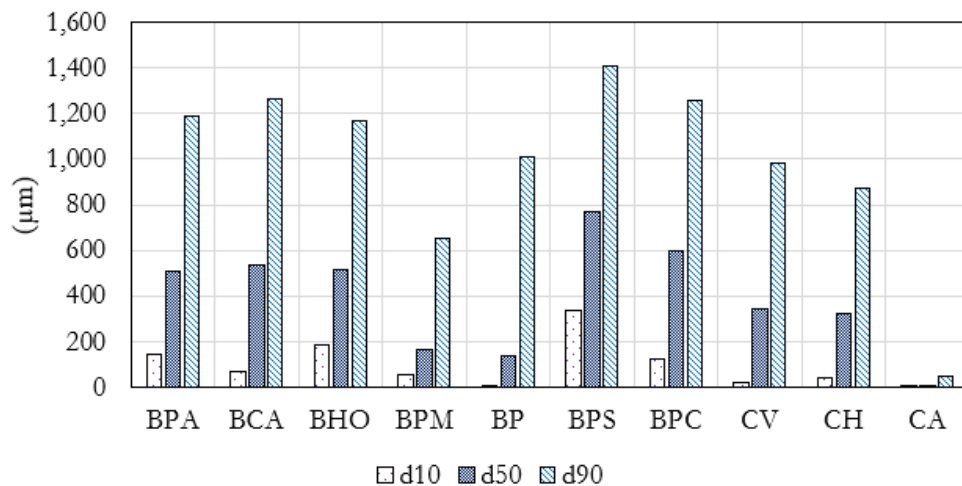


Figure 6.1. PSD for each sample

The polydispersity index revealed significant differences between the samples, which are not limited to the distinction between biomass and coals. According to Castells et al. (2023) [196], this parameter provides a more complete characterisation of dust samples than the use of a single numerical value such as the mean diameter.

BPS and BHO present the lowest indices (1.39 and 1.89, respectively), indicating a more uniform distribution that could result in a more homogeneous flame front during

combustion as particles of similar size tend to burn more uniformly. At the other extreme, BP and CA show exceptionally high indices (7.38 and 6.48), suggesting a heterogeneous size mixture that could lead to staged combustion, where the finer particles would burn first, followed by the larger ones, thus affecting the stability and uniformity of the combustion process.

As for the specific surface area (SSA), while CA presents the highest SSA ($1.60 \text{ m}^2/\text{g}$), consistent with its coal nature, BP shows a surprisingly high value ($0.235 \text{ m}^2/\text{g}$) for biomass, being closer to those values' characteristic of coals. This parameter represents a critical factor as it relates to flammability and explosivity. According to Castells et al. (2023) and Huéscar Medina et al. (2015) [196,197], it is inversely related to particle size and directly influences explosivity. A higher SSA generally correlates with a higher explosion severity.

Figure 6.2 and Figure 6.3 illustrate the trend between the polydispersity index and specific surface area for all samples. It shows that both parameters follow similar trends for all samples.

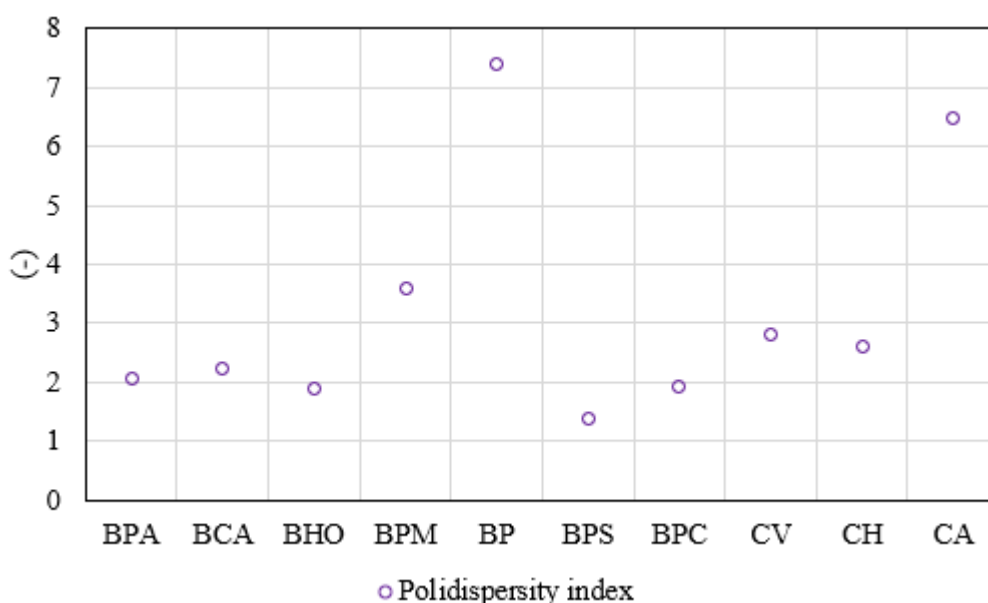


Figure 6.2. Polydispersity index for each sample

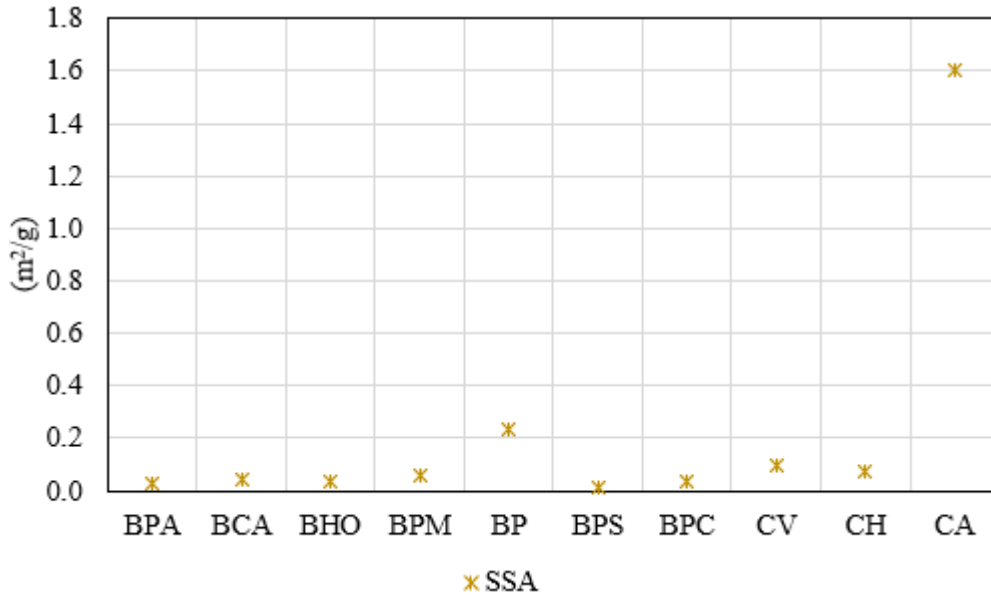


Figure 6.3. SSA for each sample

The Sauter ($d[3,2]$) and De Brouckere ($d[4,3]$) mean diameters, as shown in Figure 6.4, provide additional insights into the particle structure.

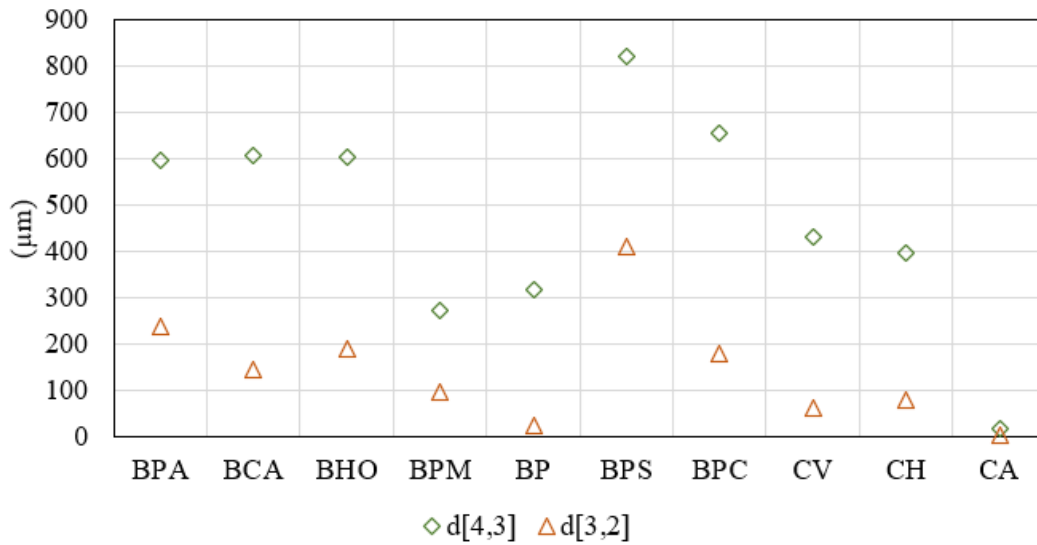


Figure 6.4. $d[4,3]$ and $d[3,2]$

BPS stands out with the highest values for both parameters ($d[3,2] = 409.37 \mu\text{m}$, $d[4,3] = 822.75 \mu\text{m}$), indicating a predominance of large particles which could result in slower ignition but longer combustion. In contrast, CA shows the lowest values ($d[3,2] = 3.75 \mu\text{m}$, $d[4,3] = 17.47 \mu\text{m}$). According to Liu et al. (2018) [198], the Sauter diameter, together with the polydispersity index, represents an important parameter in the risk assessment of combustible dust, particularly when dealing with coals. This parameter indicates a higher specific surface area, which generally results in a higher maximum

explosion pressure and deflagration index. This is because finer particles ($d[3,2]$) have a larger surface area in contact with the oxidant, increasing the reaction rate and severity of the explosion.

6.2. Proximate Analysis

The findings for olive waste samples (BPA and BHO) align closely with the studies by Miranda et al. (2008) [199] and El-Sayed et al. (2024) [149] for all analysed parameters. Similarly, the values obtained for the almond shell sample, BCA, were practically identical to those reported by Rasool et al. (2021) [200], especially for the volatile matter content (VM: 68.0 vs. 69.6%, respectively).

The wood sample (BPM) resulted in slightly higher values than those reported by Park et al. (2023) [201] in their research on building a prediction model of proximate analysis components in biomass using ultimate analysis. In the case of the straw sample, BP, the results are slightly lower than those reported by Wang et al. (2020) [202], except for the ash content, which is higher in the present study (18.7 vs. 3.37-15.55%, respectively). These variations may be due to a combination of intrinsic crop factors, soil and climatic conditions and agricultural practices, with the addition of methodological variations in sample preparation and processing, among other factors.

The soybean sample, BPS, results in similar values to those reported by Garcia et al. (2013) [203] or grain soybeans for all values, mentioning that in that case, their sample had higher moisture content (7.35 vs. 10.4%).

Finally, the cork sample, BPC, showed values similar to those reported by Pereira et al. (2017) [204] in fixed carbon and ash, while comparing the volatile matter content, a deviation was observed (59.0 vs. 67.1%). This deviation may be due to the moisture content of the sample, as this research reported a moisture content of 2.7% compared to the experimentally obtained value of 10.20%.

For the group of coals (CV, CH, and CA), it was observed that all parameters of the proximate analysis were similar and were in line with those reported by Yi et al. (2017) [205] for bituminous coal, and anthracite. As for charcoal, the *FC* content is lower than reported by García et al. (2014) [206], possibly due to the large amount of ash.

The studied biomass samples (BPA, BCA, BHO, BPM, BP, BPS, and BPC) exhibited high volatile matter (VM) contents, ranging from 58.99% to 80.28%. This characteristic is particularly relevant for flammability because a higher volatile content is generally associated with easier ignition and faster flame spread. A high volatile content results in a high fuel/oxidiser ratio, triggering easy ignition. According to Zhang et al. (2021) [207], the volatile content reflects the content of the active components, which oppositely affects the flame-retardant effect of ashes. However, above 30% volatile matter, the influence on the ignition temperature becomes more complex as various combustion-related factors come into play and must be considered.

In contrast, the coals (CV, CH, and CA) showed a significantly lower VM content, ranging from 11.17% for CA to 39.11% for CH. This difference in the volatile content between biomass and coal suggests that the ignition and flame propagation mechanisms

might be different. Anthracite (CA), with its low *VM* content, probably requires more severe ignition conditions than biomass and other coals.

The fixed carbon (*FC*) content showed an inverse trend to that of *VM*, being generally lower in biomass (between 12.48% and 20.60%) than in coals, especially in CA (79.98%). On the one hand, biomass with a lower fixed carbon content tends to have a lower ignition temperature and easier burnout temperature owing to their high volatile matter content. The result was a higher thermal reactivity compared to coals [208].

However, in the biomass samples with a high fixed carbon content, two distinct combustion phases were observed: a first stage in which combustion of volatile matter takes place, followed by a second phase characterized by the combustion of fixed carbon. The latter corresponds to the triggering of heterogeneous reactions and always follows the volatile matter combustion phase [209]. Moreover, in this phase, the particles show a relatively stable behaviour, reaching the maximum combustion temperature in this range and depending mainly on the fixed carbon content.

In contrast, as previously pointed out, coals have a higher fixed carbon content than biomass. This fact contributes to the higher decomposition temperature, as the binding energy required to break the C-C bonds is higher than that required to break C-O or C-H bonds. Accordingly, the longer burning time of coals is mainly attributed to the stronger C-C bond [209].

The ash content (*ASH*) varied considerably between samples, from values as low as 1.02% at BPM to 31.81% at CV. Ash can act as a heat sink during combustion, potentially reducing the flame temperature and propagation velocity [210]. However, in some cases, certain ash compositions can have catalytic effects on combustion reactions. Furthermore, according to Smolka-Danielowska et al. (2022) [211], a high ash content leads to lower calorific values and potentially slower combustion rates, as well as higher ignition temperatures and lower flammability due to the insulating properties of ash [207].

The ternary diagram shown in Figure 6.5, provides a visualisation of how these samples are distributed in terms of their proximate composition. This diagram reveals the clustering of the biomass in a region characterised by high *VM* and low *FC*, whereas the coals are distributed over a wider range, reflecting the variation in their range and degree of carbonisation. The position of each sample in this diagram may be indicative of its potential behaviour during ignition and combustion [212].

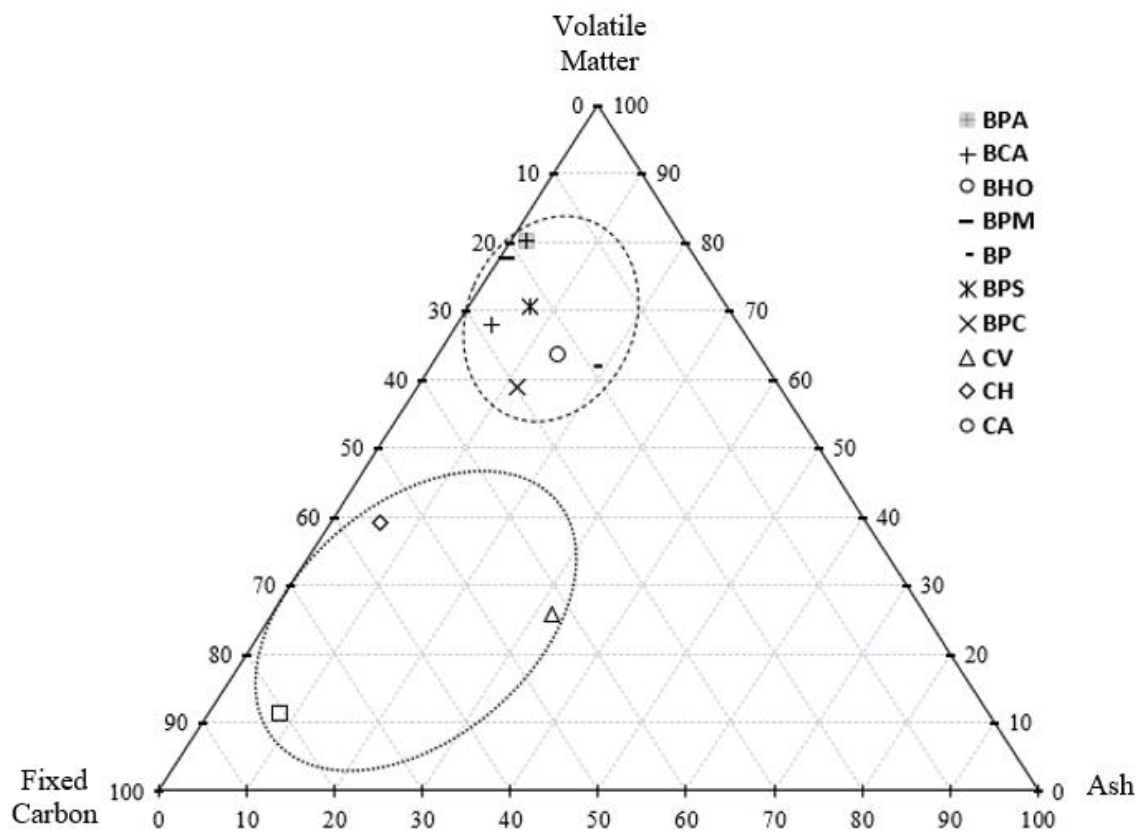


Figure 6.5. Ternary diagram

6.3.Composition Analysis

6.3.1. Elemental Analysis

Biomass shows a characteristic elemental composition, as can be seen in Figure 6.6, with a relatively lower carbon content (36.74%–45.79%) and higher oxygen levels (27.82%–38.59%) than coals. This composition is reflected in the high H/C (1.32 - 1.48) and O/C (0.70 - 0.84) ratios, placing these samples in the upper right region of the Van Krevelen diagram, depicted in Figure 6.7.

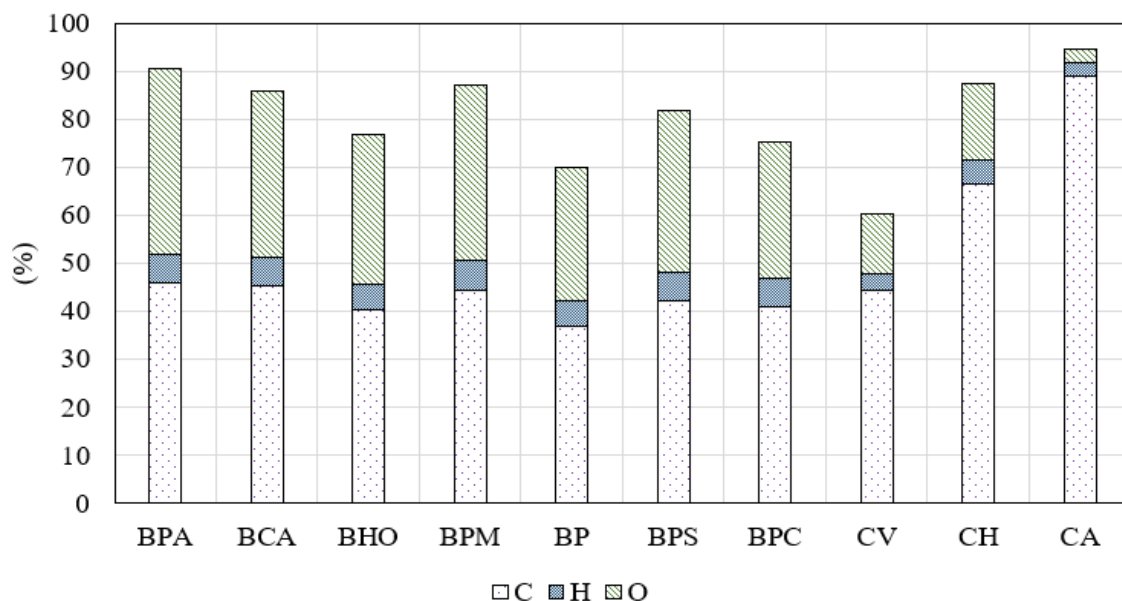


Figure 6.6. CHO percentage composition for each sample

The high proportion of oxygen in biomass has significant implications for its flammability. Oxygen present in the molecular structure of biomass can act as an internal oxidant during combustion, facilitating ignition and accelerating flame propagation. This phenomenon, for example, is especially observed in atmospheres with high oxygen concentrations, where the ignition of volatiles starts earlier, and the flames of volatiles are less bright owing to the more prominent oxidation of soot [213].

In addition, the presence of oxygenated functional groups may result in the formation of highly reactive volatile compounds during pyrolysis, which could increase the susceptibility to spontaneous ignition and the rate of explosion propagation [214,215]. These volatile compounds are released from biomass particles and may include carbon dioxide, carbon monoxide, hydrogen, methane, and other hydrocarbons. However, as discussed above, the susceptibility to spontaneous ignition and the rate of propagation can be increased by these factors. In experimental combustion tests, it was observed that biomass particles undergo two distinct phases: first, the volatiles evolve and burn in low-luminosity spherical enveloping flames; then, after the extinction of these flames, the char residues ignite and burn in short periods.

The olive-derived samples exhibited distinctive compositional characteristics. On the one hand, BPA showed higher contents in all parameters when compared to the remaining olive sample, BHO. Nevertheless, the reported values of BPA were consistent with those reported by Prins et al. (2007) [216]. In contrast, BHO showed a considerable discrepancy in carbon content, approximately 8% lower than that documented by other authors [217].

Almond shell (BCA) and wood pellets (BPM) presented elemental compositions close to those reported by Garzón et al. (2022) [218] and Fraga et al. (2022) [219].

For the straw sample (BP), the obtained values agreed with those reported by Montero et al. (2016) [220], except for the oxygen content. The soybean sample, BPS, also showed a discrepancy in oxygen content, up to 12.6% lower than that reported by Brandić et al. (2023) [221]. Finally, the cork sample BPC, except for the carbon content, fully aligns with the results reported by Rodrigues et al. (2017) [222]. These deviations can be attributed mainly to two factors. The first corresponds to the limitations of the chosen model (GP-Model), and the second to the natural variability of biomass composition due to factors such as growing conditions or post-harvest handling.

However, as demonstrated, the deviations do not have a significant impact on the trends presented in this study, as the results detailed in the Van Krevelen diagram are in line with the values reported by various authors.

In contrast, the coals (CV, CH, and CA) exhibited a clear progression in their elemental composition, reflecting different degrees of carbonisation, as shown in Figure 6.6. Charcoal (CV) showed intermediate characteristics, whereas bituminous coal (CH) and anthracite (CA) had significantly higher carbon contents (66.70% and 89.09%, respectively) and much lower levels of hydrogen and oxygen. This translates into decreasing H/C and O/C ratios, placing these samples at the bottom left of the Van Krevelen diagram (Figure 6.7). Furthermore, the data presented for the CV and CH samples were in full agreement with the ranges presented by Suttibak et al. (2018) [223] and Zapata et al. (2014) [224], respectively, as well as those of the CA sample, close to those presented by Chai et al. (2019) [225].

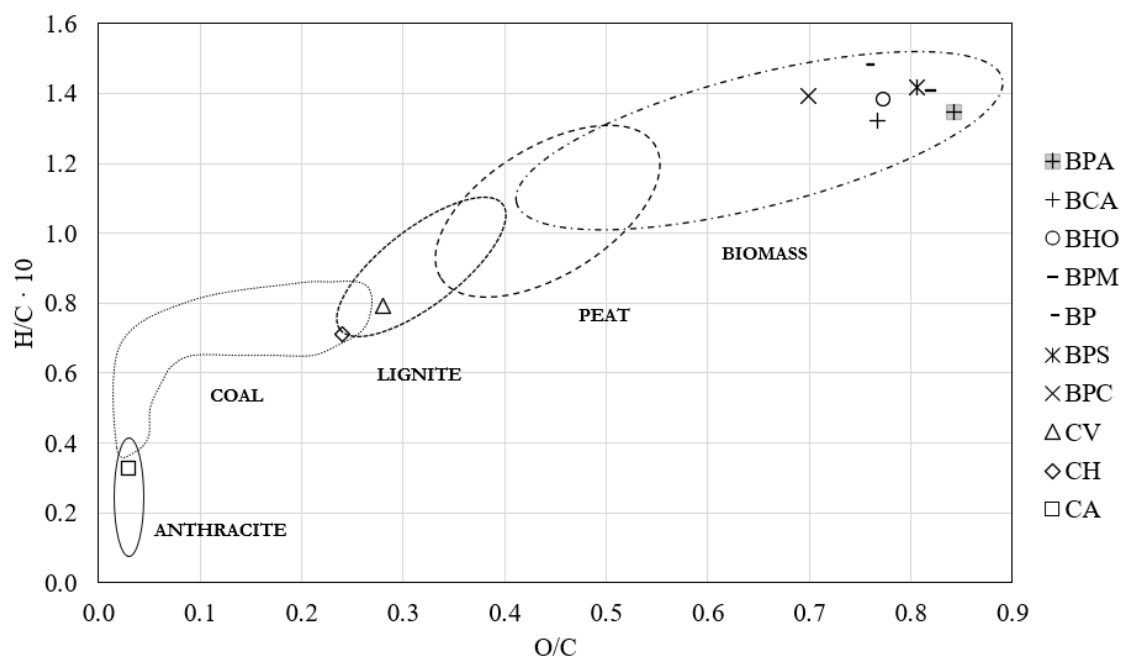


Figure 6.7. Composition ratios for each sample [226]

The CA position at the bottom left of the diagram, with a H/C ratio of 0.33 and O/C of 0.03, indicates a highly carbonised material with a predominantly aromatic molecular structure. This composition typically results in lower reactivity and higher ignition resistance [227]. However, it is important to note that low reactivity does not necessarily imply a lower risk of dust explosion, as other factors such as particle size and dispersion are also crucial parameters.

6.4. Thermogravimetric Analysis

6.4.1. TGA Flammability Points

The analysis of the data shows trends in the thermal behaviour of the samples when different heating rates are applied. On the one hand, there is an upward trend in both induction or onset temperatures (IT) and burnout temperatures (T_b) as the heating rate increases. This thermal lag is caused by the fact that as the ratio increases, the time required for the sample to reach room temperature is reduced [228], leading to higher temperatures [229]. Furthermore, the higher the value, the higher the energy required by the sample to initiate combustion.

Similarly, $MWLT$ shows a parallel trend, due to the shift of the curve. When contrasting the samples, it was observed that the olive samples (BPA-BHO), as well as the wood sample (BPM), exhibited higher $MWLT$ values than the others. This phenomenon is due to the higher concentration of hemicellulose, which shifts the curve to the right. For this reason, the $MWLT$ also varies, corresponding to the temperature of maximum cellulose volatilisation.

The temperature of maximum devolatilization of hemicellulose, cellulose, and lignin fluctuates proportionally with the heating rate. However, as this parameter increased, the shoulders corresponding to the decomposition of hemicellulose became less noticeable. This is because at higher speeds, the decomposition of the first two polymers (hemicellulose-cellulose) overlaps. In particular, in the case of the almond shell sample BCA, the peak of maximum lignin and hemicellulose decomposition from a heating rate of 7 K/min upwards cannot be differentiated.

This phenomenon is noticeable in the wood pellet sample, where the peak of maximum devolatilisation of hemicellulose is not fully differentiable. That corresponds to holocellulose (the mixture of cellulose and hemicellulose) which undergoes volatilisation within a narrow temperature range, making it difficult to differentiate between them.

An overall trend can be observed by comparing the graphs in Appendix 1. As the heating rate increased, the peaks became higher and sharper. Similarly, in the straw sample, at 7 K/min, it is also not possible to identify the peak associated with the maximum devolatilisation of hemicellulose.

Although both BPA and BHO samples were obtained from olive trees, it should be noted that the BPA results obtained in this study slightly exceeded those reported by Castells et al. (2023) [68]. However, the BHO is close to the results obtained by El-Sayed et al. (2024) [149] for IT and $MWLT$ and slightly lower for T_b .

When comparing the BCA, BPM, and BP samples with the results reported by García Torrent et al. (2016) [93], it is evident that the temperatures of the parameters analysed in the BCA and BPM samples are lower than those reported in the current study.

On the other hand, regarding the soybean powder sample, BPS, the values are consistent with the parameters documented by other researchers [96,230].

Finally, for the cork sample, BPC, the *MWLT* obtained in this study was slightly higher than that reported by Pilao et al. (2006) [231] as well as the peak cellulose decomposition temperature (*MWLT*: 346.74 vs. ≈ 380 °C). However, the induction temperature (*IT*) is identical to that reported by Escribano-Uriarte et al. (2024) [232], while the burnout temperature (T_b) is higher than that obtained experimentally in this investigation.

For the coal samples (CV, CH, and CA), the results reported for the anthracite sample agree with those reported by Tang et al. (2022) [233]. CH, on the other hand, exhibited *IT* and *MWLT* values similar to those reported by Garcia et al. (2022) [234] as well as a comparatively lower burnout temperature (T_b). Finally, the charcoal sample (CV) exhibited lower values for the parameters compared to those reported by Rainho et al. (2011) [235].

In the biomass group, a certain homogeneity in terms of thermal parameters was observed. The onset (*IT*) and burnout temperatures (T_b) obtained from the TG curve show a clear distinction between biomass and coal, as shown in Figure 6.8. Biomass generally shows lower *IT* and T_b values, indicating that thermal decomposition starts and ends at lower temperatures compared to coals. For example, BP shows the highest *IT* among the biomass (305.04 °C), while BPC has the lowest (236.77 °C), in accordance with its insulating tendency [192]. This variation within the biomass can be attributed to differences in the elemental composition and structure. BP, with the lowest carbon content (36.74%) and the highest *H/C* ratio (1.48), exhibits distinctive thermal behaviour.

In contrast, coals, especially anthracite (CA), show significantly higher temperatures (*IT*: 575.45 °C, T_b : 722.46 °C). This correlates with their higher fixed carbon content and lower oxygen content, as shown by elemental analysis and their position in the Van Krevelen diagram. The more stable and aromatic molecular structure of CA, with its high carbon content (89.09%) and low *H/C* (0.33) and *O/C* (0.03) ratios, requires more energy to initiate thermal decomposition.

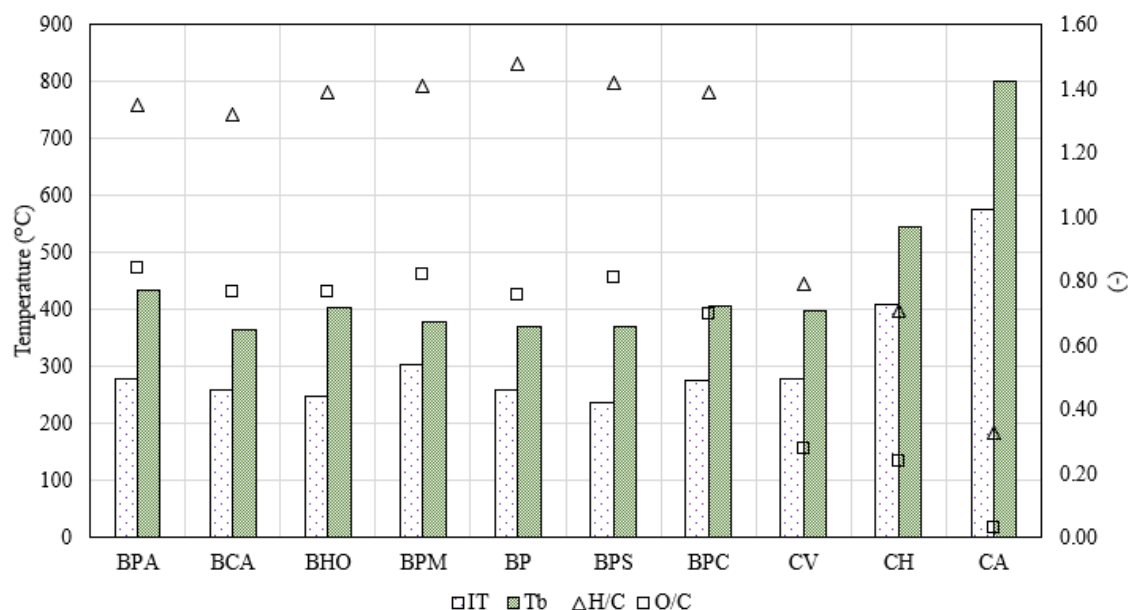


Figure 6.8. TGA parameters vs. H/C and O/C ratios

The maximum weight loss temperature (*MWLT*) obtained from the DTG curve followed a similar trend. Among the biomass, BPM shows the highest *MWLT* (350.92 °C), while BPS shows the lowest (304.86 °C). This difference was related to their different volatile matter contents: 77.60% for BPM and 70.50% for BPS. The CA sample exhibits the highest *MWLT* (722.46 °C), correlating with its low volatile matter content (11.17%) and a high proportion of fixed carbon (79.98%), as shown in Figure 6.9.

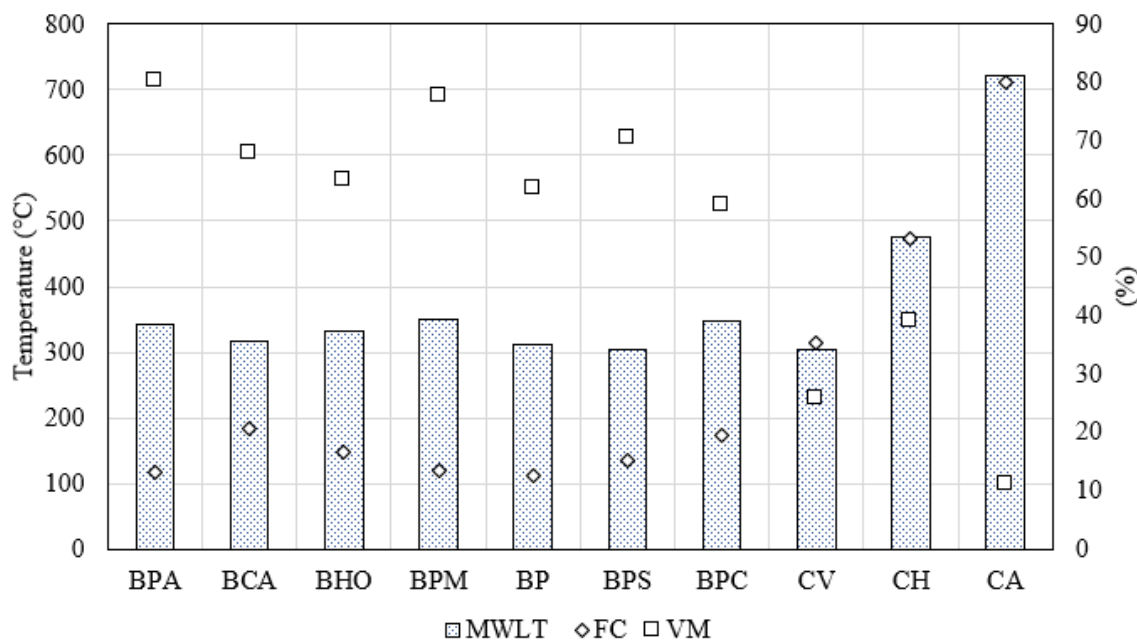


Figure 6.9. MWLT vs. FC and VM content

Analysis of the DDTG curve for the biomass revealed information on the decomposition of hemicellulose, cellulose, and lignin. BPM shows the highest temperatures for the hemicellulose (288.13 °C) and cellulose (350.92 °C) peaks, while BP shows the highest lignin peak (483.94 °C).

Significant variation in the decomposition temperatures of lignocellulosic components is observed between different biomass, which does not always correlate directly with particle size. For example, BPS, with the highest values of $d[3,2]$ (409.37 μm) and $d[4,3]$ (822.75 μm), has the lowest decomposition temperatures for hemicellulose (210.24 °C) and cellulose (304.86 °C), but one of the highest for lignin (463.67 °C). In contrast, BPM, with considerably lower $d[3,2]$ and $d[4,3]$ values (97.73 μm and 272.77 μm respectively), shows the highest temperatures for hemicellulose (288.13 °C) and cellulose (350.92 °C).

BP presents a mixed case, with the lowest $d[3,2]$ and $d[4,3]$ values (25.48 μm and 318.05 μm), but the highest lignin decomposition temperature (483.94 °C).

BPA and BHO, with similar particle sizes ($d[3,2]$ of 238.20 μm and 188.33 μm , respectively), show comparable decomposition temperatures for cellulose and lignin but differ for hemicellulose.

6.4.2. Fraser-Suzuki Analysis

Figure 6.10 shows the lignocellulosic composition of the biomass, and Appendix 3 shows the Fraser-Suzuki deconvolutions, highlighting the variations between samples.

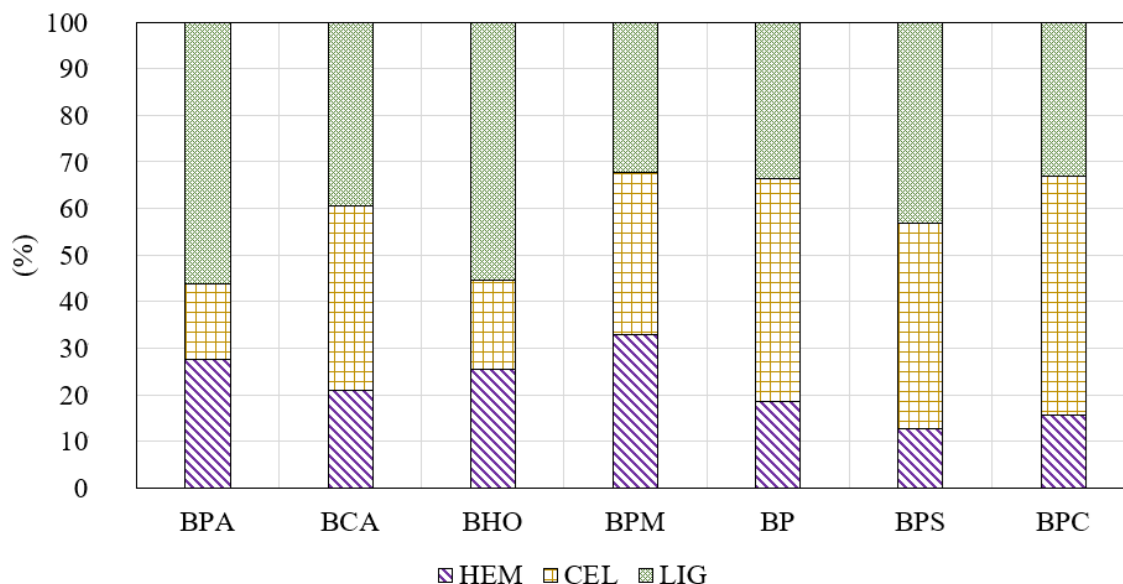


Figure 6.10. Fraser-Suzuki composition results for each sample

According to the values presented, the distributions of the olive samples (BPA and BHO) showed a marked difference with respect to the others. These samples registered cellulose contents of 16.41% and 19.13%, respectively, being the lowest values of all the samples analysed. BHO had the lowest R^2 value, indicating that the fitting technique may not be sufficiently accurate. Although the cellulose content in the BCA sample was significantly higher at 39.61%, the hemicellulose percentage was comparable to that of BPA and BHO (27.52% and 25.36%, respectively).

The findings show that cellulose and lignin were the most common polymers in samples unrelated to olives. The cellulose percentage was the highest in the BP sample and then in the BPS sample. In terms of lignin, BPA and BHO had the highest percentages of this polymer.

The BPA sample was similar to the data presented by Danzi et al. (2021) [236], according to a comparison of the results with data gathered from the literature. Although the cellulose and lignin contents reported in this study are higher, the BCA sample exhibits similarities with the hemicellulose content reported by Vidal et al. (2019) [237].

The percentage of lignin found by Sobek et al. (2020) [238] was only marginally consistent with that of the BPM sample. Given that the type of wood, origin, and other factors affect the composition, this could be explained by the fact that wood pellets can come from a variety of sources. The amounts of hemicellulose in the BP and BPS samples were comparable. However, no pertinent information was found in the literature to

compare with the soybean sample; only the cellulose content of the wheat straw sample was consistent with that reported by Baltierra-Trejo et al. (2016) [239].

A positive correlation is observed between the hemicellulose content and the maximum weight loss temperature (*MWLT*), as well as with the onset temperature (*IT*), as can be seen in Figure 6.11.

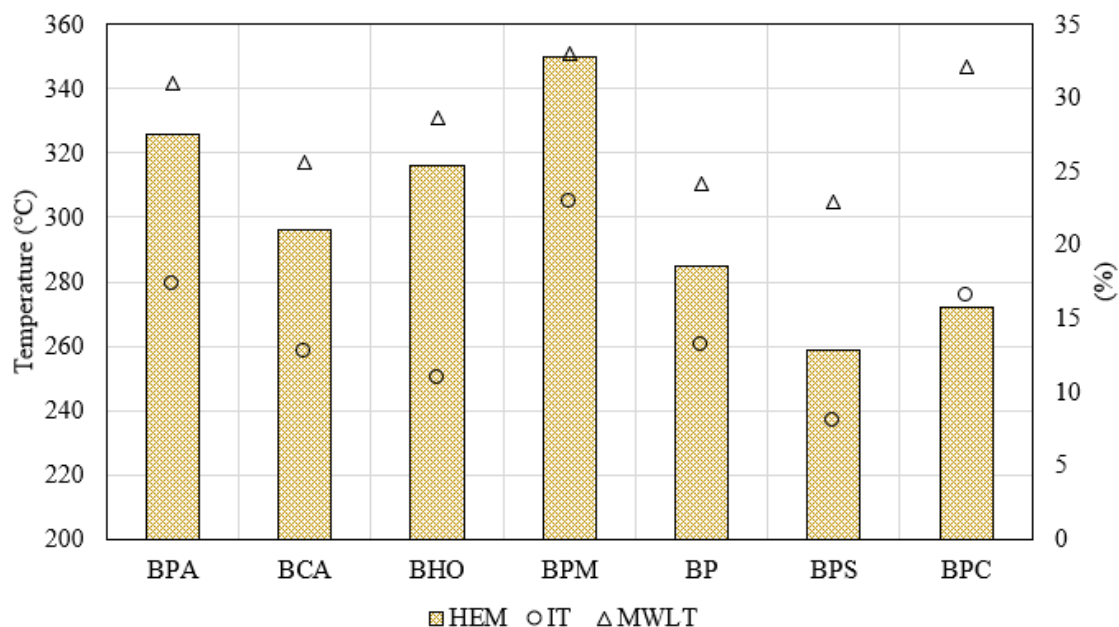


Figure 6.11. Hemicellulose vs. TGA temperature characteristic parameters

BPM, with the highest hemicellulose content (32.80%), shows the highest *MWLT* (350.92 °C) and the second highest *IT* (298.60 °C) among the biomass. This trend is maintained for BPA, which has the second-highest hemicellulose content (27.52%) and shows one of the highest *MWLT* (341.92 °C) and a relatively high *IT* (279.20 °C). This correlation suggests that hemicellulose could play an important role in the initial heat resistance and the temperature at which the maximum thermal decomposition occurs, according to Danzi et al. (2023) and Portarapillo et al. (2021) [240,241]. Hemicellulose mainly releases CO₂ during combustion, which acts as an inert heat sink, whereas cellulose and lignin generate flammable volatiles (CO and CH₄, respectively). Therefore, a higher hemicellulose content results in a higher production of CO₂ during thermal decomposition, which inhibits the ignition process and increases the temperature required for ignition to occur.

6.4.3. Reactivity Analysis

According to the TG_{spi} results presented in Table 5.7, the relationship between the slope, microscopic devolatilisation rate (Ψ), and TG_{spi} is shown in Figure 6.12.

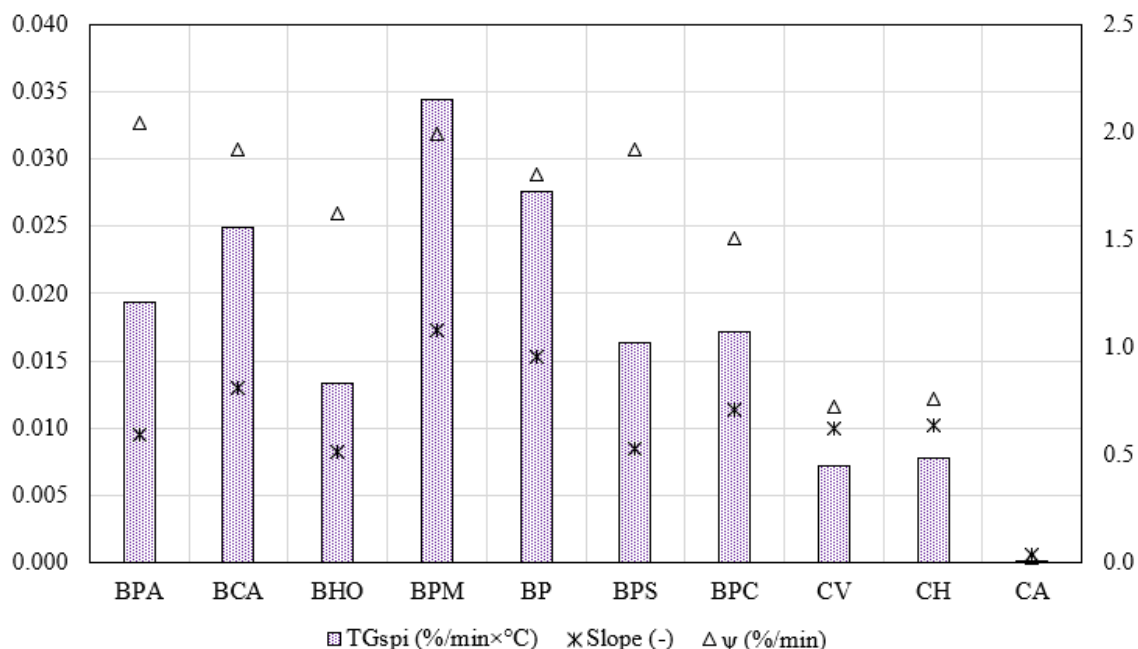


Figure 6.12. TG_{spi} vs. slope and microscopic devolatilization rate (Ψ)

Among the biomass, BPM stands out as the only sample classified as ‘Reactive’ with a TG_{spi} of 0.0344. This high reactivity is correlated with its physical and chemical characteristics. BPM has a relatively small particle size ($d_{50} = 167.51 \mu m$), which increases its specific surface area and thus its reactivity. In addition, its balanced composition of hemicellulose (32.80%), cellulose (34.96%), and lignin (32.24%) could contribute to a more uniform and sustained thermal decomposition, as reflected in its high slope value (0.0173).

BPA, BCA, and BP are classified as low reactive. BPA, despite having the highest Ψ value (2.0419), shows a lower TG_{spi} (0.0194) owing to its lower slope (0.0095). This could be attributed to its high lignin (56.07%) content, which contributes to higher thermal stability, as generally observed in Figure 6.13. BP, with the highest TG_{spi} in this group (0.0276), showed a combination of high cellulose content (47.83%) and volatile matter (61.90%), which could facilitate the faster release of volatiles during heating.

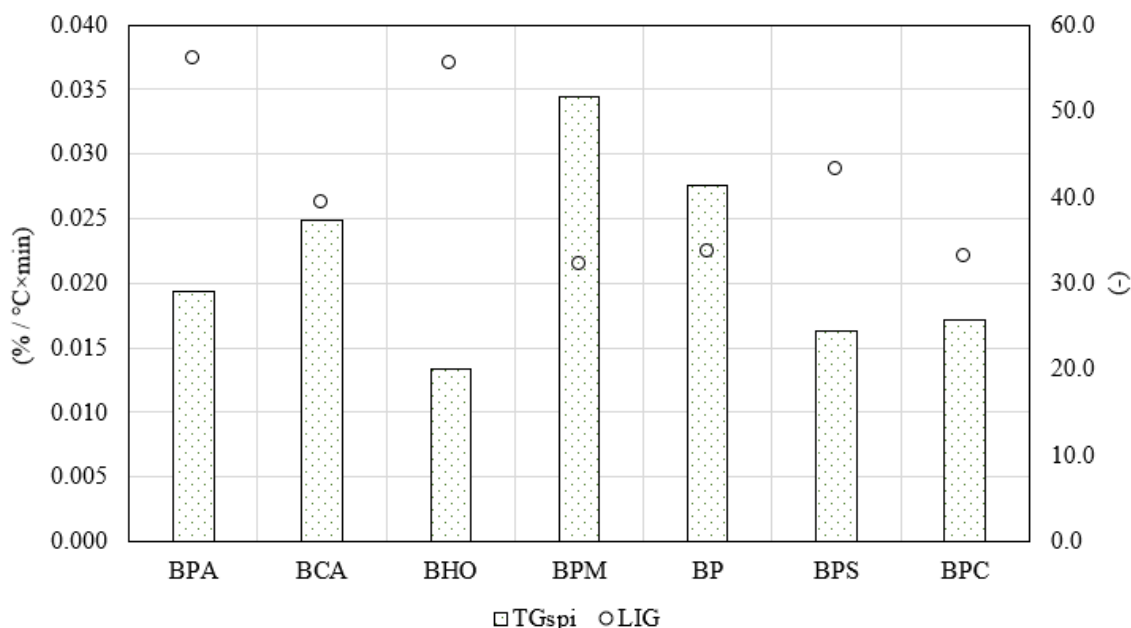


Figure 6.13. TG_{spi} vs. Lignin content

It is interesting to note that BHO, BPS, and BPC are classified as ‘Non-reactive’ despite being biomass. BHO, with its high lignin content (55.51%), similar to that of BPA, shows a lower reactivity. Despite their high cellulose contents, BPS and BPC show low reactivity, mainly due to their particular conditions as thermal insulating components [242,243].

The coals (CV, CH, CA) showed significantly higher resistance to spontaneous combustion, all classified as ‘Non-reactive’. This correlates with the higher fixed carbon content and lower volatile matter content observed in the proximate analysis. Anthracite (CA), with the lowest TG_{spi} (0.00001), demonstrates extreme resistance to auto-ignition, consistent with its high degree of carbonisation, high carbon content (89.09%), and low H/C ratio (0.33) observed in the elemental analysis.

On the other hand, analysing the results of the RB Index, Figure 6.14 reveals an inverse relationship between the thermogravimetric analysis (TGA) characteristic temperatures and the RB Index. Generally, lower onset temperatures (*IT*) are associated with a higher RB Index, which is consistent with the idea that materials that begin to decompose at lower temperatures are more prone to spontaneous combustion [244].

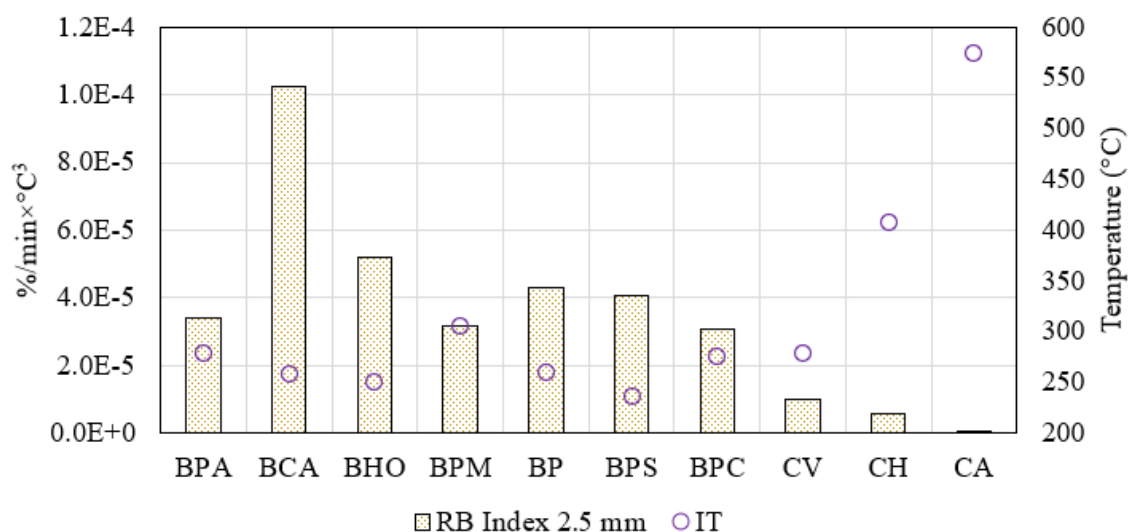


Figure 6.14. RB Index vs. IT

BCA, with an *IT* of 258.59 °C, exhibits the highest RB Index, while CA, with an *IT* of 575.45 °C, shows the lowest RB Index. The BPM sample presents an interesting exception to this trend. Despite having one of the highest *IT* values among the biomass (298.60 °C), it maintains a relatively high RB Index. This anomaly could be explained by its specific composition, particularly its high hemicellulose content (32.80%), which could result in a more intense release of volatiles once decomposition started, thus compensating for its higher *IT*.

Figure 6.15 illustrates how the RB Index varies between biomass and coals. Biomass had consistently higher RB Index values than coals for all radii analysed. The higher reactivity of biomass, reflected in their higher RB Index, can be attributed to their higher volatile matter content and less condensed molecular structure compared to coals. These characteristics facilitate the faster release of volatile compounds and a higher susceptibility to oxidation, thus increasing the risk of spontaneous combustion.

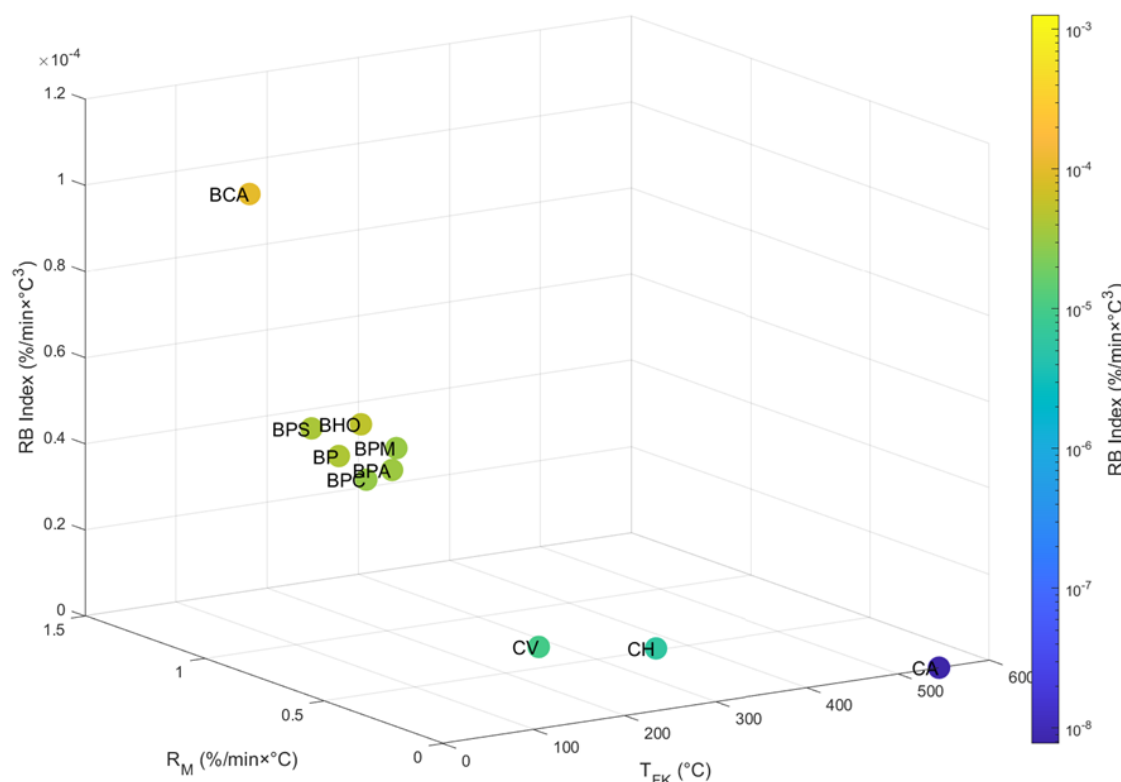


Figure 6.15. RB Index (0.0025 m)

Figure 6.15, Figure 6.16, Figure 6.17, and Figure 6.18 show a trend of increasing RB Index with increasing radius considered, from 2.5 mm to 1 m, respectively. This relationship was consistently observed in all samples, although the magnitude of the increase varied between samples. The increase in the RB Index with radius reflects the heat accumulation in larger volumes of material. In larger piles or stockpiles, heat dissipation becomes more difficult, thereby increasing the risk of spontaneous combustion.

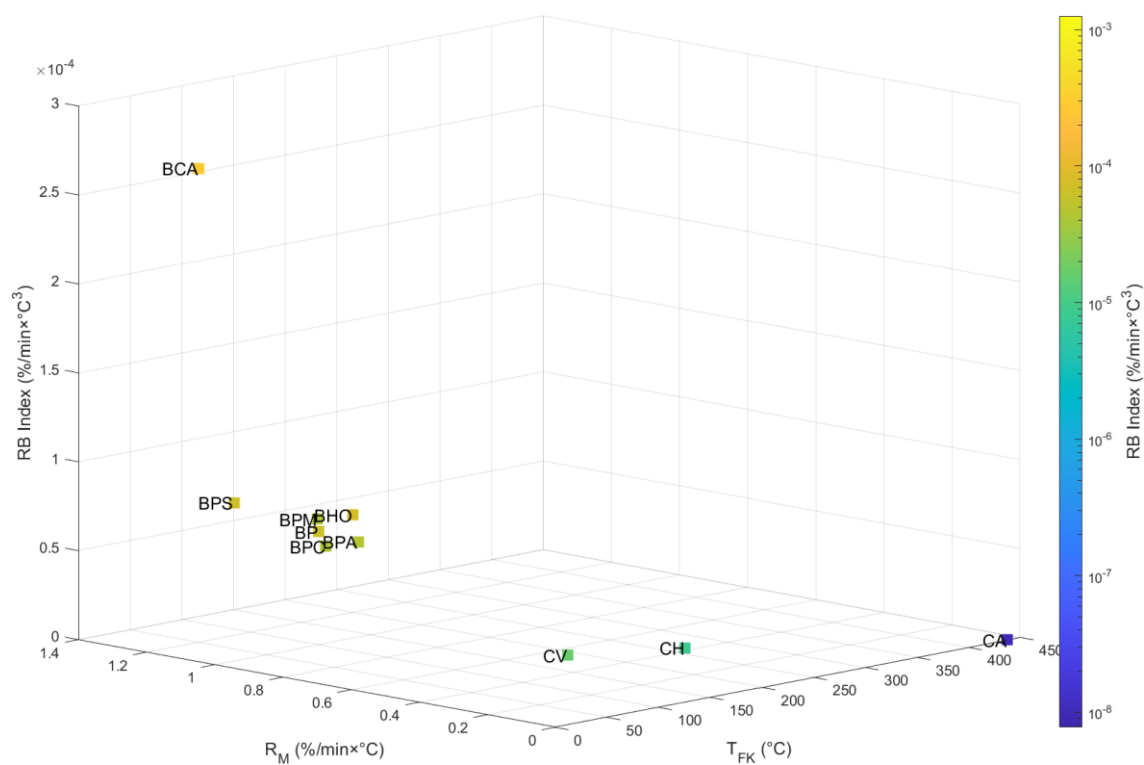


Figure 6.16. RB Index (0.1 m)

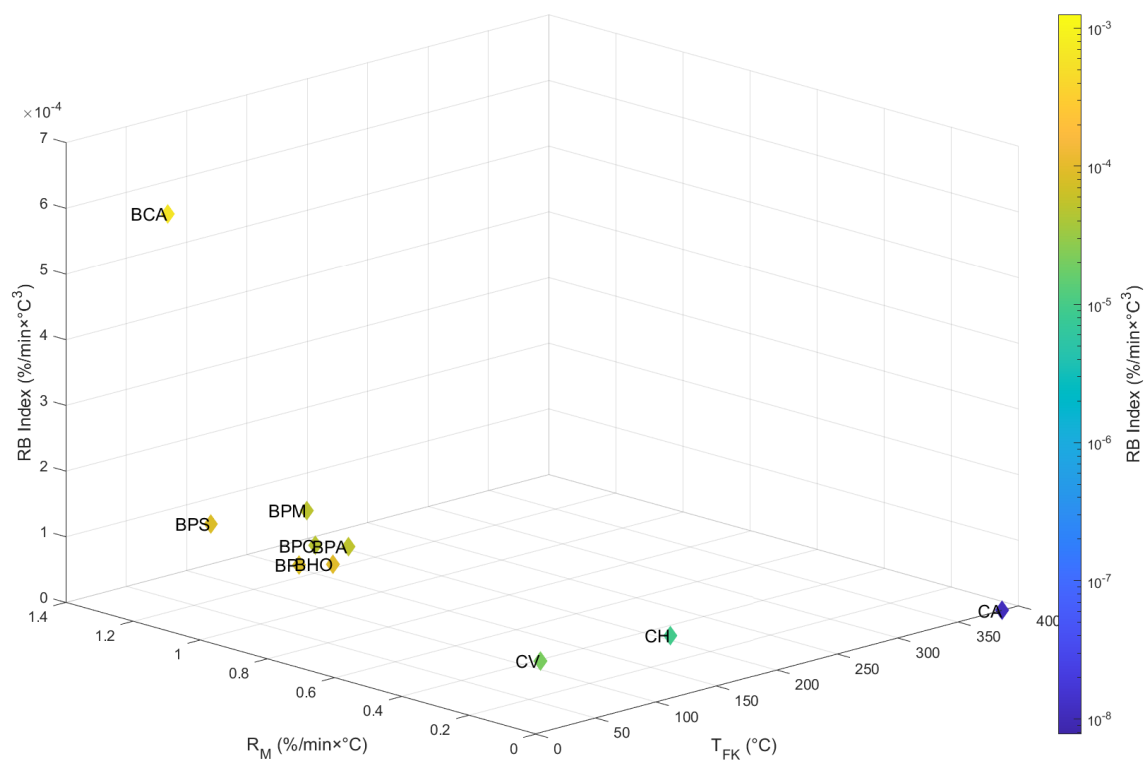
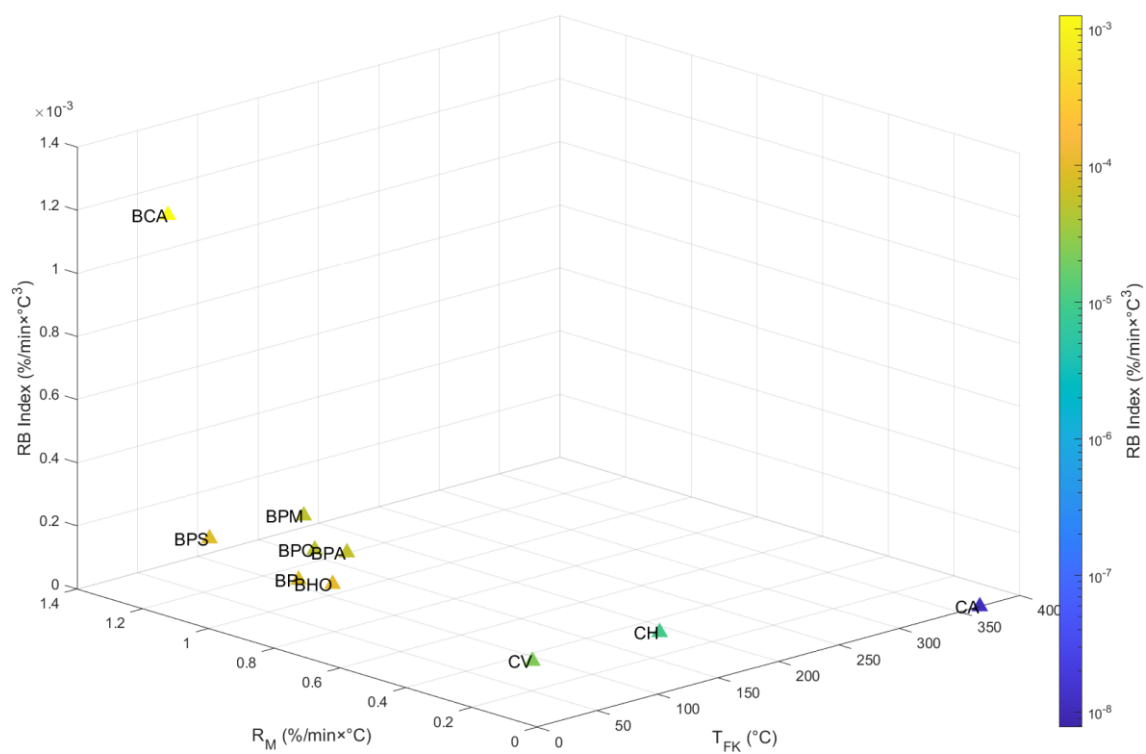


Figure 6.17. RB Index (0.5 m)

**Figure 6.18.** RB Index (1 m)

6.4.4. Kinetic Analysis

The results obtained for the kinetics of olive pomace (BPA) agreed with the values reported by Castells et al. (2023) [68] in their study on the ignition and explosion characteristics of olive-derived biomass. It can be seen how the values quoted by Friedman's method are lower than those reported in this study (294.19 vs. 252.44 kJ/mol) and close to those reported for the remaining methods (KAS: 251.72 vs. 242.07 kJ/mol; FWO: 248.17 vs. 239.78 kJ/mol).

On the other hand, according to the results reported by Wang et al. (2019) [245], the results obtained in this research are practically identical (5.29×10^{22} vs. $5.45 \times 10^{22} \text{ s}^{-1}$ for FWO, respectively).

In addition, comparing the values with the other olive sample, BHO, it is observed that they are lower than those previously reported for E_a and slightly higher for A (Friedman: 215.38 kJ/mol - $1.57 \times 10^{27} \text{ s}^{-1}$; KAS: 207.33 kJ/mol - $1.46 \times 10^{24} \text{ s}^{-1}$; FWO: 131.92 kJ/mol - $4.28 \times 10^{23} \text{ s}^{-1}$).

As for the almond shell sample (BCA), the values reported by Rasool et al. (2021) [200] are slightly higher for E_a and A compared to those reported in this study (152.02 vs. 131.92 kJ/mol, respectively; and 3.41×10^{18} vs. $8.54 \times 10^{16} \text{ s}^{-1}$, respectively, for FWO).

The wood sample, BPM, closely resembles the kinetic values reported by Magdziarz et al. (2017) [246] for their 'B2' raw sample (Friedman: 232.2 - 214.55 kJ/mol / 9.90×10^{18} - $1.03 \times 10^{18} \text{ s}^{-1}$; KAS: 215.30 - 213.29 kJ/mol / 9.20×10^{17} - $7.93 \times 10^{17} \text{ s}^{-1}$; FWO: 214.60 - 212.32 kJ/mol / 6.20×10^{17} - $6.34 \times 10^{17} \text{ s}^{-1}$).

In contrast, the BP sample showed higher activation energy values for all methods (e.g. 236.62 vs. 199.48 kJ/mol) than those reported by Zhang et al. (2019) [247] in an air (N_2/O_2) atmosphere. In contrast, for the pre-exponential factor, the values reported in this research are up to 10 orders of magnitude higher.

For the soybean sample (BPS), the values reported by Zhou et al. (2020) [248] (e.g. Friedman: 168.98 kJ/mol - FWO: 165.44 kJ/mol) are very close to those reported in this study (Friedman: 163.72 kJ/mol - FWO: 158.71 kJ/mol). However, the values reported in this study for the pre-exponential factor are higher than those reported by Emiola-Sadiq et al. (2021) [249].

Finally with the biomass group, the cork sample, BPC, shows values very close to those reported by Ribeiro et al. (2022) [250] for the range $0.1 < \alpha < 0.7$ (FWO: 236.79 - 245.61 kJ/mol; KAS: 239.19 - 246.68 kJ/mol, respectively).

For the group of coal samples, the charcoal and bituminous samples fell within the range of activation energy values reported by Várhegyi et al. (2020) [251] and Mureddu et al. (2018) [162], respectively. In contrast, the activation energy values for the anthracite sample were close to those reported by Kim et al. (1996) [252]. Regarding the pre-

exponential factor, the values reported in this study were higher than those reported by Li et al. (2019) [253], except for anthracite, which was similar.

Analysing the kinetic parameters with the results of the chemical composition of the samples, it was observed that in the biomass group, there was a correlation between the pre-exponential factor and the ash content (as shown in Figure 6.19). This can be attributed to the catalytic effect of the minerals present in the ash, which favours the formation of active sites and increases the probability of effective collisions during thermal decomposition [254].

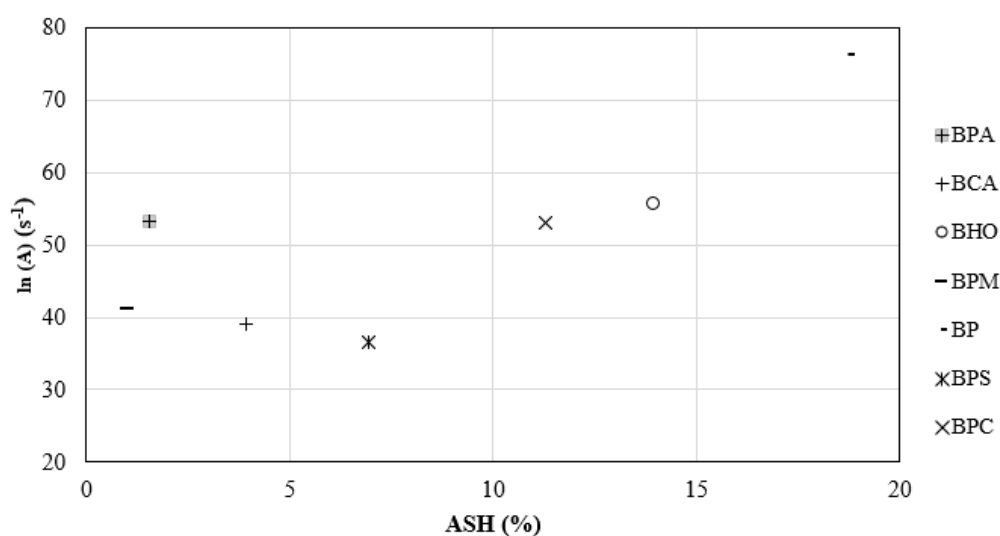


Figure 6.19. $\ln(A)$ vs. ASH

In addition, a trend was observed with the carbon content, where the higher the pre-exponential factor, the lower the carbon content (as shown in Figure 6.20). This is related to the presence of more functional groups and reactive sites in structures where carbonisation is lower, thus facilitating molecular interactions during the decomposition process.

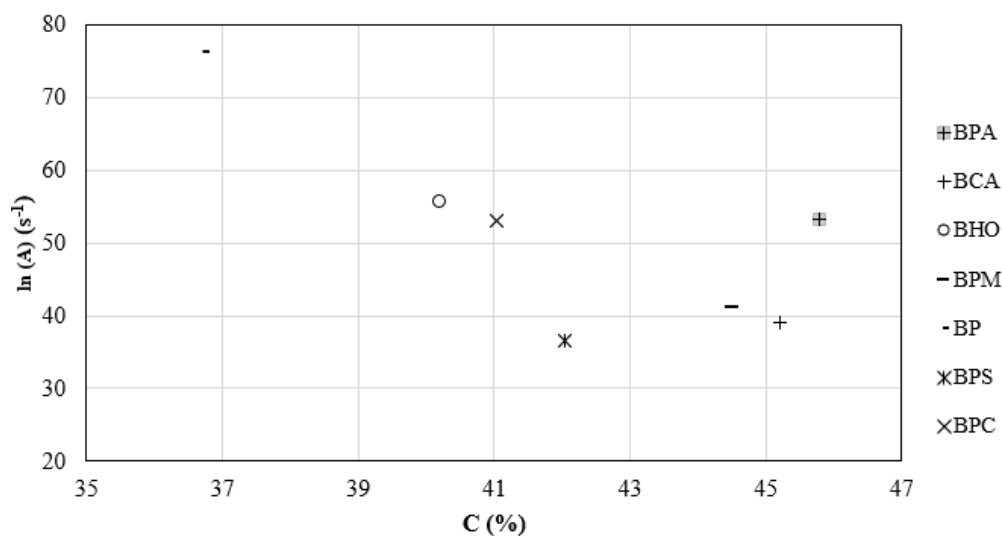


Figure 6.20. $\ln(A)$ vs. C

However, the comparison with the carbon group showed stronger trends. The activation energy shows a robust relationship with the fixed carbon and carbon content; the higher the value of fixed carbon and carbon, the higher the thermal stability of the ordered carbonaceous structures, and thus the higher the energy required (as shown in Figure 6.21 and Figure 6.22). This trend is consistent with the relationships observed for the H/C and O/C ratios (as shown in Figure 6.23), indicating that more aromatic and condensed structures with fewer functional groups require more energy to decompose.

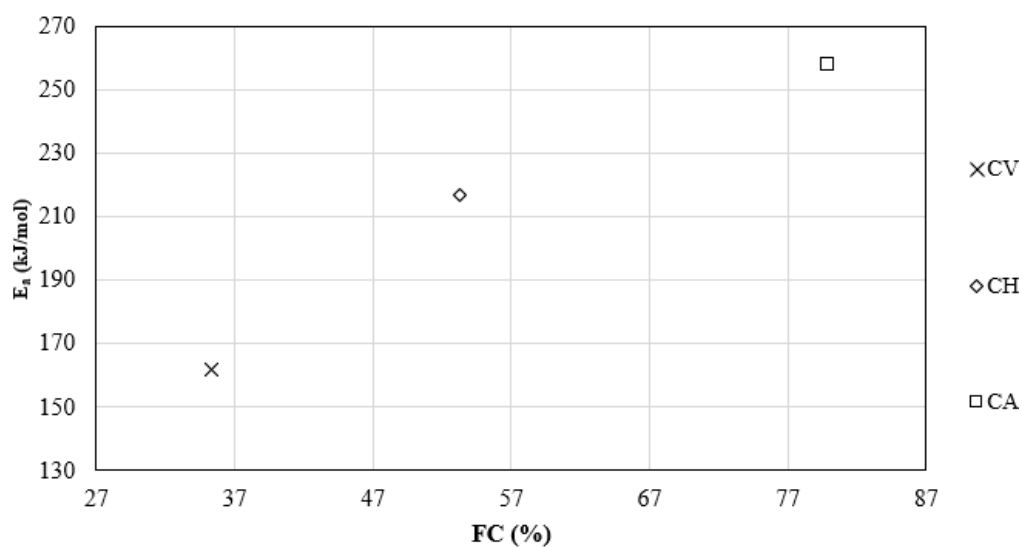
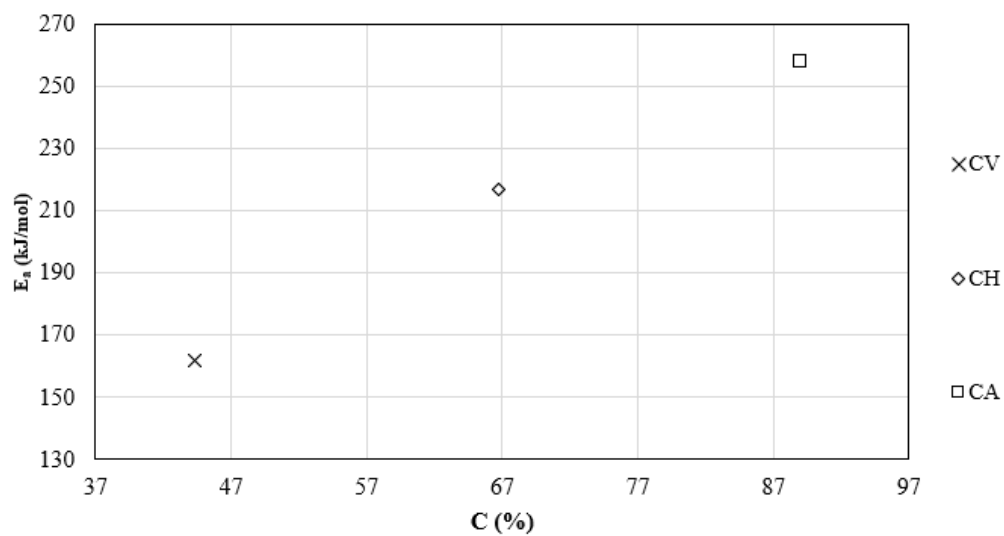
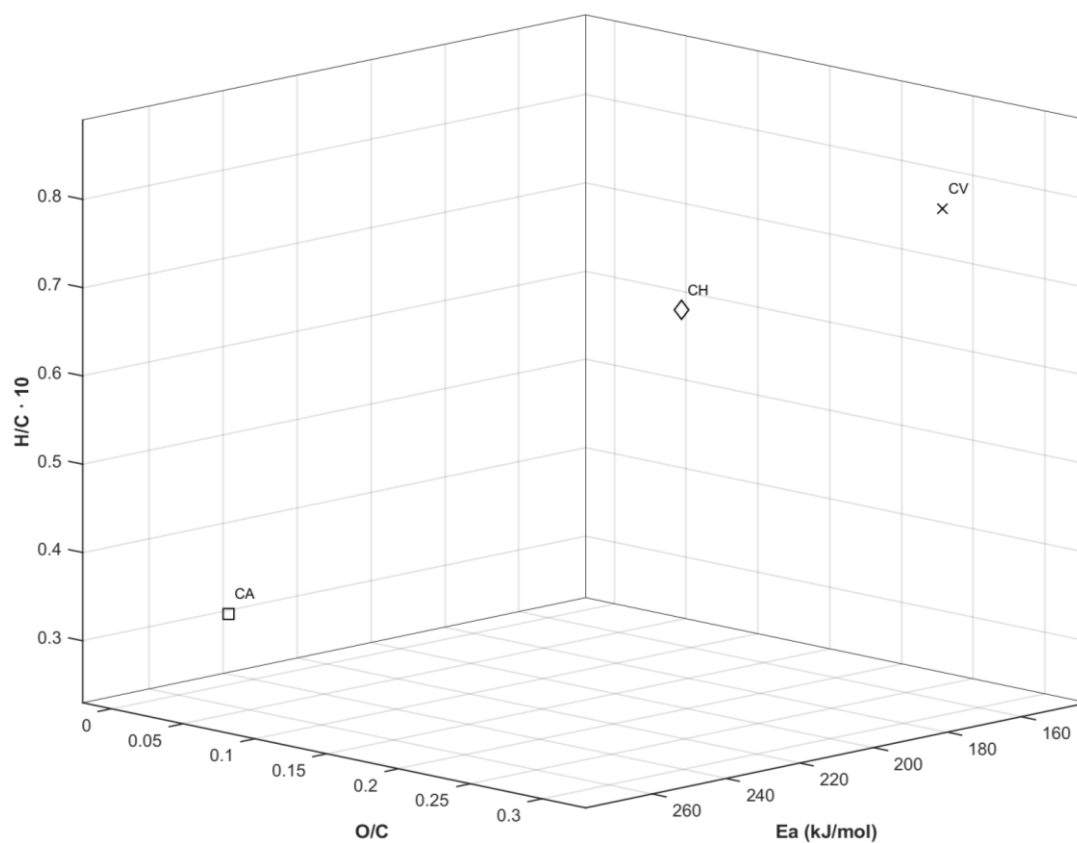


Figure 6.21. E_a vs. FC

**Figure 6.22.** E_a vs. C**Figure 6.23.** E_a vs. H/C and O/C

The pre-exponential factor shows relationships with volatile matter and hydrogen and oxygen contents, as both volatile matter and functional groups (represented by H and O) provide active sites for the reaction, increasing the probability of effective molecular collisions during the thermal decomposition process (as shown in Figure 6.24, Figure 6.25, and Figure 6.26). It is important to highlight the novelty that lies in these results, as such tendencies between preexponential factor and composition has not been previously studied.

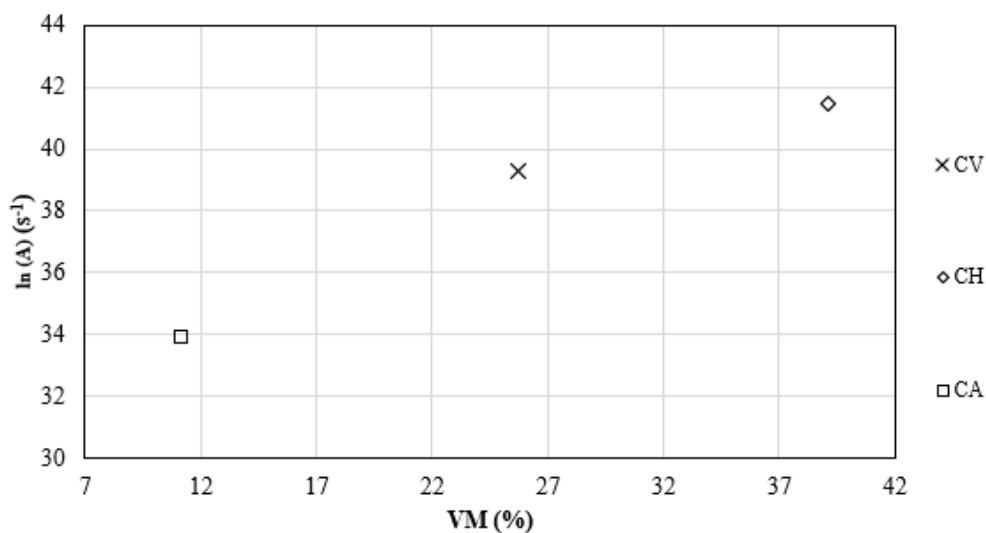


Figure 6.24. $\ln(A)$ vs. VM

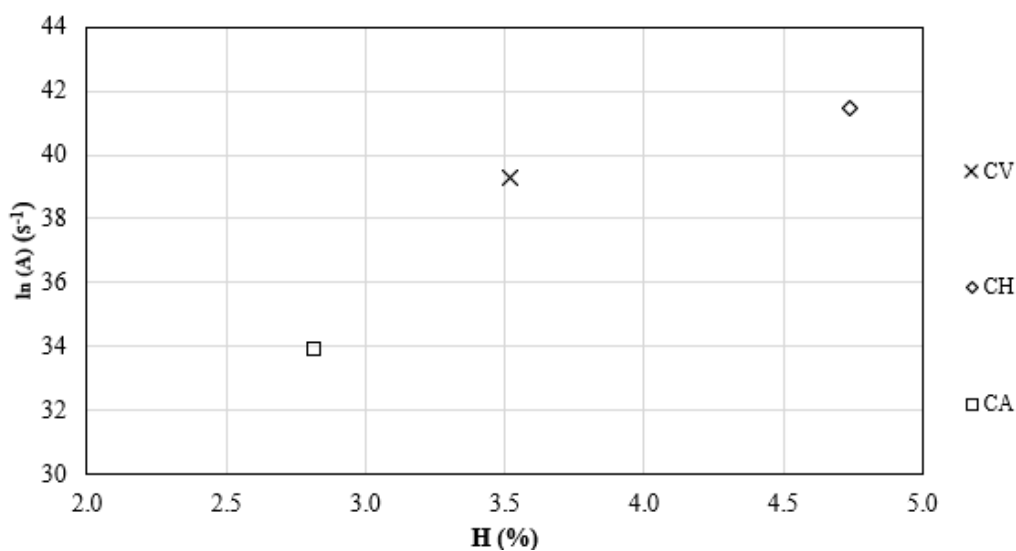


Figure 6.25. $\ln(A)$ vs. H

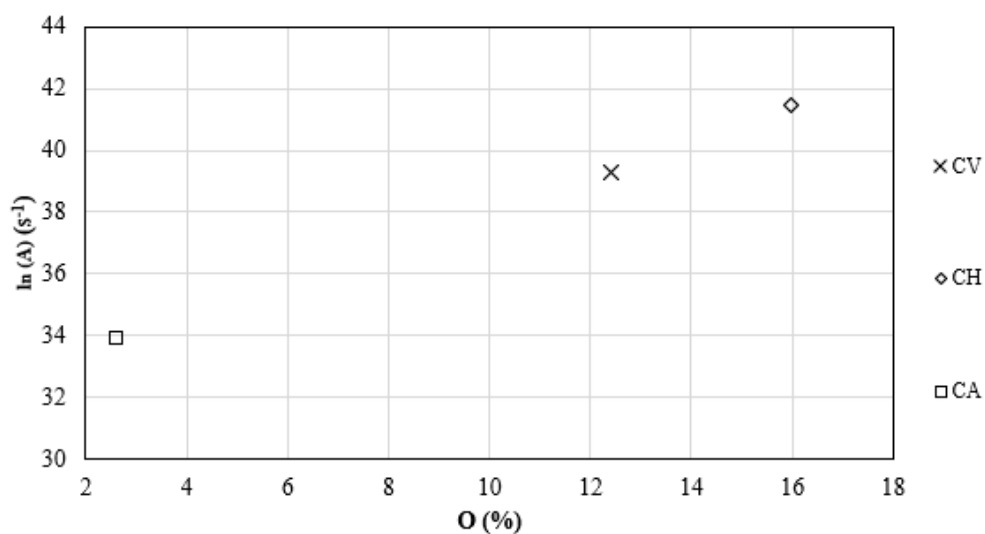


Figure 6.26. $\ln(A)$ vs. O

Analysing the data obtained in this research with thermal parameters, a correlation between the activation energy and burnout temperature can be observed, as shown in Figure 6.27. This correlation may be due to the fact that, by definition, the burnout temperature represents the temperature at which the combustion of the material is completed, directly related to the energy required to decompose the more stable structures of the fuel. In the case of coals, this is particularly evident, due to their more ordered molecular structure and more stable bonds. For example, anthracite, with its high aromaticity and highly ordered carbonaceous structure, requires more energy to break its bonds (higher E_a) and therefore requires higher temperatures to complete combustion (higher T_b).

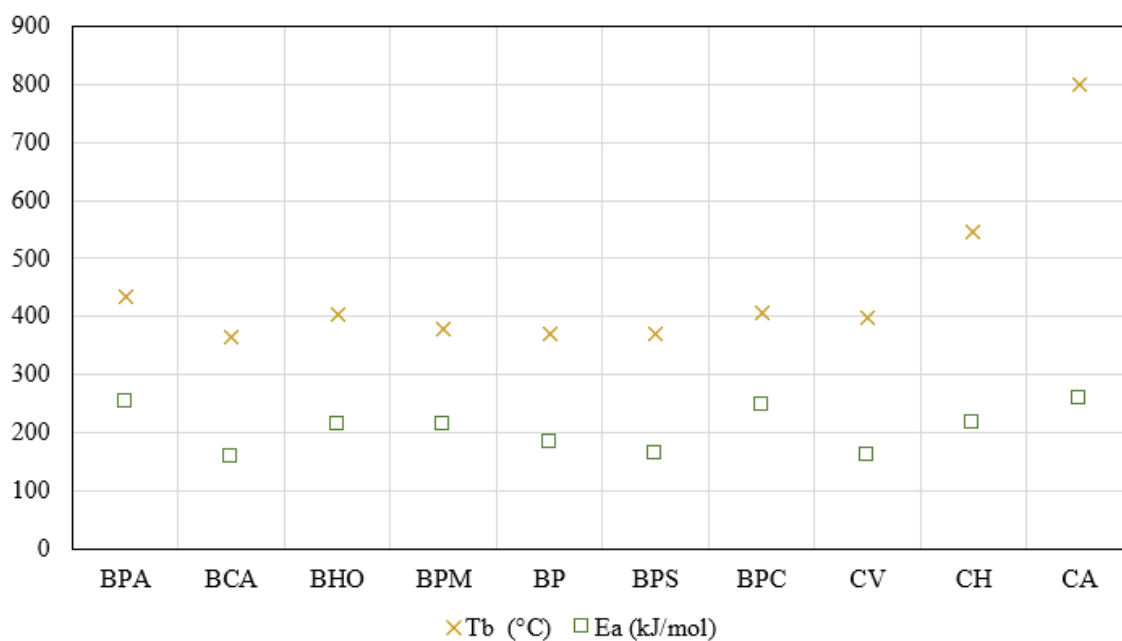


Figure 6.27. E_a vs. T_b

On the other hand, the trend in E_a ($CV < CH < CA$) correlates well with the increase in coal rank, reflected in their increasing fixed carbon content (35.28%, 53.32%, 79.98%) and decreasing volatile matter content (25.72%, 39.11%, 11.17%). This progression also aligns with their increasing ignition temperatures (IT) (278.43 °C, 408.20 °C, 575.45 °C) and decreasing RB index ($r = 0.0025$ m), according to Figure 6.28, indicating an increasing resistance to ignition and spontaneous combustion.

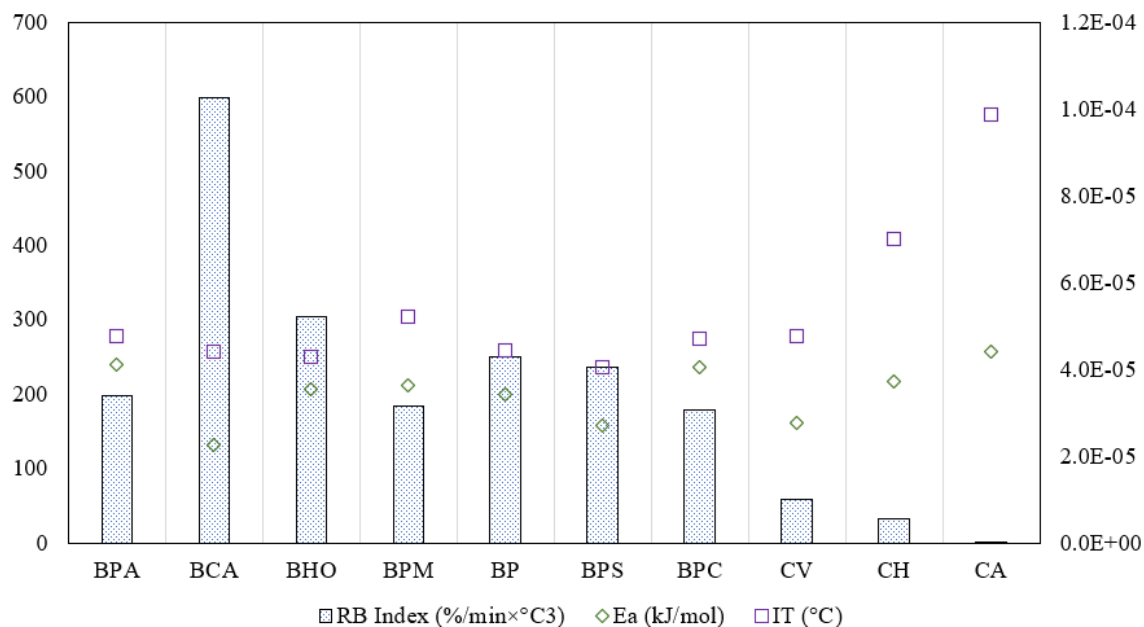


Figure 6.28. RB Index vs. E_a vs. IT

6.4.5. Thermodynamic Analysis

The thermodynamic parameters of the olive samples (BPA-BHO) were slightly higher than those reported by Wang et al. (2019) [245] for enthalpy and Gibbs free energy, whereas for entropy, the values were practically identical.

On the other hand, for the almond shell sample, according to the values reported by Rasool et al. (2021) [200] for KAS and FWO, the results of this research are closely matched for enthalpy (ΔH) and entropy (ΔS) and slightly higher for Gibbs free energy (ΔG).

The wood dust sample, BPM, shows slightly higher results, but within the expected accuracy, than those reported by Xu et al. (2021) [255] for the FWO kinetic method (ΔH : 201.79 vs. 181.61 kJ/mol; ΔG : 170.41 vs. 155.08 kJ/mol; ΔS : 0.051 vs. 0.04306 kJ/mol $\times$ K).

As for the straw sample, BP and, as in the wood sample, slightly higher results than those reported by Singh et al. (2022) are observed [256] for ΔH and ΔG , while for ΔS the values for KAS and FWO are very close (KAS: 0.029 vs. 0.02 kJ/mol $\times$ K; FWO: 0.028 vs. 0.02 kJ/mol $\times$ K).

For the soybean sample, BPS, the calculated value for ΔH is higher than that reported by Agnihotri et al. (2024) [257] and lower in terms of ΔS . However, comparing the ΔG , a similarity between values is found (167.23 vs. 153.31 kJ/mol).

Finally, in the biomass group, the results of the cork sample, BPC, could not be compared with those in the literature. However, according to the previous point where the discussion of the kinetics is presented, these values are similar to those obtained in this research; therefore, the thermodynamic results will be similar, as they depend intrinsically on the kinetic values.

Regarding the group of coals, the values reported by Florentino-Madiedo et al. (2021) [258] for bituminous coal (CH) were very close to the ΔH and ΔG parameters and were higher to the ΔS value (0.033 vs. 0.01149 kJ/mol $\times$ K). On the other hand, the analysis of the results obtained from the charcoal sample (CV) revealed a slight overestimation for ΔH , ΔG and ΔS with those reported by Kumar et al. (2022) [259].

Finally, for the anthracite sample, CA, agreed with the ranges reported by He et al. (2018) [260] for all parameters except ΔS , where the values obtained were lower than those reported.

However, according to many authors, the difference between E_a and ΔH should be approximately ± 5 kJ/mol, indicating a small potential energy barrier to achieve product formation, which implies greater ease of product formation [261,262]. The comparison is shown in Figure 6.29 and Figure 6.30. Moreover, the average difference between methods is less than 5 kJ/mol (Friedman: 4.72 kJ/mol; KAS: 4.90 kJ/mol; FWO: 4.51 kJ/mol).

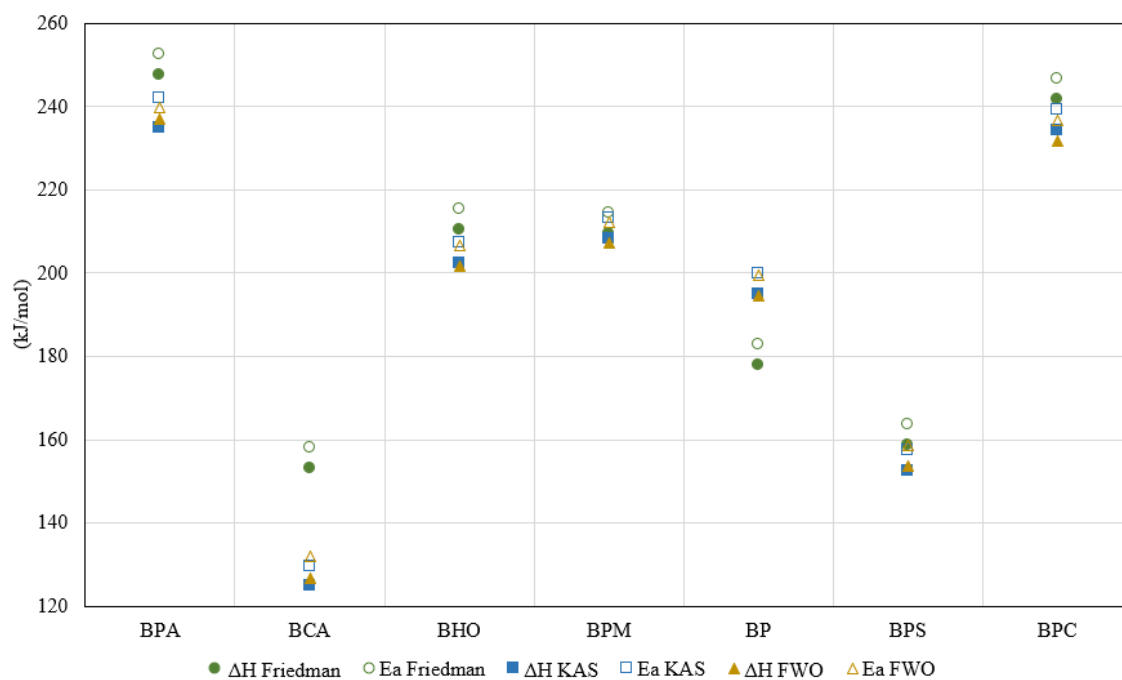


Figure 6.29. ΔH vs. E_a for biomass samples and method

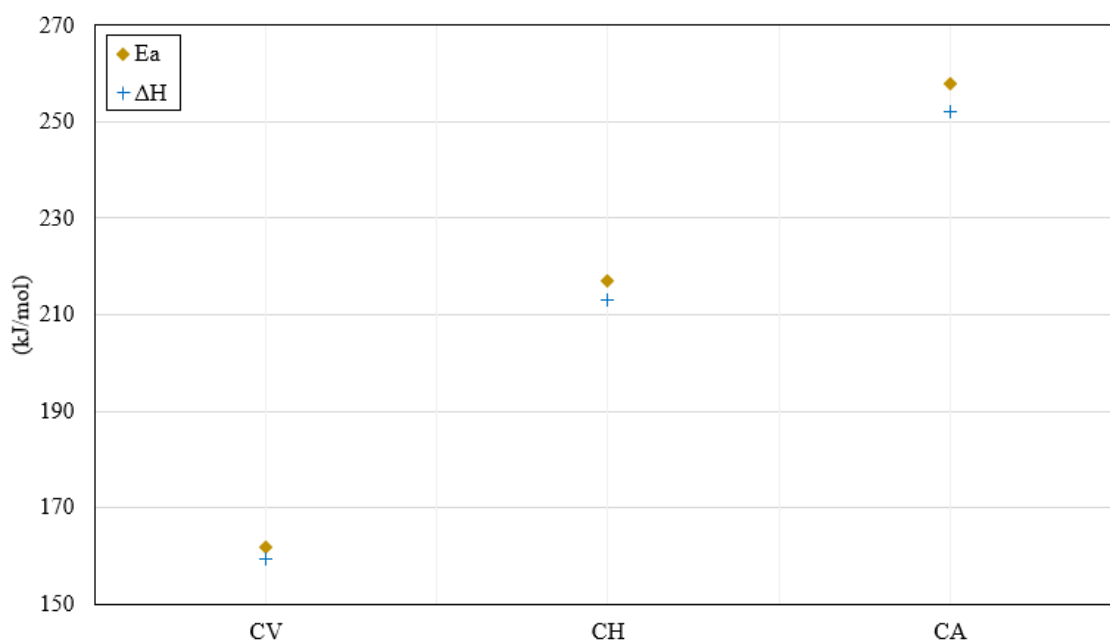


Figure 6.30. ΔH vs. E_a for coal samples and method

By analysing the thermodynamic parameters with the rest of the parameters studied, various relationships were observed.

First, in the biomass group, considering the burnout temperature (T_b), a positive correlation was observed with ΔH , ΔG , and ΔS . This is because a higher enthalpy (ΔH) requires a higher temperature to complete combustion. A higher Gibbs free energy (ΔG)

requires a higher temperature, and an increase in entropy (ΔS) requires a higher temperature to reach the final combustion state (Figure 6.31).

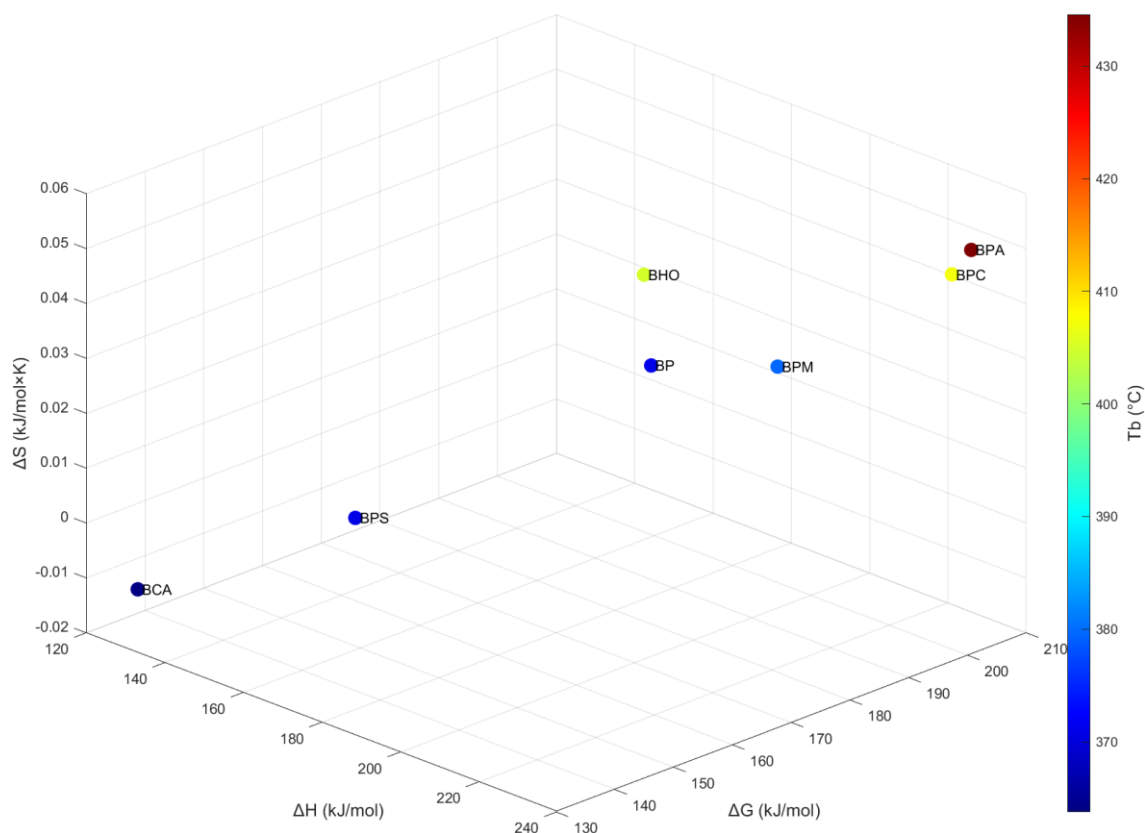


Figure 6.31. ΔH , ΔG and ΔS (FWO) vs. T_b

Regarding reactivity and establishing trends with the RB Index, there is mainly evidence of a negative trend with both enthalpy and Gibbs free energy (as shown in Figure 6.32). This is because an increase in enthalpy indicates greater energy stability of the system, reducing its reactivity. Similarly, an increase in ΔG implies that a larger energy barrier must be overcome to initiate the reaction, thereby decreasing the reactivity of the system and, therefore, decreasing RB index.

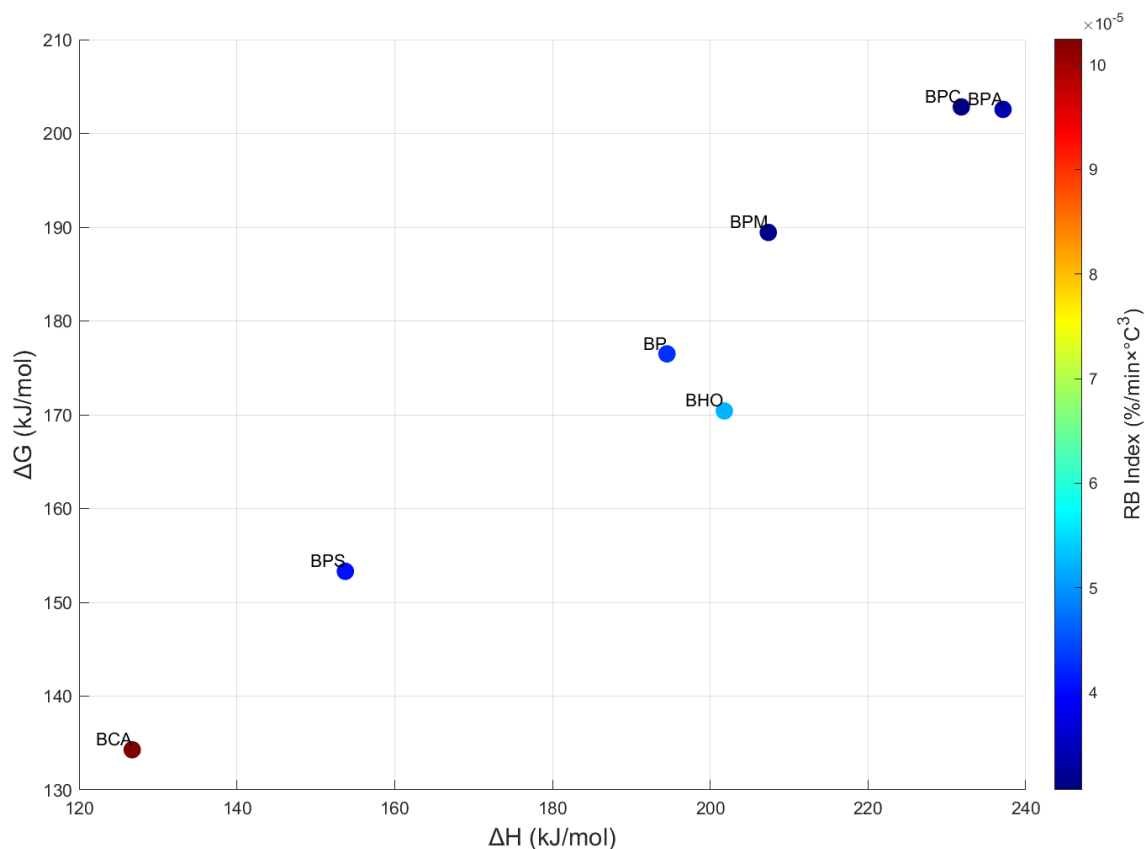
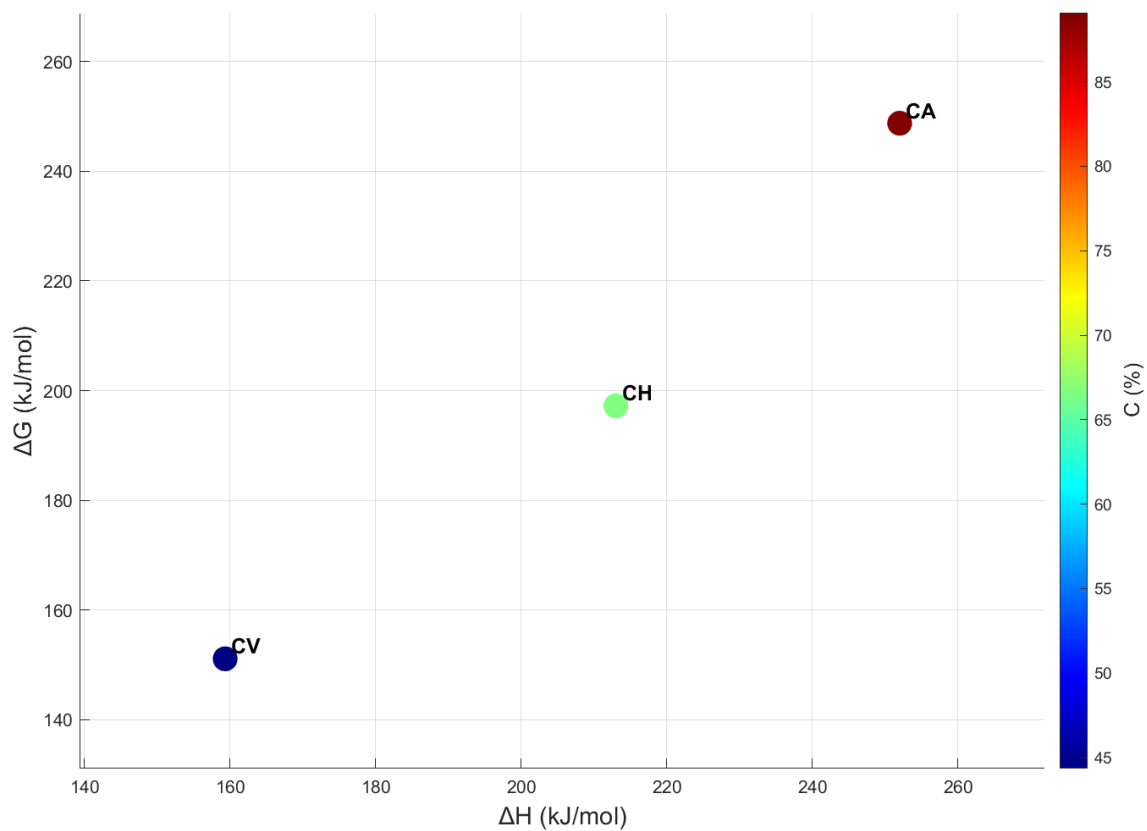
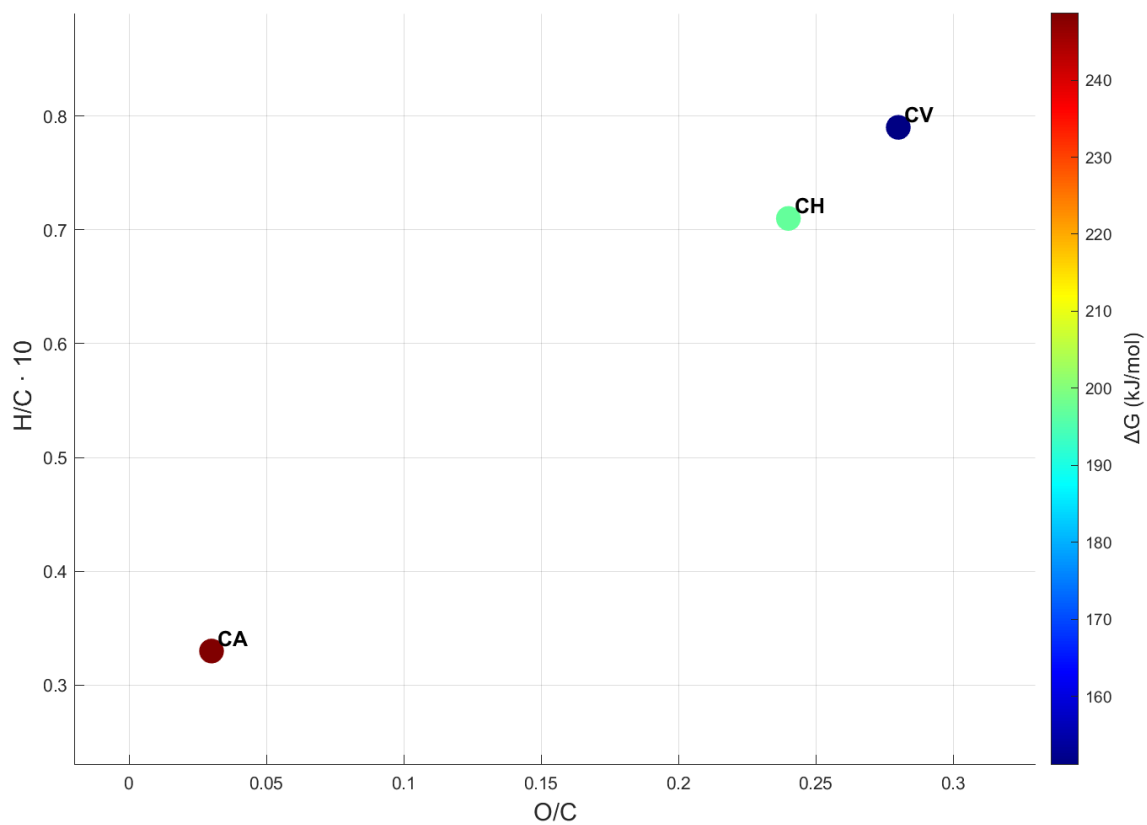


Figure 6.32. ΔH and ΔG (FWO) vs. RB Index

For the coal group, clear trends were observed. The correlations with the composition and structure of the carbon samples reveal that both ΔH and ΔG show a positive trend with fixed carbon and C content, as it reflects the higher energy content associated with more evolved carbonaceous structures (Figure 6.33). In contrast, H/C and O/C exhibited negative trends with ΔG (Figure 6.34). In addition, entropy shows a positive trend with volatile matter (VM) and oxygen content because these parameters are associated with greater disorder in the structure (Figure 6.35).

**Figure 6.33.** ΔH and ΔG vs. carbon content**Figure 6.34.** ΔG vs. H/C and O/C

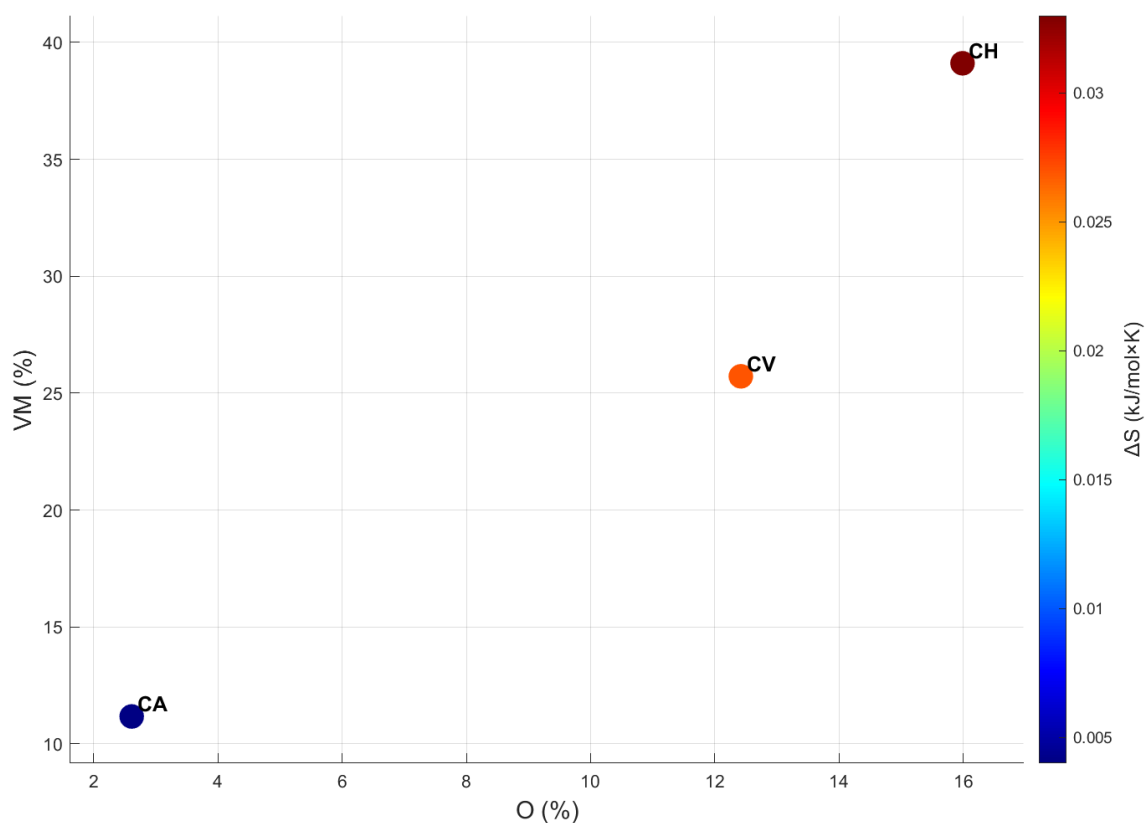
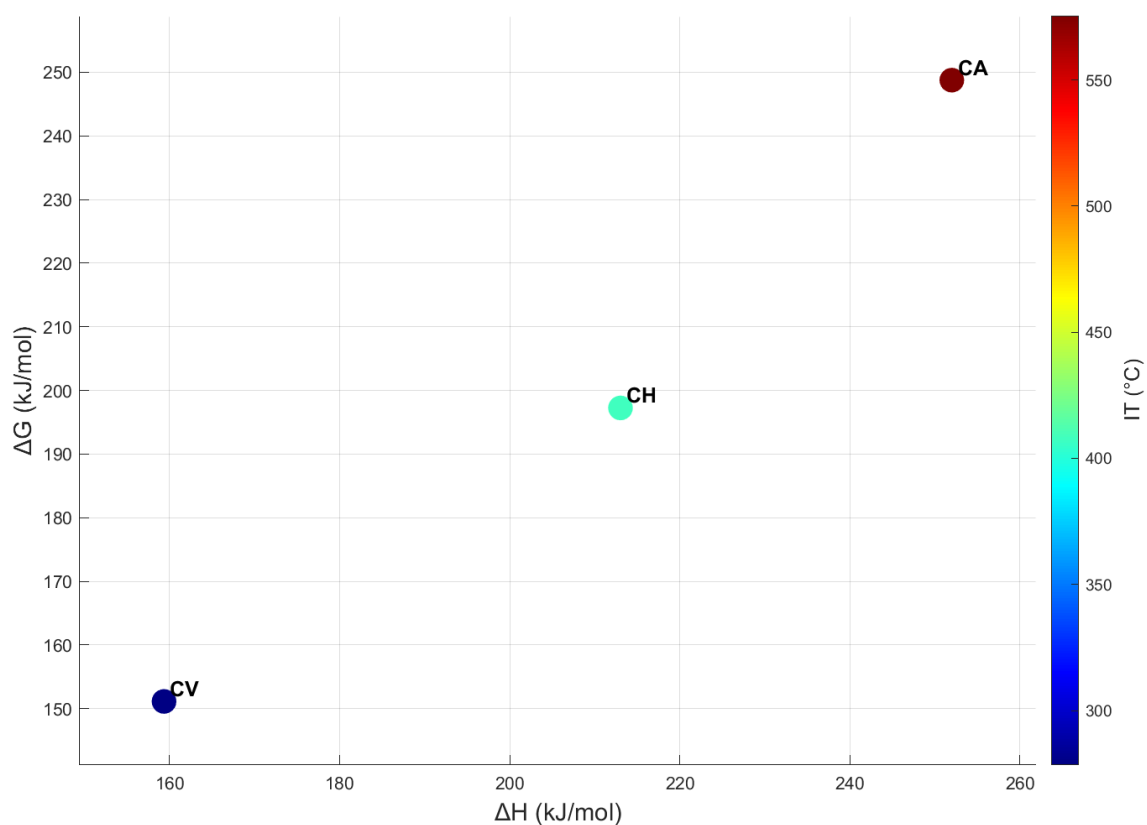
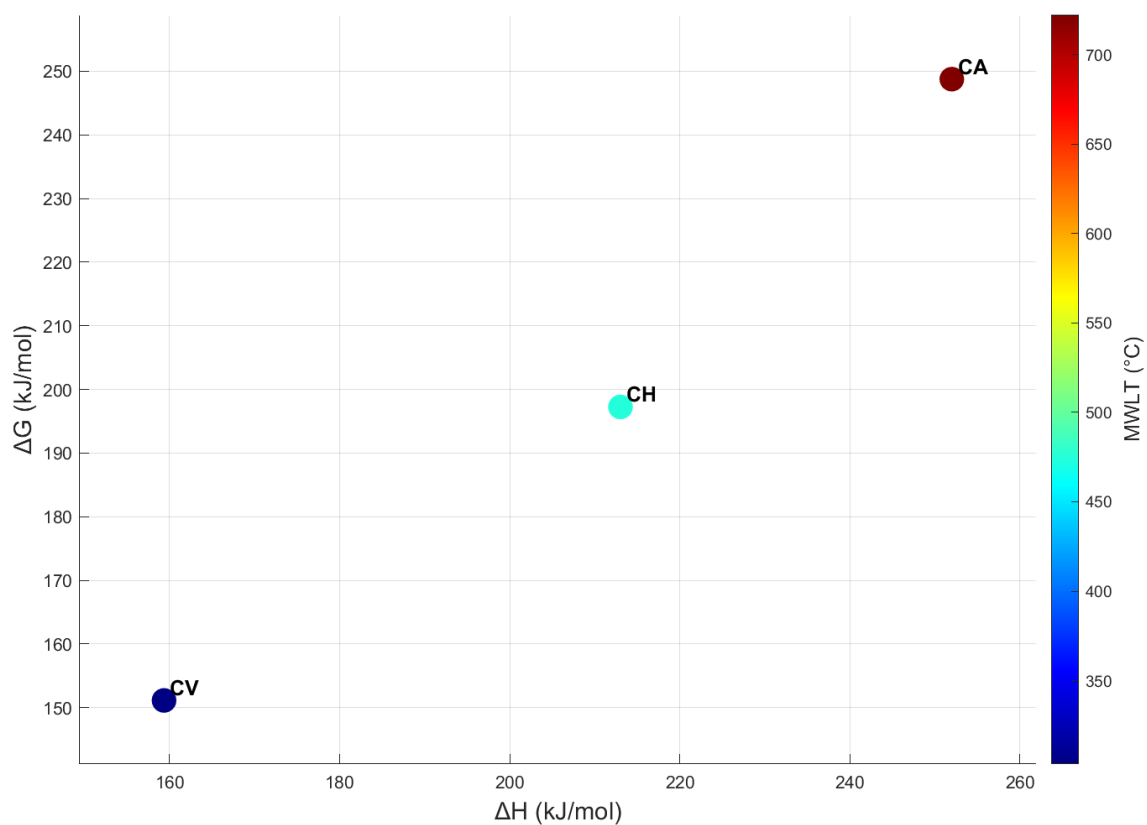


Figure 6.35. ΔS vs. VM and O

Regarding the characteristic temperatures (IT , $MWLT$, and T_b), both ΔH and ΔG show positive trends; that is, higher energy contents and higher Gibbs-free energy require higher temperatures to initiate and complete the thermal degradation processes (as shown in Figure 6.36, Figure 6.37, and Figure 6.38).

**Figure 6.36.** ΔH and ΔG vs. IT**Figure 6.37.** ΔH and ΔG vs. MWLT

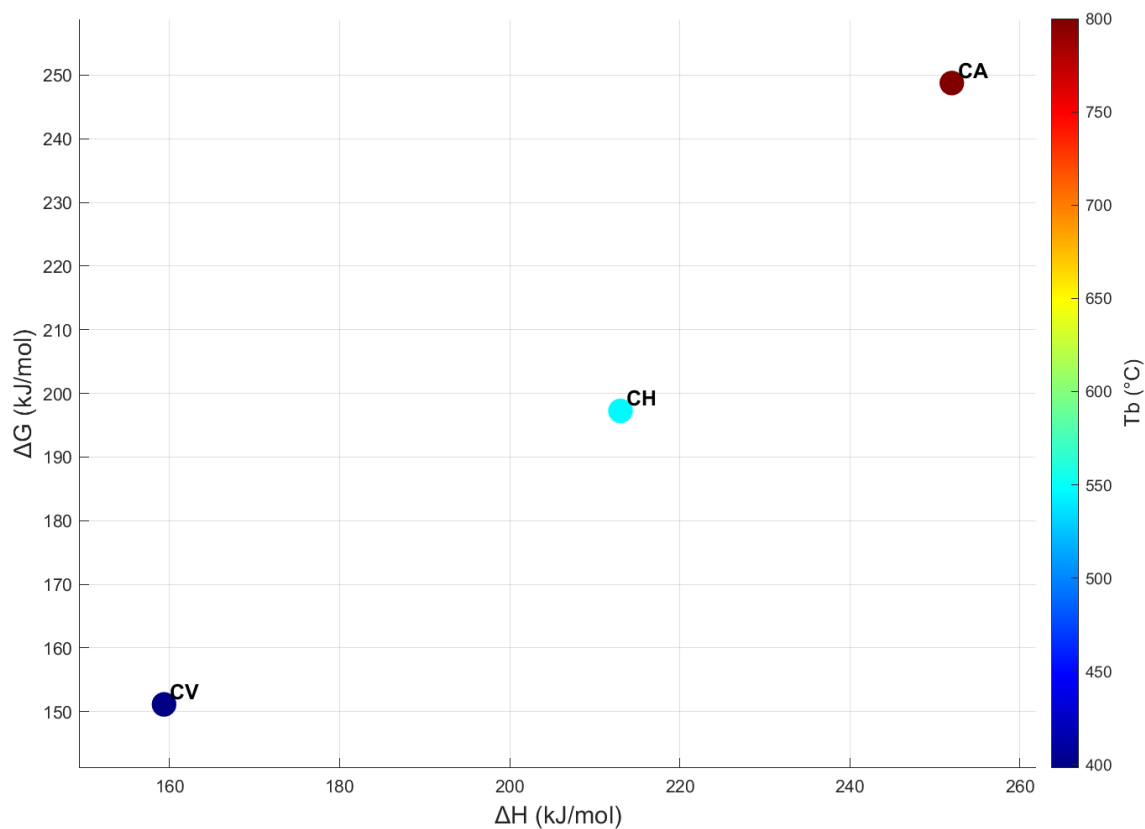


Figure 6.38. ΔH and ΔG vs. T_b

Conversely, the reactivity of the samples decreased with increasing ΔH and ΔG values, whereas high ΔS values facilitated thermal transformations, increasing the reactivity (TG_{spi}) of the system (Figure 6.39).

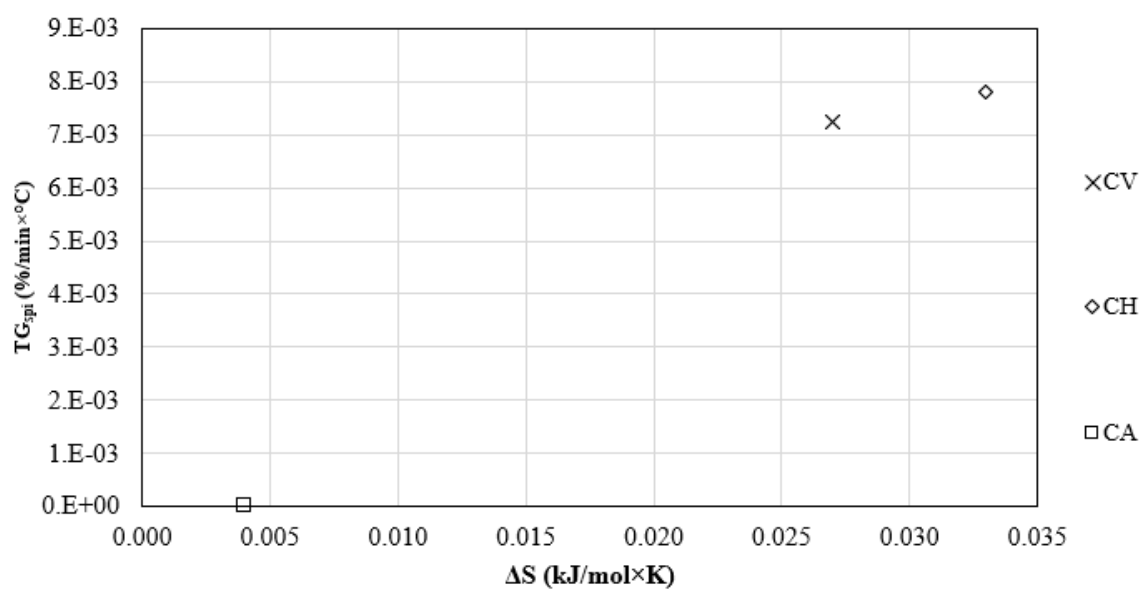


Figure 6.39. ΔS (FWO) vs. TG_{spi}

Finally, the kinetic behaviour, represented by the pre-exponential factor, shows a positive correlation with entropy, consistent with the theory of collisions and the principle of kinetic compensation in heterogeneous reactions, because the greater the collision of particles, the greater the instability (Figure 6.40).

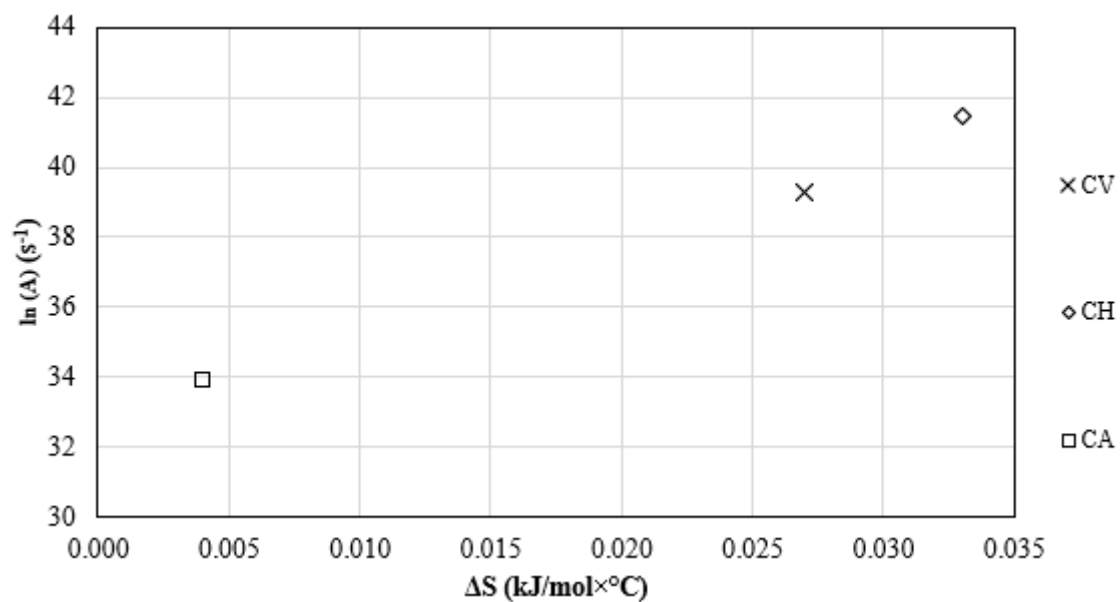


Figure 6.40. ΔS vs. $\ln(A)$

6.4.6. Combustion Indices Analysis

The combustibility index (CI) showed a clear distinction between the lignocellulosic and coal samples, with a distribution close to that established in the Van Krevelen diagram.

Lignocellulosic samples exhibit significantly higher values, ranging from 3.2 to 6.12 (BPC and BPA, respectively), suggesting that the higher the volatile matter content, the higher the rate of release of flammable products, favouring ignition and flame spread. A higher CI results in faster ignition and more intense energy release in the initial states, creating a fuel-rich atmosphere around the particles and promoting a more efficient flame spread.

In contrast, the coal samples exhibited lower values (CA: 0.14, CH and CV: 0.73). This results in a slower release of volatile components at the onset of heating, and thus higher temperatures are needed to achieve ignition.

The ignition index (D_i) and burnout index (D_b) exhibited similar trends. Biomass exhibited higher values for both indices than coal, which agrees with Mahanta et al. (2020) [263]. In terms of biomass, the BPM trial exhibited the highest D_i ($1.35 \times 10^{-2} \text{ \%}/\text{min}^3$), and the BCA trial exhibited the highest D_b ($8.74 \times 10^{-4} \text{ \%}/\text{min}^4$). On the other hand, anthracite (CA) had the lowest values for both variables (D_i : $1.17 \times 10^{-4} \text{ \%}/\text{min}^3$, D_b : $2.83 \times 10^{-6} \text{ \%}/\text{min}^4$).

The comprehensive combustion index (S) and flammability index (C) showed similar patterns to the CI . According to Aniza et al. (2024) [264] and Qin et al. (2021) [160], biomass samples showed higher values for both indices S ($2.14 \times 10^{-7} \text{ \%}^2/\text{min}^2 \times \text{°C}^3$) and C ($7.25 \times 10^{-5} \text{ \%}/\text{min} \times \text{°C}^2$). This is because biomass has a higher volatile matter content, facilitating ignition and thus improving combustion efficiency. In addition, they also require lower ignition temperatures and higher reactivity compared to coals.

Coal, particularly anthracite, exhibited lower values (CA: $S = 7.02 \times 10^{-11} \text{ \%}^2/\text{min}^2 \times \text{°C}^3$, $C = 6.02 \times 10^{-7} \text{ \%}/\text{min} \times \text{°C}^2$). According to Bilkic et al. (2023) [161], the combustion index (H_f) shows an inverse trend compared to the other indices, where the results obtained for the biomass group are higher than those obtained for the coal group. This can be explained due to the lower the value of H_f , the better the combustion characteristics. Coal, especially anthracite, showed the highest values (CA: $3,894.25 \text{ °C} \times \text{min}^2/\text{°C}$) whereas biomass exhibited lower and more uniform values ($1,074.65$ – $1,354.93 \text{ °C} \times \text{min}^2/\text{°C}$). This is consistent with the less reactive nature of coal compared to biomass.

The combustion stability index (D_w) showed a similar trend to that of CI , with higher values for biomass (with a maximum of $6.14 \times 10^{-5} \text{ \%}/\text{min} \times \text{°C}^2$ for BPM) and lower values for coal (with a minimum of $4.68 \times 10^{-7} \text{ \%}/\text{min} \times \text{°C}^2$ for CA) [161]. According to Demirbas et al. (2004) [265], biomass shows high volatility and reactivity, which gives it more stable and continuous combustion than coals which is consistent with the values

obtained in this study, where biomass samples showed values two orders of magnitude higher ($3.17\text{--}6.14 \times 10^{-5} \text{ \%/min} \times ^\circ\text{C}^2$) than coals ($1.27 \times 10^{-5}\text{--}4.68 \times 10^{-7} \text{ \%/min} \times ^\circ\text{C}^2$).

However, several correlations were observed between combustion rates and other parameters reported in this research.

The *CI*, defined above as the ratio of volatile matter to fixed carbon, provides a direct measure of the volatilisation potential of solid fuel. That is, a high *CI* indicates a higher proportion of compounds likely to be released during heating relative to the carbonaceous matrix and thus translates experimentally into higher devolatilisation rates, as observed in Figure 6.41, when comparing this parameter with the microscopic devolatilisation ratio (ψ). For example, the olive sample BPA, with the highest *CI* (6.12), also exhibited the highest microscopic devolatilisation rate (2.0419).

Furthermore, a generalised trend is found for both biomass and coal samples, with the latter showing a similarly consistent correlation (*CI*: 0.14–0.73; ψ : 0.019–0.74). However, deviations are observed for soybean and kernel samples (BPS and BCA, respectively), where devolatilisation rates are higher than expected according to their *CI*. This may be due to the insulating properties of soy and the low activation energy of the almond sample.

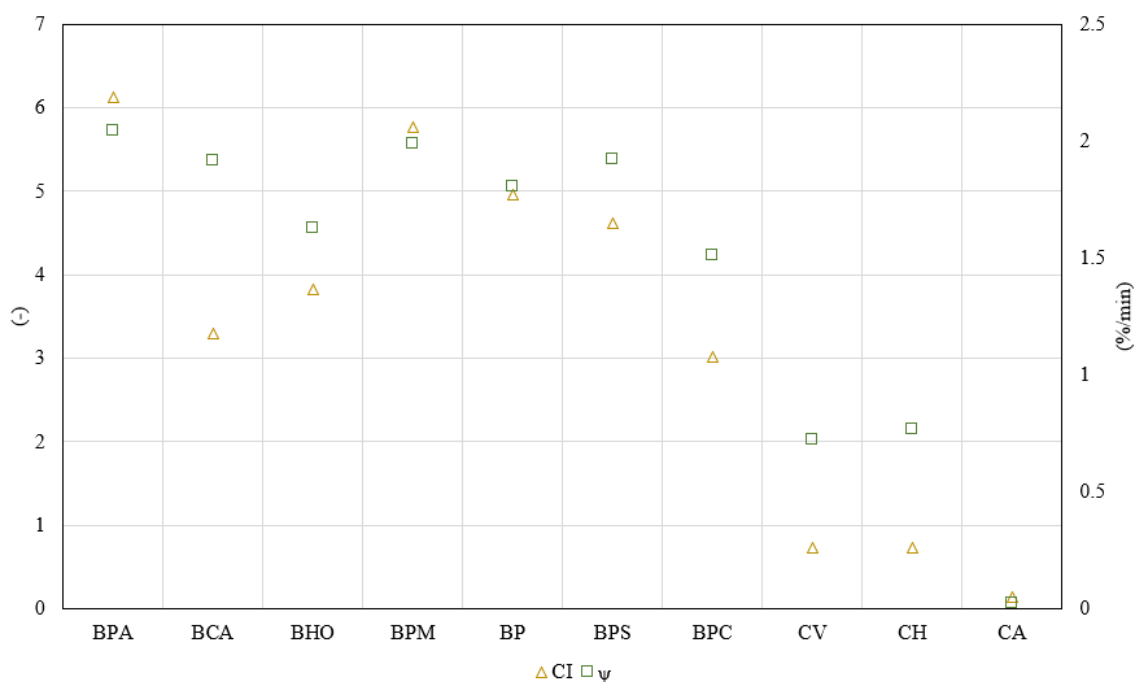


Figure 6.41. *CI* vs. ψ

On the other hand, a close relationship is also observed between the ignition index (D_i), which evaluates the ease of ignition of the sample and the devolatilisation of the fuel, with the reactivity in terms of spontaneous combustion in both the lignocellulosic samples and the coal samples, according to Figure 6.42. However, it can be observed that

the cork sample, BPC, reported a lower TG_{spi} index than it would tend to. This is because of the insulating properties of cork, resulting in a lower tendency for self-ignition.

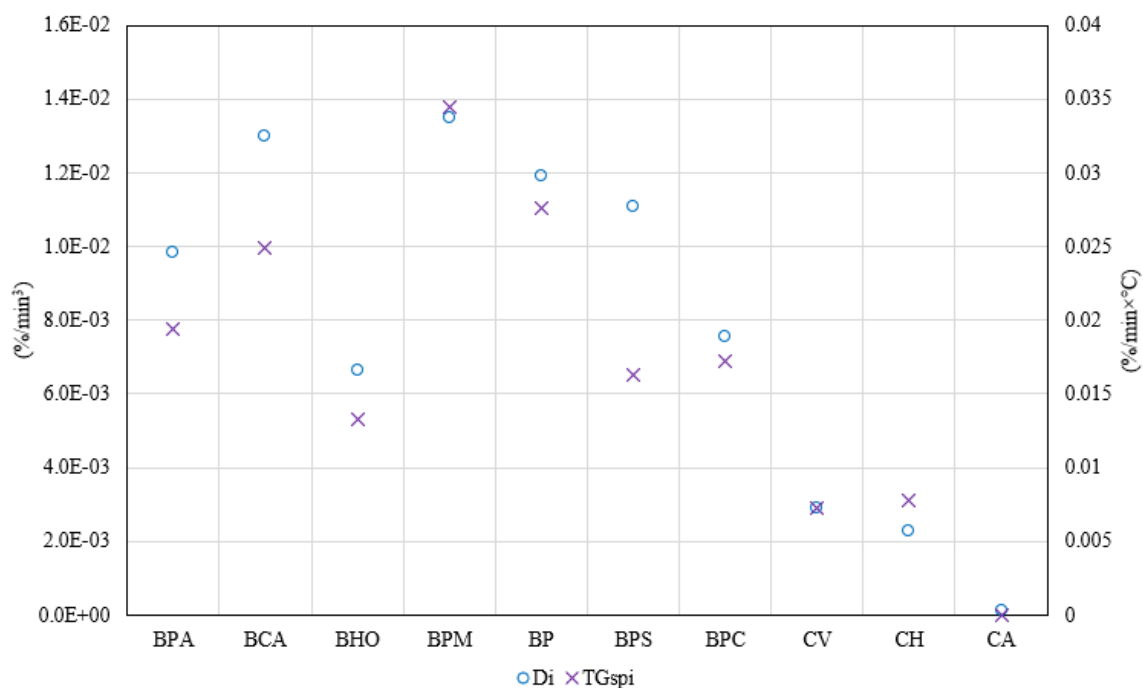


Figure 6.42. D_i vs. TG_{spi}

For the burnout index (D_b), a general inverse correlation was observed in the samples when compared with the burnout temperature (T_b), as shown in Figure 6.43. This index evaluates the ease with which ignition ends; therefore, a higher value of this parameter results in a lower burnout temperature.

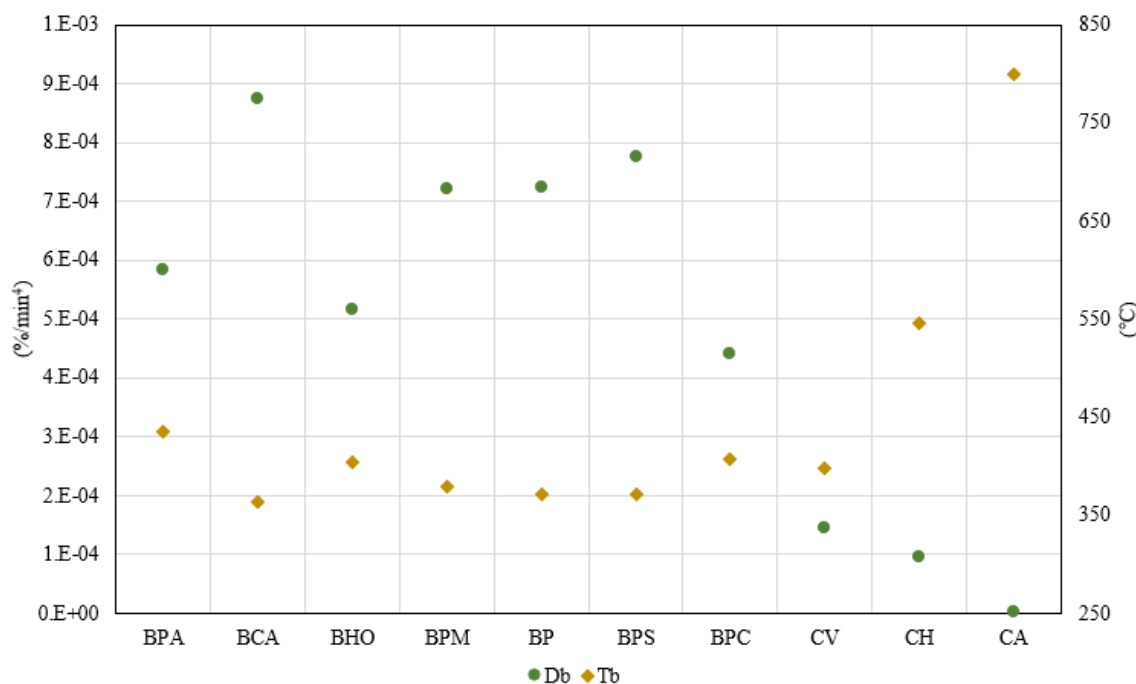


Figure 6.43. D_b vs. T_b

Comparing H_f and $MWLT$, a general trend was observed, as shown in Figure 6.44, the higher the H_f , the higher the temperature of maximum weight loss. This is because when a material is subjected to a gradual increase in temperature, the supplied thermal energy translates into an increase in the molecular kinetic energy. This gradual increase eventually exceeded the activation energy required to break the chemical bonds, triggering the thermal decomposition process.

Data analysis corroborates this interpretation, as biomass samples, characterised by relatively simple organic structures, show lower values of both $MWLT$ and H_f , indicating more efficient combustion processes. In contrast, materials with more complex or stable molecular structures (coals) showed higher values for both parameters, representing a higher resistance to thermal decomposition and less efficient combustion processes.

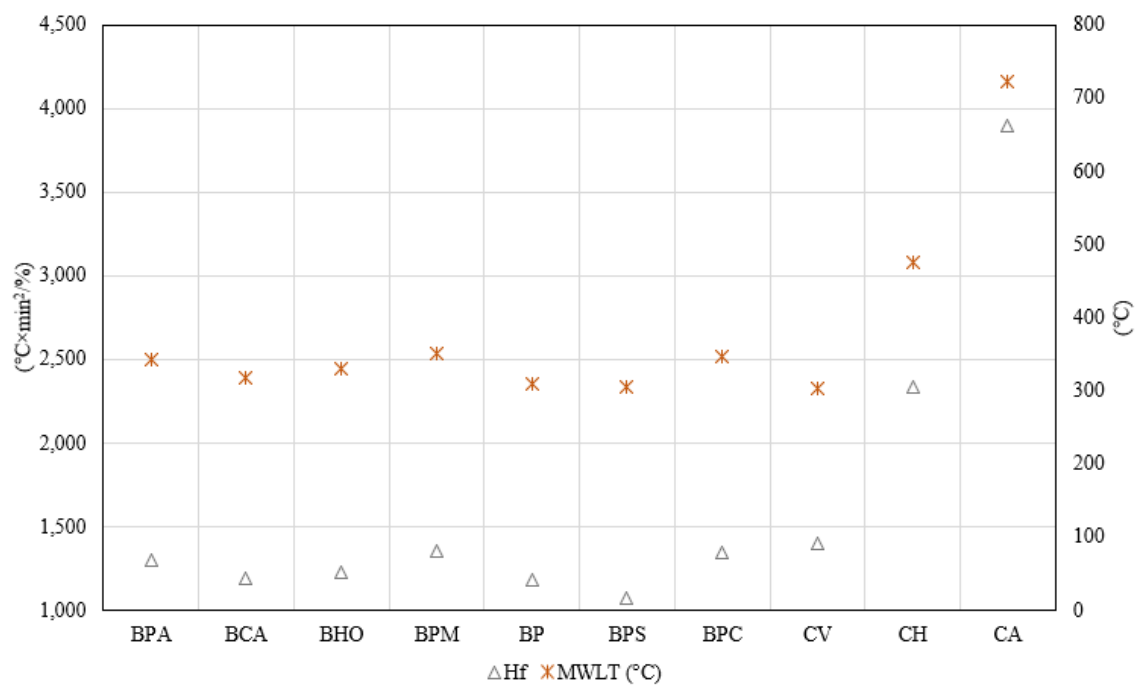


Figure 6.44. H_f vs. MWLT

6.5. ATEX Parameters

6.5.1. Minimum Ignition Temperature of Dust Layer

By analysing the experimental results obtained for the minimum ignition temperature of dust layer for both groups, a clear distinction between biomass and coal samples can be observed.

In the biomass group, the soybean sample, BPS, exhibited the lowest value (270 °C), resulting in the sample with the highest ease of ignition under hot surface deposition conditions at a thickness of 5 mm. On the contrary, the wood pellet sample, BPM, obtained the highest temperature (340 °C), resulting in the lowest predisposition to ignition in such a situation.

In the coal group, the charcoal sample exhibited a temperature that coincided with the range of biomass, specifically with that reported for almond shells (BCA) and straw (BP), both at 290 °C.

Comparing the results with other authors, it can be seen that, for the olive samples, both Castells et al. (2023) [68] and Fernandez-Anez et al. (2019) [266] reported values of 300 °C, which was slightly lower than the one obtained during this research (310-320 °C). On the other hand, the value reported by the same authors [266], 290 °C, for the almond shell sample is completely in line with that reported in this study (BCA: 290 °C). Similarly, the value for the wood sample, BPM, is in line with that reported by Jaskółowski et al. (2014) [267] for their three wood powder samples (340 °C).

The straw sample, BP, showed a slight discordance with that reported by Fernandez-Anez et al. (2019) [266], 320 °C vs. 290 °C. Similarly, the value obtained for the soybean sample, BPS, was slightly lower than that reported by Ramírez et al. (2009) [79] (270 vs. 300 °C, respectively). The cork sample, BPC, was also slightly lower than that reported by Park (2006) [268] for a 5 mm thickness, but similar to the value for a 10 mm layer thickness.

Finally, the charcoal sample, CV, showed an experimental value very close to that reported by Institute For Occupational Safety and Health of the German Social Accident Insurance (IFA GESTIS-DUST Ex Database) [269]. The remaining coal samples (CH and CA) did not ignite within the test range established by the standard.

As presented in Chapter 5, for the modelling of this method, only heating rates of 3, 5, and 7 K/min were considered, as greater heating rates might introduce errors due to the thermal lag. The numerical modelling from the differential analysis of the thermogravimetric curves, according to Figure 6.45, and the data reported in Appendix 6, it is noteworthy that the maximum error occurred in the cork sample, BPC, at a heating rate of 7 K/min. When comparing this casuistry with the other samples, it can be deduced that the highest errors generally occur at this heating rate because it is the highest because of the thermal lag phenomenon. On the other hand, this phenomenon is also due to the fact that the decomposition of the different polymers overlaps as the heating rate

increases, so, for example, in the BCA and BP samples at 7 K/min, it was not possible to appreciate the point at which the parameter approached.

The experimental test standard established an interval of 10 K difference between the value where ignition occurred and the value where it did not occur. However, in order to report more accurate results, the tests were carried out with a 5 K interval. Therefore, an uncertainty of ± 5 K was considered. However, the uncertainty of the value applying - 5 K is irrelevant because ignition will not occur at $MIT_L - 5$ K at all. Therefore, if this temperature is outside this range, it is because $MIT_{Lapproach} > \text{Ignition temperature}$.

Remarkably, the mean error of the results applying heating rates of 3 and 5 K/min was similar, presenting values of 2.37-2.38%, respectively. The average of the temperatures leads to the figure closest to the experimental one, with an average error of 2.25%, which allows this temperature to be established as the $MIT_{Lapproach}$ according to Equation 6.1, representing the average of the results obtained for each point evaluated in the second derivative of the thermogravimetric curve at heating rates of 3, 5, and 7 K/min.

$$MIT_{Lapproach} = \frac{\sum_{\beta=(3, 5, 7)|_{K \times min^{-1}}} MIT_{Lapproach\beta}}{length(\beta)} \quad 6.1$$

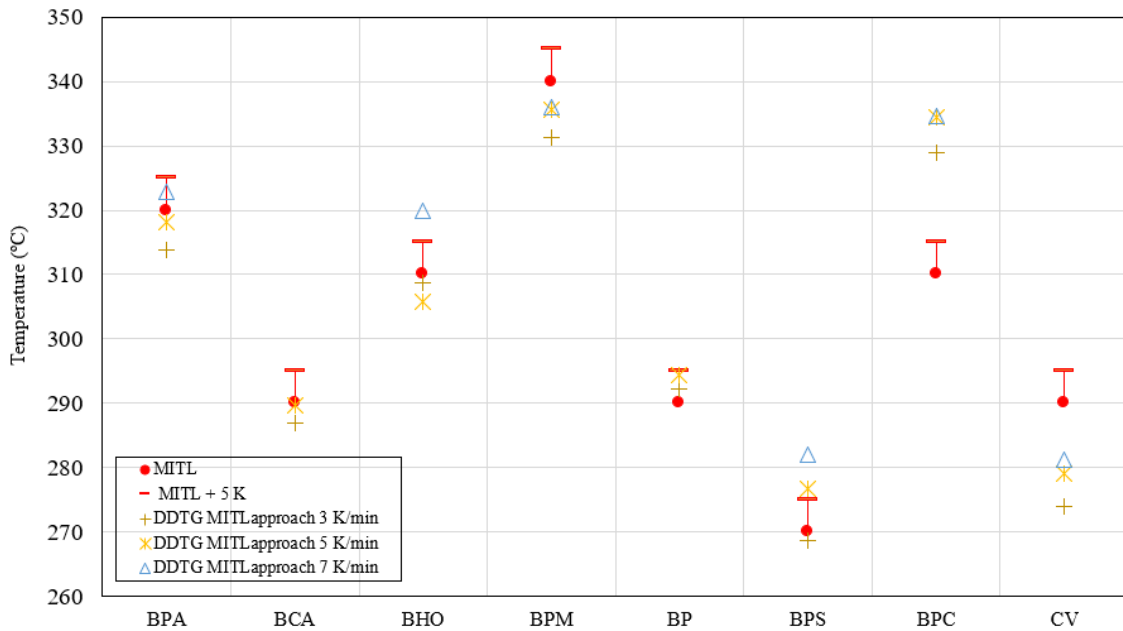


Figure 6.45. $MIT_{Lapproach}$ results

Comparing the experimental values of the minimum ignition temperature in the powder layer with various parameters of this research, strong correlations were observed, specifically with the hemicellulose content.

The correlation between hemicellulose content and this parameter was almost direct, as shown in Figure 6.46, with a high correlation coefficient ($R^2 = 0.98$). This correlation can be explained by the thermal decomposition of polymers in the lignocellulosic samples.

As previously pointed out, the decomposition of hemicellulose mainly releases CO_2 , which functions as an inert heat absorber, whereas the decomposition of cellulose and lignin produces combustible volatiles (CO and CH_4) [240,241]. Therefore, a higher hemicellulose content leads to a higher production of CO_2 during thermal decomposition, hindering the ignition process and thus increasing the temperature required for this process to take place.

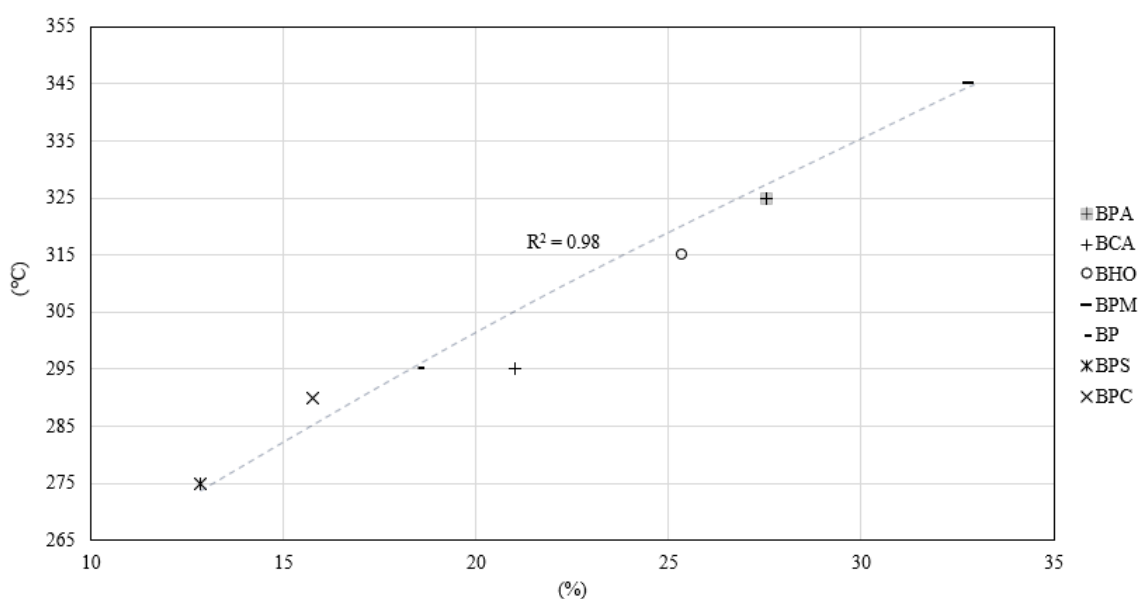


Figure 6.46. MIT_L vs. hemicellulose content

6.5.2. Minimum Ignition Temperature of Dust Cloud

Comparing the experimentally obtained values with those reported by other authors, it was observed that the results for the olive samples were slightly lower than those reported by Castells et al. (2023) [68] (BPA: 440 °C, BHO: 400 °C, vs. 470 °C, respectively).

Interestingly, the experimental values obtained for the almond shell (BCA) and straw (BP) samples differed by 150 °C and 60 °C, respectively, from the values reported by García Torrent et al. (2016) [270]. However, the wood sample BPM resulted in a similar value (400 vs. 380 °C, respectively).

On the other hand, the soybean sample, BPS, reported a lower value than that exhibited by Ramírez et al. (2009) [79], as well as a value close to that exhibited by the Institute For Occupational Safety and Health of the German Social Accident Insurance (IFA GESTIS-DUST Ex Database) [269] for the cork sample, BPC, (440 °C vs. 470 °C).

Regarding the coal group, CV and CH reported values similar to those reported by the Institute For Occupational Safety and Health of the German Social Accident Insurance (IFA GESTIS-DUST Ex Database) [269] (680 °C vs. 710 °C, respectively).

As for the numerical modelling, according to the data reported in Table 5.14 and Figure 6.47, the improvement is substantial when including the parameter ψ , which correlates various intrinsic properties of the substances, in the calculation of the minimum dust cloud ignition temperature.

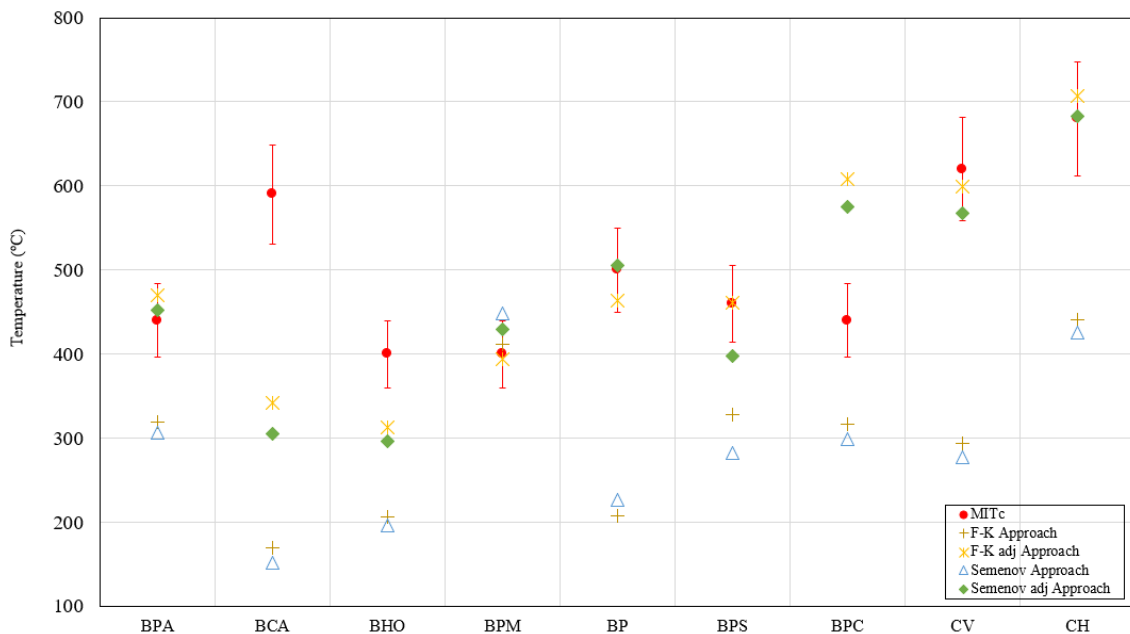


Figure 6.47. MIT_C results

This parameter, calculated according to Equation 3.31, was set according to the values obtained for a - e for Frank–Kamenetskii and Semenov (Table 6.1).

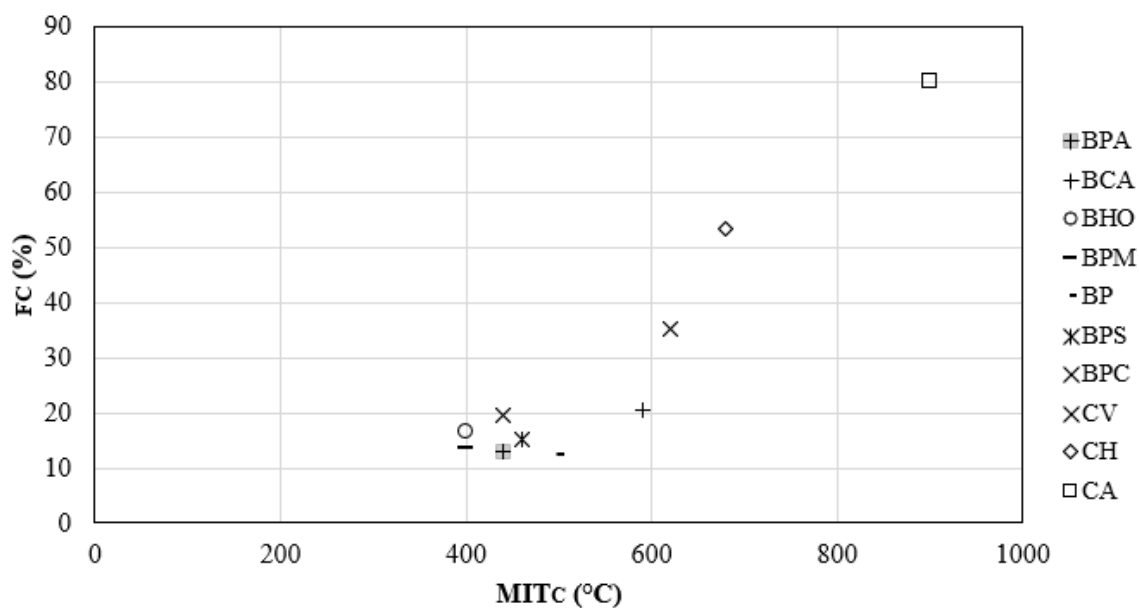
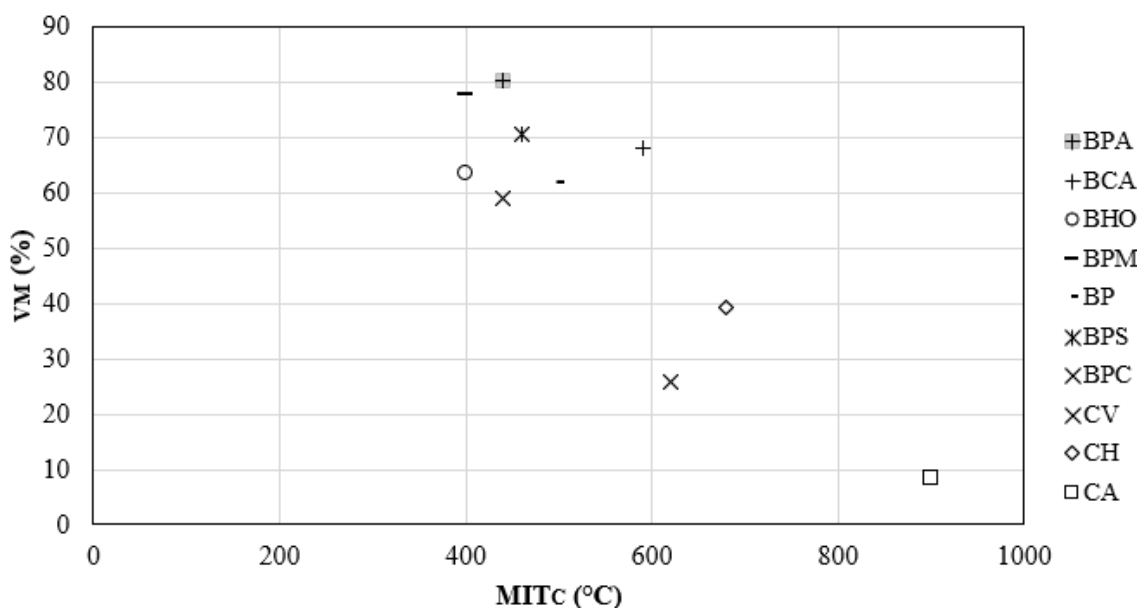
Table 6.1. Optimal values

Parameters	Optimal values
a	1.622538
b	-0.275564
c	1.475685
d	6.106496
e	-4.194847

Comparing the experimental results with the final modelled results, that is, with the application of the fitting parameter, different trends were observed in the different groups. In the group of biomasses, the lowest average error was achieved when applying the Frank-Kamenetskii approximation, highlighting the good approximation in samples such as BPM (400 vs. 394.10 °C) and BPS (460 vs. 460.70 °C). However, regarding Semenov's method, the precision in samples such as BPA (440 vs. 451.70 °C) and BP (500 vs. 505.20 °C) stand out. As for the group of coals (CV and CH), the mean error between both methods is similar, although, as in the case of the group of biomolecules, with lower values when applying the Frank-Kamenetskii approximation (3.65 vs. 4.49%, respectively).

Several correlations were established by comparing the results obtained with the composition values, characteristic temperatures, various reactivity parameters, and combustion indices. For a better comparison between the samples, the MIT_C of anthracite (CA) was assumed to be 900 °C and not > 900 °C.

Regarding the comparison with composition, Figure 6.48 shows a direct trend between MIT_C and fixed carbon content, as well as an inverse trend with respect to volatile matter (Figure 6.49). This is mainly due to the fact that fixed carbon requires higher activation energies for its oxidation due to its more ordered structure and more stable C-C bonds, resulting in higher ignition temperatures.

Figure 6.48. MIT_C vs. FCFigure 6.49. MIT_C vs. VM

However, the same trend as that with volatile matter exists when comparing the MIT_C with the ratios of the Van Krevelen diagram (H/C and O/C). This is because higher ratios indicate a predominance of aliphatic structures over aromatic ones, and therefore, a higher presence of oxygenated functional groups, facilitating thermal breakdown and oxidation, which triggers lower MIT_C values (Figure 6.50).

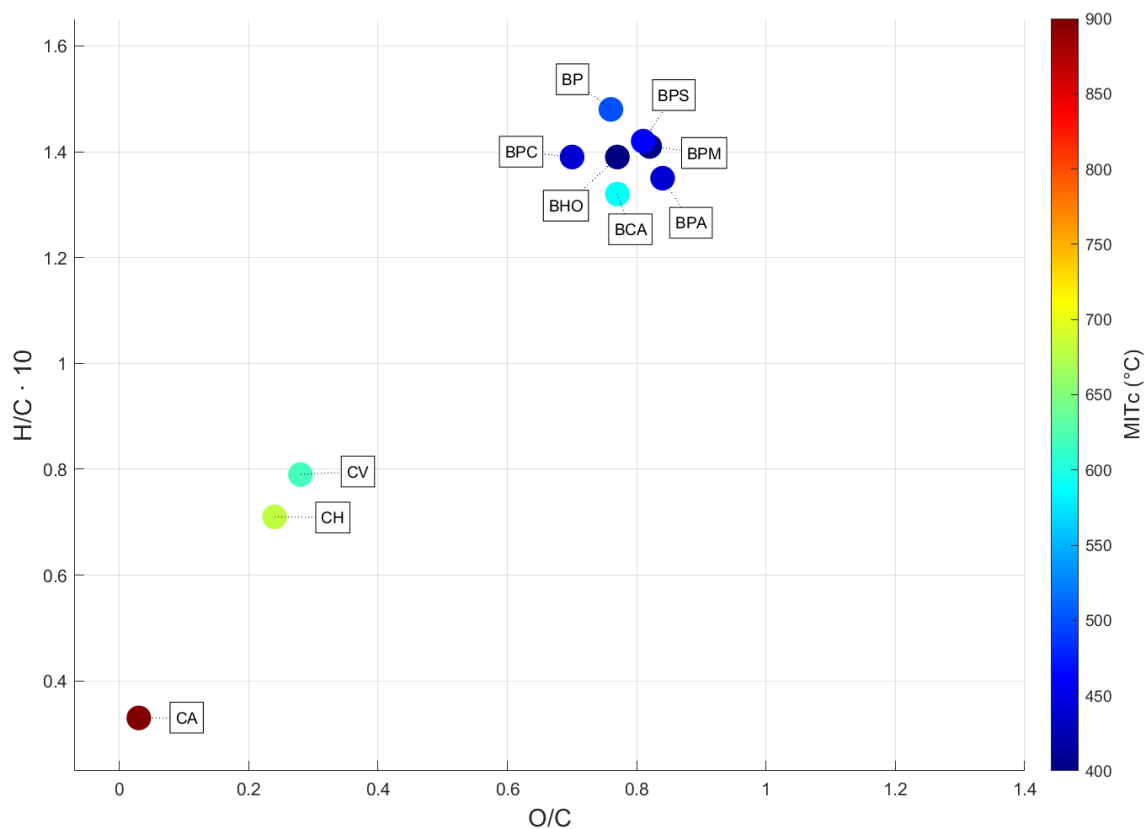


Figure 6.50. MIT_c vs. H/C and O/C

If the MIT_c values obtained are compared with some of the reactivity parameters (microscopic devolatilisation rate- Ψ -, OB , and OB^*), the trend is the same. This trend is inverse, that is, the lower the MIT_c , the higher the reactivity (as shown in Figure 6.51, Figure 6.52, and Figure 6.53).

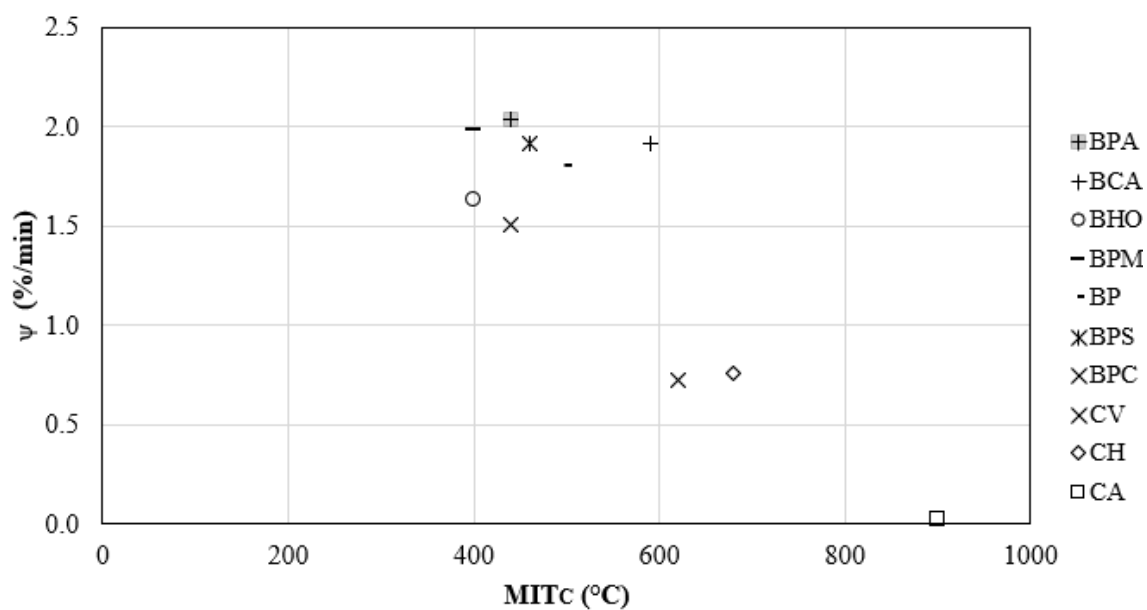
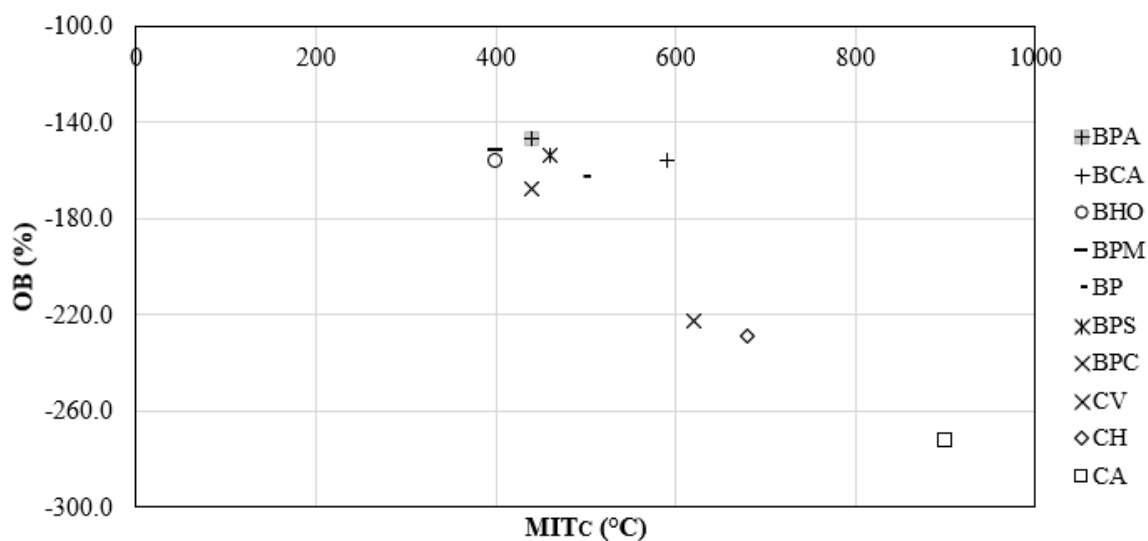
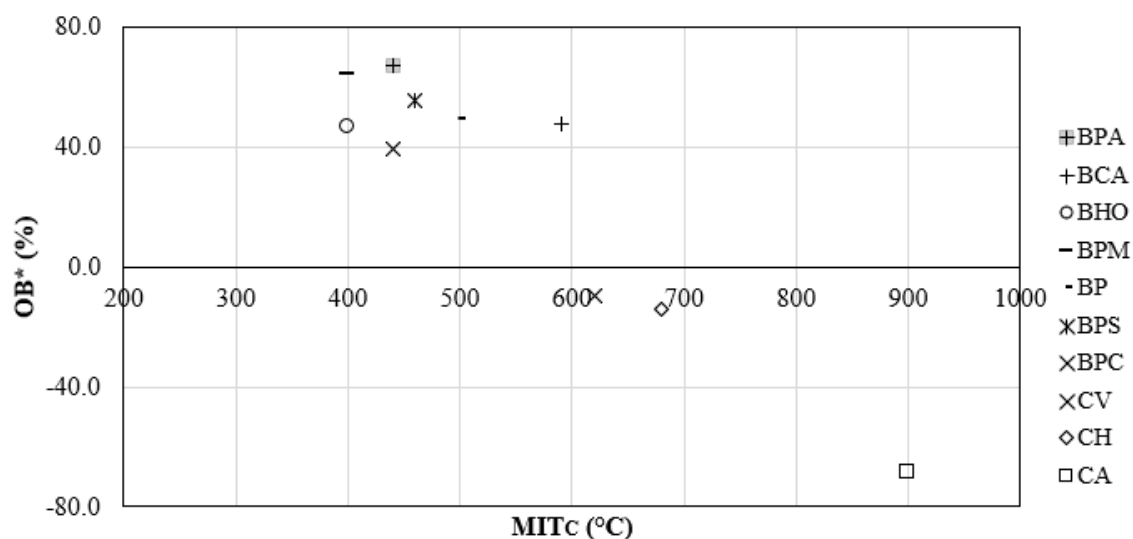
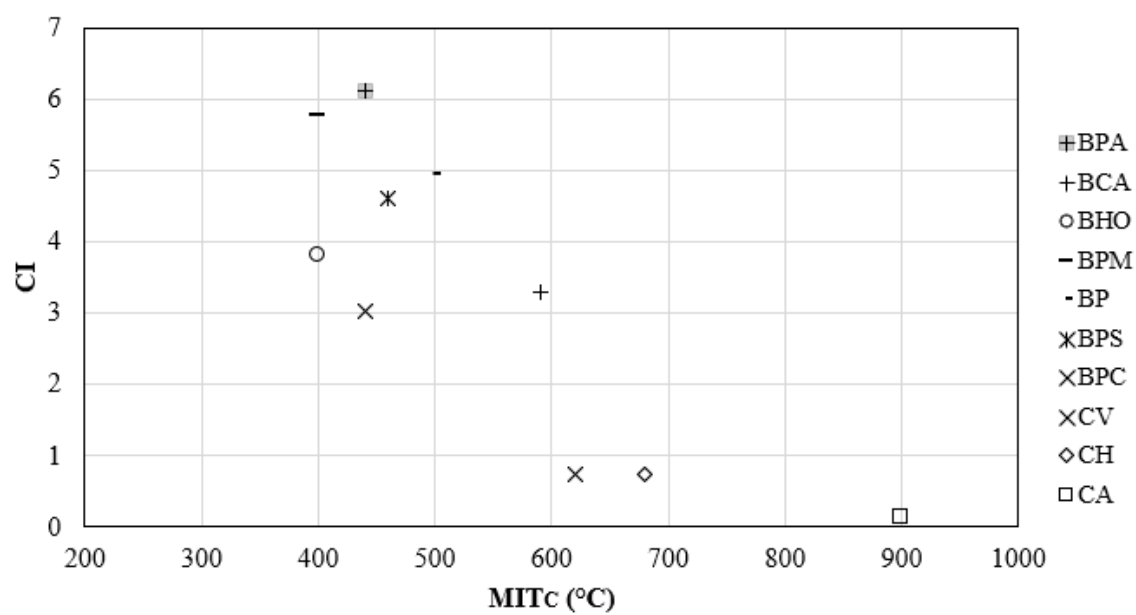


Figure 6.51. MIT_c vs. Ψ

Figure 6.52. MIT_C vs. OBFigure 6.53. MIT_C vs. OB*

As for the comparison with the combustion indices, there were clear relationships with the *CI* index, with opposite trends. The relationship with *CI* is inverse: the higher the *MIT_C*, the lower the *CI*. This fact can be explained as the *CI* ratio can be established as the quotient between *VM* and *FC*. A lower ratio implies a predominance of stable carbonaceous structures over volatile compounds, thus requiring higher temperatures to reach the activation energy required for ignition (Figure 6.54).

**Figure 6.54.** MIT_c vs. Cl

6.5.3. Severity

According to the results presented in Section 5.5.3, biomass samples can be classified according to their oxygen balance, simulating their use as explosives or high-energy components. As can be seen in Figure 6.55, all biomass, as well as two of the coal samples, CV and CH, were in the medium hazard range, following the classification given in Table 3.6, and with the results obtained by other authors [271].

Anthracite, as mentioned above, is a very unreactive and highly aromatic material with a very ordered chemical structure, which leads to an oxygen balance above -240% (low level).

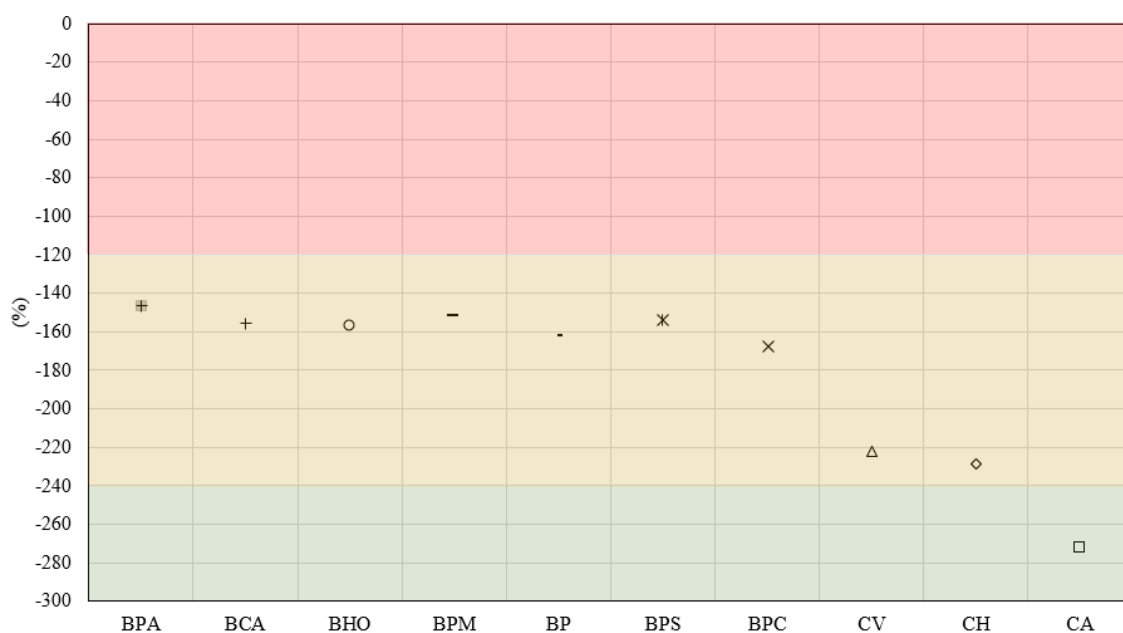


Figure 6.55. OB classification for each sample

The oxygen balance measures the existence of the necessary amount of oxygen to achieve total oxidation of the reaction products and, therefore, the comparison with other parameters results in remarkable relationships, as shown in Figure 6.56, Figure 6.57, and Figure 6.58. These include the relationship of this parameter with volatile matter and fixed carbon, with an $R^2 = 0.94$, and, in particular, as quantification of reactivity when compared to the microscopic devolatilisation ratio (ψ) with an $R^2 = 0.98$.

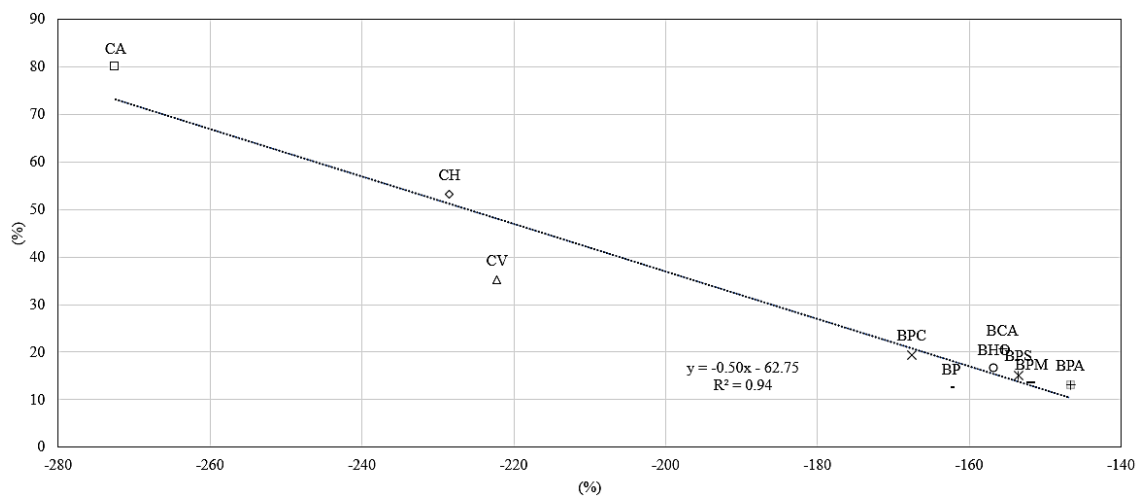


Figure 6.56. OB vs. VM

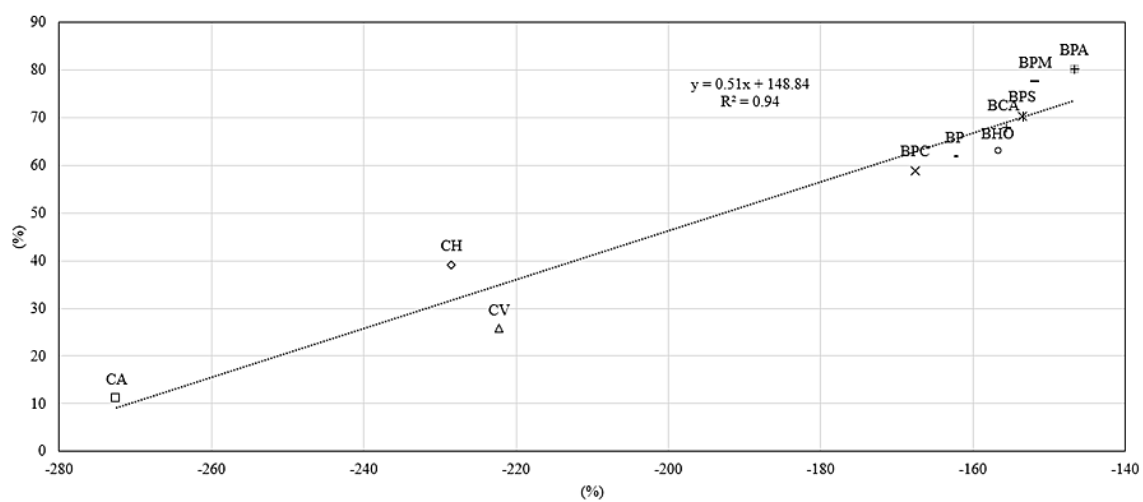
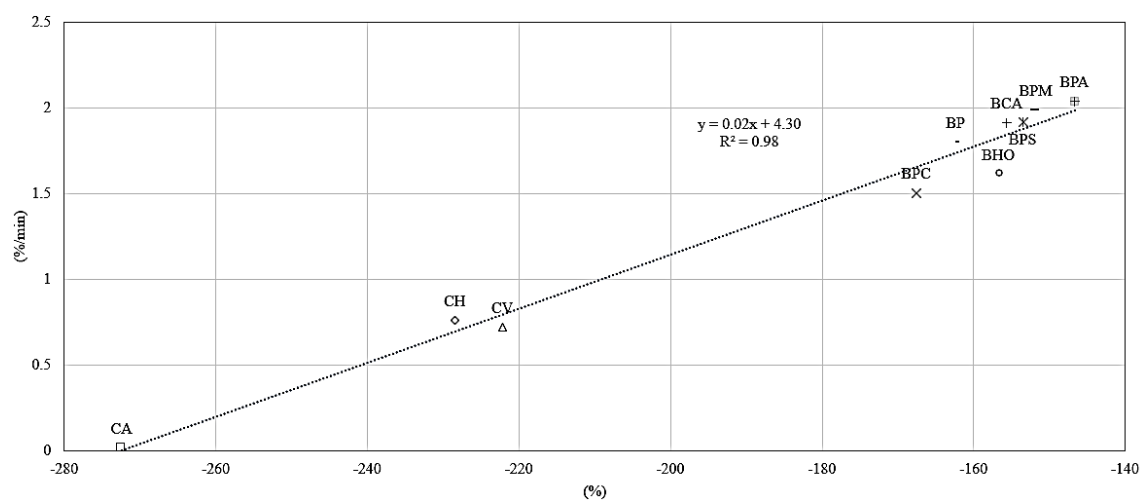


Figure 6.57. OB vs. FC

Figure 6.58. OB vs. Ψ

The observed inverse correlation between the compared near-analysis parameters, *FC* and *VM* ($R^2 = 0.94$), represents a fundamental relationship in the characterisation of these materials. This correlation can be explained by the underlying physicochemical mechanisms. Volatile matter, mainly composed of light hydrocarbons and oxygenated compounds, positively contributes to the oxygen balance due to the presence of oxygenated functional groups in its molecular structure. In contrast, fixed carbon, which represents more stable and condensed carbonaceous structures, increases the stoichiometric oxygen demand for complete combustion.

Therefore, the relationship between these two variables can be represented by a composite function according to the following expression:

$$OB^*(\%) = f(VM) - g(FC) \quad 6.2$$

where $f(VM)$ represents the positive contribution of volatile matter to the oxygen balance, while $g(FC)$ quantifies the oxygen demand associated with the fixed carbon. Thus, this mathematical relationship reflects the fundamental physicochemical processes that occur during the thermal oxidation of the substance, reflecting an $R^2 = 0.99$ when applied, as shown in Figure 6.59, where the data from Table 6.2 is represented.

Table 6.2. OB^* results

<i>Sample</i>	<i>OB*</i>
BPA	67.16
BCA	47.41
BHO	46.73
BPM	64.17
BP	49.42
BPS	55.23
BPC	39.48
CV	-9.56
CH	-14.21
CA	-68.81

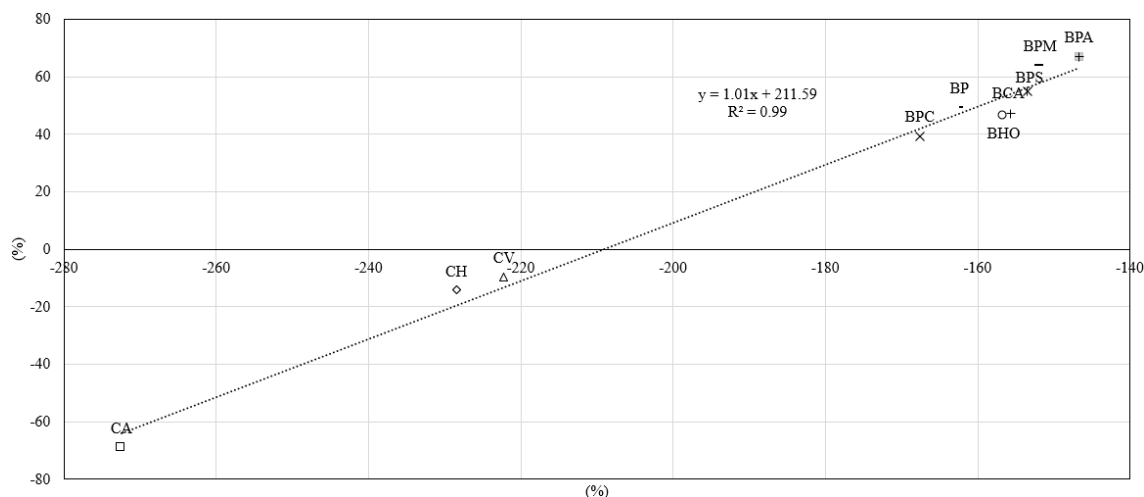


Figure 6.59. OB* vs. OB

The difference between volatile matter and fixed carbon (OB*) can then be interpreted as an indicator of the degree of potential oxidation of the material. In other words, when this difference is greater ($VM > FC$), it indicates the presence of more oxygenated compounds and less condensed molecular structures. In contrast, when the difference is smaller or negative ($VM < FC$), it suggests more condensed structures and a lower structural oxygen content.

This is because volatile matter in biomass is mainly composed of oxygenated structures such as cellulose ($C_6H_{10}O_5$)_n, hemicellulose, as xylan, ($C_5H_8O_4$)_n, and lignin [$C_9H_{10}O_3(OCH_3)_{0.9-1.7}$]_n, with significantly higher O/C ratios than fixed carbon structures, which consist mainly of polycondensed aromatic rings with less oxygen content [190].

Furthermore, their relationship to the molecular mechanism arises because, during proximal analysis, the determination of volatile matter occurs at temperatures where the weaker C-O and C-C bonds are broken, releasing oxygenated compounds. Fixed carbon, on the other hand, represents more stable structures that require higher temperatures for decomposition, and thermal stability is directly related to the oxygen content in each fraction.

On the other hand, as mentioned above, the explosion severity test was performed by obtaining three key parameters: P_{max} (Figure 6.60), $(dP/dt)_{max}$ (Figure 6.61 and Figure 6.62), and the deflagration index K_{ST} (Figure 6.63 and Figure 6.64).

Comparing these parameters with the literature for the olive, BPA, and BHO samples, we can see that the overpressure results obtained in the 20-litre sphere test are similar to those reported by Pietraccini et al. (2021) [236]. However, comparing the deflagration index, K_{ST} , a deviation is observed in the BHO sample, where experimentally in this research, a value of 119 bar×m/s (St 2) versus 49 bar×m/s (St 1) is reported.

Similarly, the almond shell (BCA), wood (BPM), straw (BP), and cork (BPC) samples exhibit similar maximum overpressure values to those reported by García Torrent et al. (2016) [270], Callé et al. (2005) [272], García Torrent et al. (2016) [270] and Pilao et al. (2006) [231]. However, certain deviations were observed in the K_{ST} parameters.

These deviations can be attributed to several factors. While differences in the laminar combustion velocity of the dust sample play a crucial role, other significant factors can lead to differences between experimental results and models, such as the use of different standardised test vessel volumes, measurement uncertainty inherent to the testing methods, and variations in the ignition source (igniters) used during testing.

For the soybean sample BPS, the results in this case were similar, both for the maximum explosion overpressure and for the K_{ST} parameter, when comparing the values with those reported by Ramírez et al. (2009) [79].

On the other hand, for the group of coals, all the results obtained experimentally agree with the ranges reported by Huéscar Medina et al. (2015) [197], except for the K_{ST} parameter for the CV sample, where the experimental value is lower than reported.

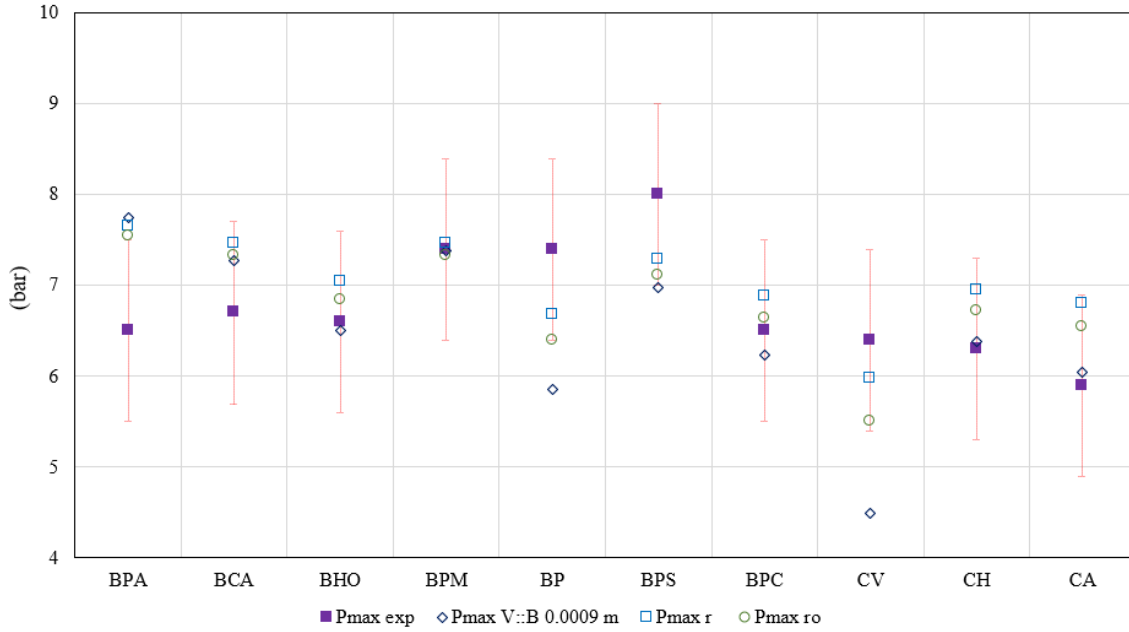


Figure 6.60. $P_{\max}$

On the other hand, the numerical modelling results using the isothermal NCV and adiabatic BM methods can be seen in Figure 6.61, Figure 6.62, Figure 6.63, and Figure 6.64, as in the previous chapter of results, how the error is quite high in the BM method compared to that obtained using NCV. It should be noted that these calculations were only performed using the results of the r_o model, as it had the lowest error in the maximum overpressure parameter and CFD results.

However, it has been proposed to improve the BM model with the mathematical addition of an empirical Ψ factor in such a way that, once applied and in a generalised way, the values fall within the permitted error range for both $(dP/dt)_{\max}$ and K_{ST} . Thus, $BM \rightarrow \Psi \times BM$, where Ψ corresponds to 1.65, a value determined empirically through result validation.

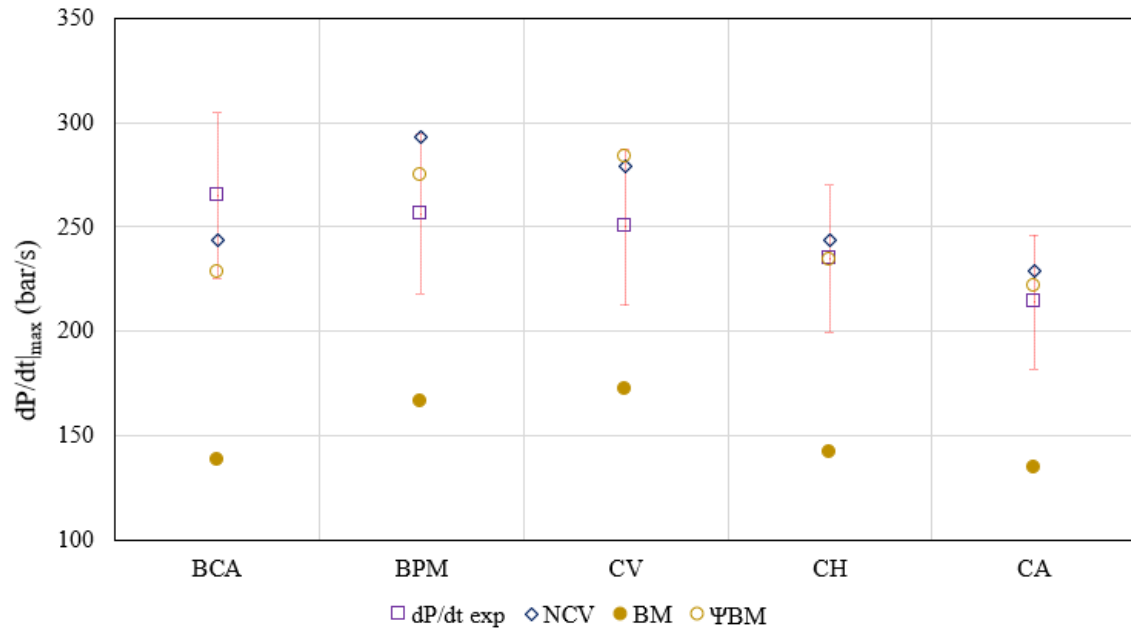


Figure 6.61. $(dP/dt)_{\max}$ result for r_0 model

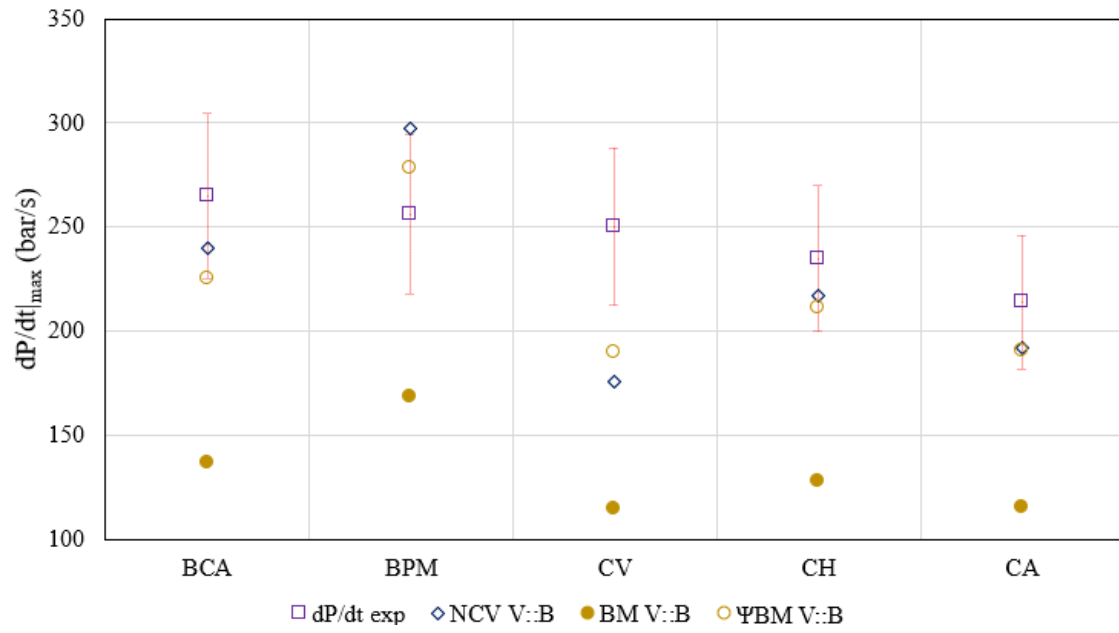


Figure 6.62. $(dP/dt)_{\max}$ result for CFD model

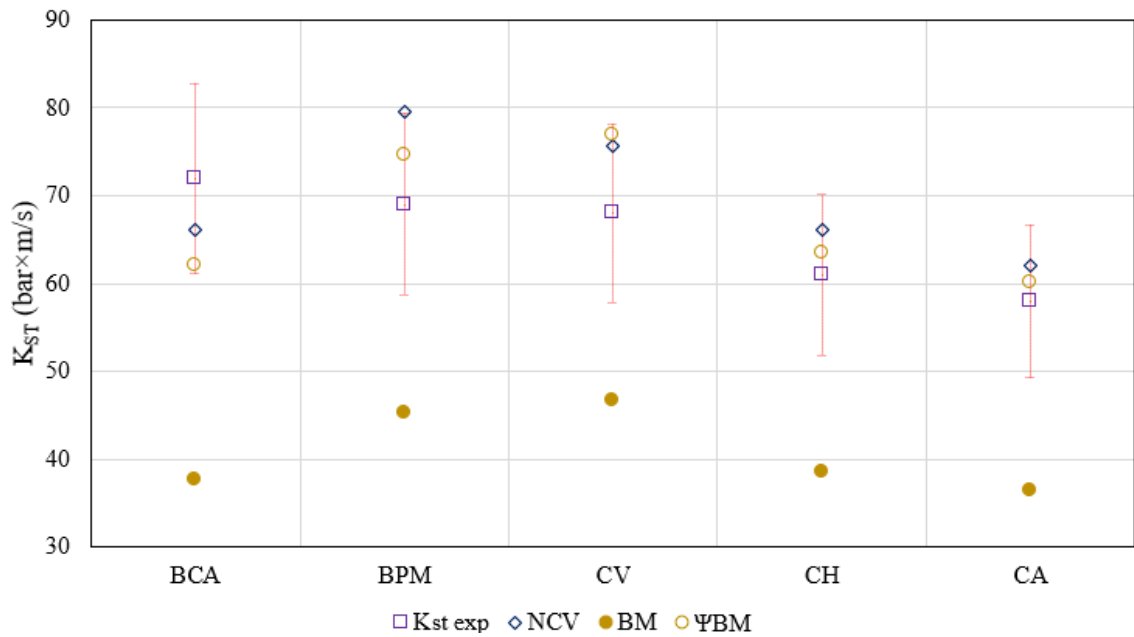


Figure 6.63. K_{ST} result for r_0 model

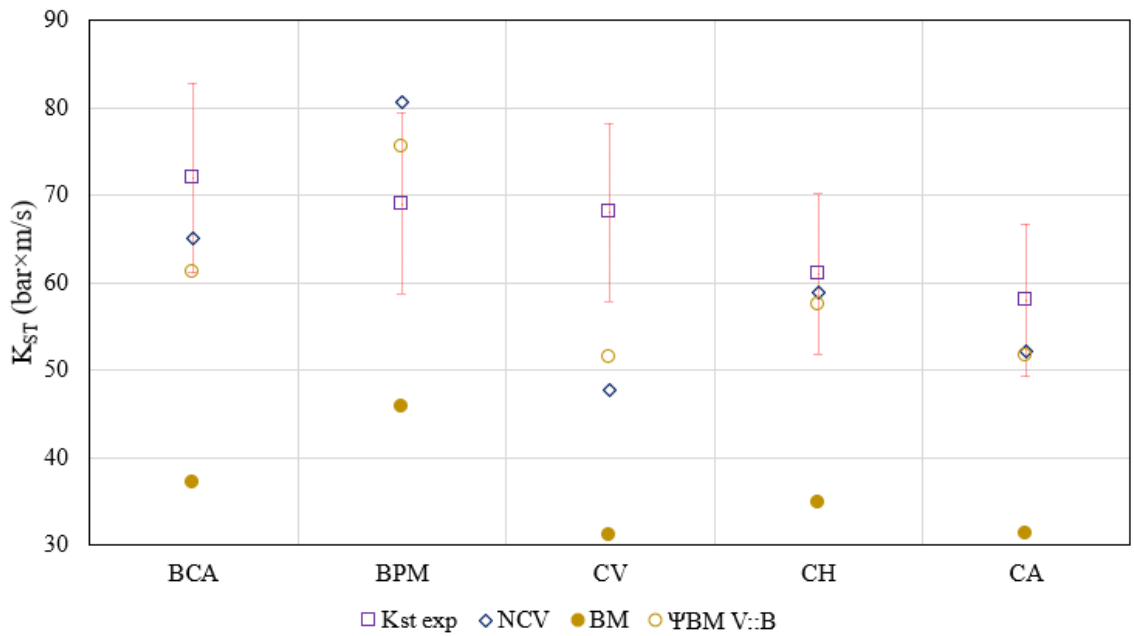


Figure 6.64. K_{ST} result for CFD model

6.5.4. BZ Burning Class Number

Comparing the BZ Burning Class Number with the other parameters obtained in this research, strong relationships can be observed.

For example, comparing the BZ Index with the proximate analysis, as shown in Figure 6.65, offers insights into the underlying mechanisms of fire propagation and combustion behaviour. On the one hand, a positive correlation with volatile matter and a negative correlation with fixed carbon is observed. These correlations are consistent with combustion principles, where volatile materials, which are more easily released during heating, favour rapid ignition and fire propagation. In contrast, fixed carbon, owing to its thermal stability, requires more extreme conditions for complete combustion.

These findings agree with those of Riaza et al. (2020) [273], who reported similar correlations between volatile matter content and fire spread propensity in their study on biomass combustion. In contrast, an especially low fire spread propensity was recorded for the anthracite CA sample, which was attributed to its high fixed carbon content and low reactivity, according to Zou et al. (2016) [274].

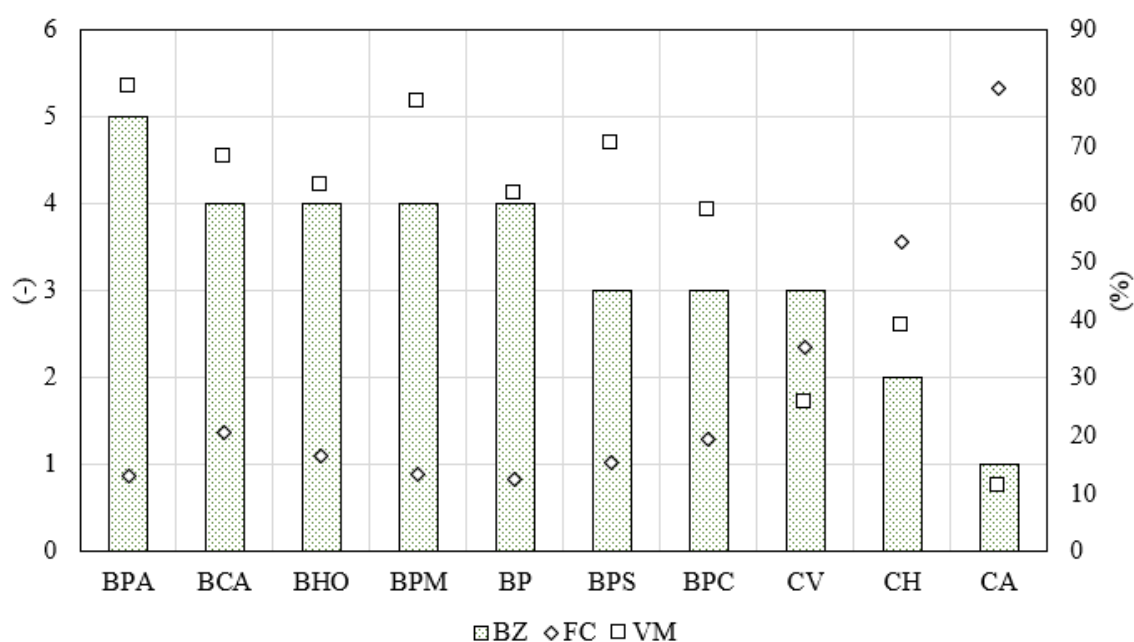


Figure 6.65. BZ Index vs. FC and VM

Figure 6.66 shows the correlation of the characteristic temperatures obtained by TGA with the BZ Index. A clear positive correlation was observed in the coals, e.g. as IT , $MWLT$, and T_b decreased, the BZ Index increased, suggesting a higher propensity for flame propagation.

In the case of the biomass samples, this relationship was less evident. However, a positive relationship between the burnout temperature (T_b) and the BZ Index can be seen, suggesting that biomass with higher resistance to total combustion tends to have a higher

flame spread. This phenomenon can be explained by the existence of more thermally stable components that, once ignited, resist combustion for longer periods.

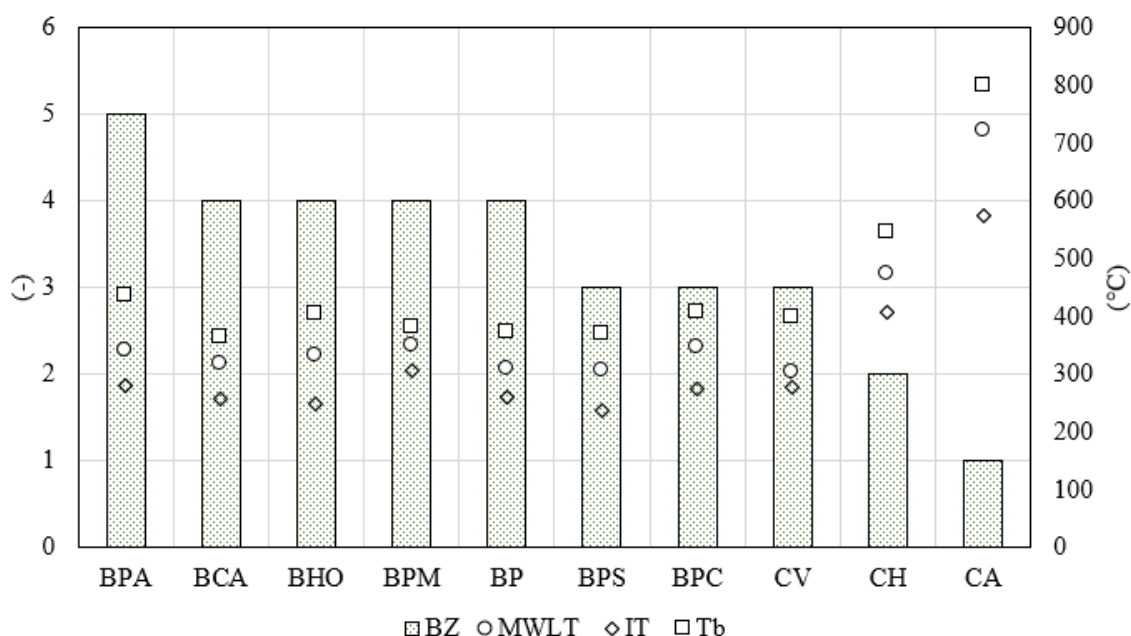


Figure 6.66. BZ Index vs. IT, MWLT and T_b

In addition, Figure 6.67 shows the correlation between the *H/C* and *O/C* ratios and the BZ Index, also revealing significant trends. The relationship with carbon content shows a decreasing trend for the coals, e.g. as the carbon content increases, the BZ Index decreases. This is especially noticeable in the anthracite (CA) sample, which has the highest carbon content (~90%) and the lowest BZ Index (BZ 1). In contrast, the biomass exhibited a carbon range between 35-45%, with a BZ between BZ 3-5, with no obvious trend.

As for their relationship with the hydrogen content, this is generally positive. Biomass, which contains a higher percentage of hydrogen, tends to have higher BZ values. In contrast, coals with a lower amount of hydrogen were shown to have a lower BZ.

The relationship with the oxygen content was consistent for both groups of samples. Biomass, with a higher oxygen content, exhibits higher BZ values than coals.

These observations underline the relevance of the equilibrium between the fuel and oxidiser (C and O, respectively) in determining the combustion behaviour. Biomass with a more balanced composition shows a higher propensity for flame propagation and thus a higher BZ Index. However, coals, particularly anthracite, show a lower propensity for flame propagation (lower BZ Index) owing to their high carbon content and low oxygen and hydrogen content.

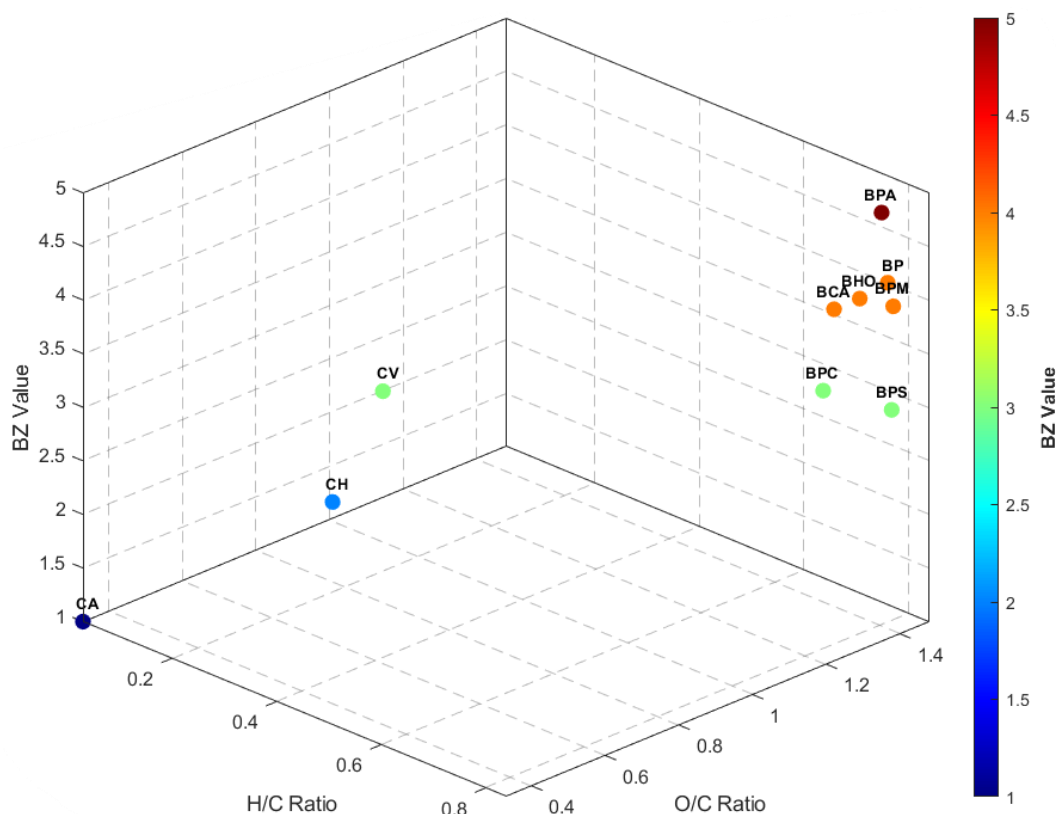


Figure 6.67. BZ Index vs. H/C and O/C

On the other hand, the biomass *CI* index exhibited considerably higher figures, suggesting a higher volatile matter content that is rapidly released during the first part of the heating, favouring ignition and accelerating fire propagation. In other words, a higher *CI* leads to faster ignition and more intense energy release during the early stages of combustion, generating a fuel-filled atmosphere around the particles, thus favouring more efficient flame propagation.

In contrast, in the coals, the *CI* was lower, and they exhibited a lower release of volatile compounds during the first part of heating. Therefore, they require higher ignition temperatures.

These similarities indicate that *CI* may be the key element in predicting flame spread, maintaining a robust correlation with the BZ Index, as shown in Figure 6.68.

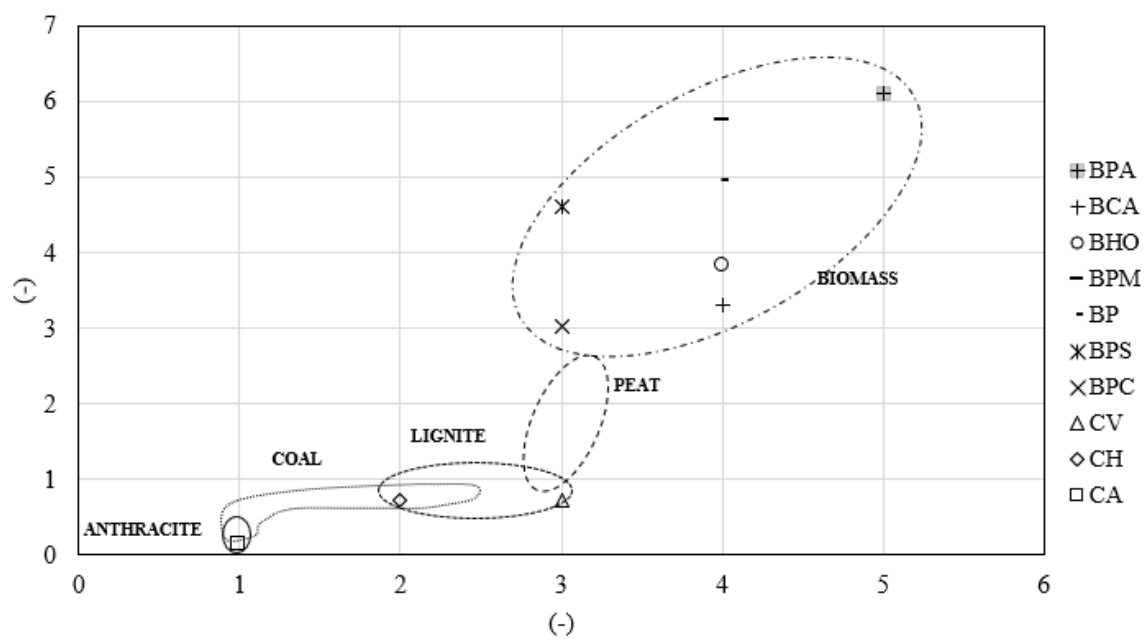


Figure 6.68. BZ vs. CI

Chapter 7

Conclusions and Future Research Lines

7.1. Conclusions

This thesis presents a comprehensive analysis of different biomass and coal samples, focusing not only on the physicochemical properties, but also in their thermochemical behaviour and its relationship to the industrial safety factors associated to their use, storage and management. Through the different analysis and tests presented in this study, different parameters have been assessed such as particle size, volatile content, polydispersity index, and thermodynamic relationships between molecular structure and ignition sensitivity or material reactivity. In these relationships lies the novelty of this work. The results presented systematically correlated different factors such as the hemicellulose percentage or ash content ignition and explosion parameters. Therefore, providing a deeper insight into how intrinsic variables (such as oxygen content or lignin properties) might be translated into easy ignition or fire resistance, depending on the material in question. This constitutes a novel approach that has not been previously addressed in such a comprehensive manner.

Moreover, this thesis developed numerical and experimental methodologies based on highly scientifically rigorous studies, which constitutes a significant advance in the field of dust combustion behavior modelling. Different thermokinetic models were applied and modified (such as Frank-Kamenetskii and Semenov models) by introducing new parameters that improve their accuracy and allow better estimations of minimum ignition temperature both in layer and cloud. This approach unifies characteristics ranging from physicochemical properties to experimental validation following standardized methodologies, which grants novelty to the study and provides a solid methodological foundation for future research in the field of process safety.

Following the objectives set out in Chapter 1, the conclusions focus on two distinct areas: the analysis of the flammability of powdered solid fuels and the application of numerical methods and computations for the modelling of experimental tests that intrinsically characterise the ignition sensitivity and explosion severity of such fuels.

In this context, the particle size and morphology of the samples have a decisive influence on flammability and explosiveness. The fibrous structure of biomass retains larger particles post-screening, increasing the surface area exposed to the oxidant and accelerating flame propagation. This fact limits the accuracy of traditional particle sizing methods for biomasses, whereas for coals, there is no such issue, as their particle distribution is more uniform.

Further characterisation and forthcoming analysis revealed that the biomass samples studied, including olive, almond shells, wood, straw, soybean, and cork, exhibit higher volatile content and lower fixed carbon than coals, easing ignition and flame propagation due to a higher fuel/oxidant ratio. Coals, with higher fixed carbon content, require more severe ignition conditions owing to their thermal stability.

Related to this, the elemental composition of biomass, characterised by high oxygen and low carbon, significantly influences its flammability. In contrast, the coals

showed a clear progression in composition, with a higher carbon content and lower levels of hydrogen and oxygen.

From the perspective of thermal composting, a comprehensive analysis revealed that the heating rate significantly impacts the induction temperature (IT) and burnout temperature (T_b). A higher heating rate resulted in a higher value for both parameters, indicating thermal lag. The relationship manifests consistently across samples, where specifically, the hemicellulose concentration in the olive and wood samples resulted in higher maximum weight loss temperature ($MWLT$) values, which shifted the curve to the right. Furthermore, a distinctive phenomenon emerges at high heating rates, where an overlap in the decomposition of hemicellulose and cellulose is observed, manifesting only as one devolatilisation process of both polymers often referred to as holocellulose.

The results of the compositional analysis by Fraser-Suzuki of the biomass samples revealed variations between samples, specifically in cellulose and lignin content. Notably, olive-derived samples showed distinctive compositions, with a lower cellulose content than other samples. Furthermore, a positive correlation was established between the hemicellulose content and various temperature characteristics (IT and $MWLT$), suggesting a fundamental role in ignition.

The TG_{spi} results showed distinct and well-defined levels of thermal reactivity. The highest value was obtained for the wood sample, which can be attributed to its balanced composition of hemicellulose, cellulose, and lignin. However, the coals exhibited significantly high resistance to the smouldering process owing to their high fixed carbon content and low volatile matter content. In particular, the anthracite (CA) sample showed extreme resistance to self-ignition phenomena, fundamentally as a consequence of its high level of carbonisation.

Complementarily, the RB Index was developed, revealing robust consistent inverse relationships with the characteristic temperatures of the thermogravimetric analysis. Notably, materials with lower onset temperatures tended to have a higher RB Index, indicating their high susceptibility to spontaneous combustion. However, the wood sample (BPM) showed an exception, which could be directly attributed to its high hemicellulose content, which during devolatilisation emits CO_2 , an inert gas. Biomass consistently showed higher RB Index values than coals, reflecting their high reactivity and oxidative susceptibility. Additionally, the RB Index increased as the height of the dust deposit increased, evidencing the thermal accumulation resulting from the accumulation of large volumes of material and the consequent high risk of spontaneous ignition.

The results of the kinetic analysis revealed a clear correlation between activation energy and burnout temperature. This correlation was particularly evident in the carbon group, where higher E_a values were required to break the stable bonds of highly ordered carbonaceous structures, resulting in higher T_b values to achieve complete combustion. In addition, the trend in activation energy aligns with the increase in coal rank, which is

reflected in the increase in fixed carbon content and decrease in volatile matter. This progression also corresponds to higher ignition temperatures and a decrease in the RB Index, indicating a higher resistance to ignition and spontaneous combustion.

On the other hand, obtaining thermodynamic parameters provided essential information for determining the ease or difficulty of product formation and the existence of energy barriers. Significantly, the mean difference between the activation energy and enthalpies was less than 5 kJ/mol, corroborating the methodological consistency of the study.

Analysis of the combustion rates revealed that the lignocellulosic samples obtained higher values than the carbon samples, suggesting a higher release rate of flammable products and faster ignition. The biomass also exhibited higher combustion and ignition ratios, as well as demonstrating more stable and continuous combustion compared to coals.

Regarding the modelling of the minimum ignition temperature of dust layer, it was observed that the hemicellulose content plays a fundamental role in the determination of the minimum ignition temperature. This relationship is explained by the different decomposition products: hemicellulose releases mainly CO₂, acting as an inert thermal sink, whereas cellulose and lignin generate flammable volatiles (CO and CH₄, respectively). The correlation between hemicellulose content and ignition temperature was validated with a correlation index $R^2 = 0.98$ which indicates the accuracy of the model and the strong relationship between the variables.

As a result, it leads to a complete thermal characterisation under hot surface dust layer conditions, validating the proposed new method for predicting the minimum ignition temperature of dust layer by differential analysis of thermogravimetric curves. This novel method provides several advantages over experimental tests: it requires only 60 mg of sample and assesses the complete thermal profile at a single temperature point. In addition, it allows simultaneous compositional analysis by deconvolution in a single test.

Advancements in modelling the minimum ignition temperature of dust clouds, specifically through the inclusion of the Ψ parameter and the development of an optimised expression of five parameters correlated to intrinsic material properties, have substantially improved the predictive accuracy. This improvement has a direct impact on the characterisation of combustible dust, providing an effective tool for the evaluation of industrial safety parameters.

The ratio of volatile matter (VM) to fixed carbon (FC) in biomass has been identified as crucial for determining the oxygen balance (OB) and oxidative potential. Oxygenated volatile matter compounds contribute positively to the oxygen balance, whereas fixed carbon increases the stoichiometric demand for complete combustion. This newly developed inverse correlation, represented by OB^* , achieved an exceptionally high correlation index of $R^2 = 0.99$, serving as an indicator of the degree of oxidative potential.

For the severity test, numerical modelling revealed higher errors in the BM (adiabatic) method than in the NCV (isothermal) method. The BM model was improved by incorporating an empirical Ψ factor of 1.65 which increased the accuracy by approximately 80% for the $(dP/dt)_{max}$ parameter with the r_o model data and by 77% for the K_{ST} parameter using the same model. Moreover, the application of the computational fluid dynamics software Viper::Blast, enhanced by including the parameters of the TNT equivalent, demonstrated a low error in the prediction of overpressure in the deflagration of solid fuels in the standard 20-litre sphere.

The results showed strong relationships between the BZ combustion class number and various physicochemical parameters. Biomass, with a balanced composition, shows a higher propensity for flame propagation, whereas coals, especially anthracite, show a lower propensity. The combustibility index (CI) showed a significant correlation with the BZ number, establishing it as a key parameter for predicting flame spread.

Finally, thermogravimetric analysis was validated as an effective predictor of combustion propagation. Coals showed a negative correlation between the BZ index and characteristic temperatures, whereas biomass showed a positive correlation. Biomass showed superior performance in multiple indices, including combustibility, flammability, burnability, and flammability, while coal, with lower values, showed more controlled combustion processes, reflected in its CI values.

The major contributions of this thesis can be summarised as follows:

- A new method of predicting the minimum ignition temperature of dust layer with an error of 2.25% with respect to experimental data was developed from the differential analysis of thermogravimetric curves and with only 60 mg of sample required.
- A correlation of $R^2 = 0.98$ was found between the hemicellulose content and the minimum ignition temperature of dust layer.
- A new index to characterise the tendency to spontaneous combustion was developed using numerical methods (RB Index).
- The minimum ignition temperature of dust cloud was modelled using an optimised expression of five parameters correlated with the intrinsic properties of the substance.
- A new index was developed that quantifies the oxidative potential of solid fuels as high-energy explosives by their volatile matter and fixed carbon content with an $R^2 = 0.99$, compared to the traditional method of obtaining the oxygen balance (OB^*).
- The computational fluid dynamics software Viper::Blast was used to model the 20-litre sphere maximum overpressure values from the TNT equivalent model.
- The combustibility index was found to be an effective predictor of flame spread compared with the Brennzahl index (BZ).

In terms of contributions to society and their practical application, the results presented in this thesis offer clear guidelines for the industry that handles powdered solids, whether biomass or coal. On the one hand, the information obtained on the risk of explosion and self-ignition conditions is essential for designing fire prevention and control systems, reducing incidents and their economic and environmental consequences. On the other hand, the proposed correlations and modelling methodologies allow industry to adapt and optimize their production, storage and transport processes of these powders, with a greater emphasis on sustainability and safety, thus contributing to more efficient and responsible industrial management.

7.2. Future Research Lines

From the results obtained in this study, several new lines of research were identified with the aim of improving the methods used, as well as improving the accuracy of the results.

On the one hand, although the kinetic methods used in this study are quite accurate, it would be interesting to focus on the kinetic behaviour using Distributed Activation Energy Models (DAEM). This multi-component approach allows each of the reactions taking place in the process to be modelled individually, thus providing a more detailed characterisation of the reaction mechanisms and their interactions.

On the other hand, thermogravimetric analysis coupled with mass spectrometry (TG-MS) would allow the identification and quantification of the gaseous species released during thermal degradation processes (volatilisation), providing information on the ignition mechanisms. This approach can provide information on the time evolution of gases released as a function of temperature, allowing correlations between the chemical nature of the volatiles and critical ignition parameters to be established. For example, it would be of great application concerning the minimum ignition temperature in a layer, where the characterisation of the decomposition products would help to better understand the transition between the pyrolysis and combustion regimes.

Improve the new RB index developed using the experimental data of Class 4.2: Substances liable to spontaneous combustion test, would be a proper continuation of this research. The main objective would be to systematically assess the influence of the container height on the self-ignition behaviour. This refinement would require a test matrix that explores different geometrical configurations, paying particular attention to the relationship between the container height and the resulting heat transfer patterns. In addition, the future integration of this new experimental data could allow the development of a more robust model that captures geometrical effects more accurately.

Finally, modelling the explosion severity test using Viper::Blast from the devolatilisation reactions would provide deeper insights in the dust explosion phenomena. In other words, the computational approach would integrate the kinetic data obtained

from the devolatilisation study with the dynamics of the explosion, providing a more complete thermochemical description of the deflagration process.

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Appendix 1

Thermogravimetric Parameters Results

Table AP 1.1. Thermogravimetric Parameters Results

Sample	Heating rate (K/min)	TG (°C)		DTG (°C)		DDTG (°C)	
		<i>IT</i>	<i>T_b</i>	<i>MWLT</i>	<i>H-Peak</i>	<i>C-Peak</i>	<i>L-Peak</i>
BPA	3	267.00	435.75	327.25	239.71	327.25	399.56
	5	270.30	446.25	333.24	248.80	333.24	411.75
	7	275.90	452.04	341.08	251.06	341.08	427.15
	10	287.28	411.05	346.68	250.72	346.68	453.28
	20	295.54	427.84	361.34	NAP	361.34	NAP
	Average	279.20	434.59	341.92	247.57	341.92	422.94
BCA	3	243.30	348.16	309.62	249.41	309.62	NAP
	5	254.00	357.38	316.02	258.86	316.02	NAP
	7	260.60	364.95	318.74	NAP	318.74	NAP
	10	267.07	373.79	323.25	NAP	323.25	NAP
	20	266.45	374.54	317.61	NAP	317.61	NAP
	Average	258.28	363.76	317.05	254.14	317.05	NAP
BHO	3	235.40	384.84	322.92	229.59	322.92	394.83
	5	238.00	404.97	324.67	233.52	324.67	406.06
	7	251.70	407.06	338.48	234.93	338.48	411.59
	10	264.64	414.89	340.10	237.10	340.10	499.60
	20	259.16	412.51	329.06	NAP	329.06	504.07
	Average	249.78	404.85	331.05	233.79	331.05	428.02
BPM	3	298.60	357.71	341.27	285.24	341.27	423.35
	5	302.00	369.06	348.85	291.02	348.85	434.83
	7	308.70	376.59	352.94	NAP	352.94	467.48
	10	310.76	384.29	355.54	NAP	355.54	NAP
	20	305.15	411.30	356.01	NAP	356.01	NAP
	Average	298.60	357.71	350.92	288.13	350.92	441.89
BP	3	298.60	357.71	305.03	257.57	305.03	471.02
	5	302.00	369.06	312.60	269.56	312.60	481.40
	7	308.70	376.59	314.18	307.55	314.18	487.53
	10	310.76	384.29	312.63	NAP	312.63	495.80
	20	305.15	411.30	307.15	NAP	307.15	520.79
	Average	305.04	379.79	310.32	278.23	310.32	483.94

Appendix 1: Thermogravimetric Parameters Results

BPS	3	251.20	341.35	290.35	204.16	290.35	434.23
	5	262.00	359.12	300.52	209.94	300.52	468.02
	7	257.60	368.30	304.23	212.37	304.23	470.61
	10	263.33	376.24	309.47	214.50	309.47	481.80
	20	266.20	411.00	319.71	NAP	319.71	NAP
	Average	260.07	371.20	304.86	210.24	304.86	463.67
BPC	3	219.60	354.66	339.11	250.23	339.11	410.21
	5	222.00	368.26	347.10	257.37	347.10	427.34
	7	234.20	370.63	349.95	259.24	349.95	431.52
	10	249.68	375.87	352.25	260.60	352.25	441.10
	20	258.39	385.31	345.30	NAP	345.30	NAP
	Average	236.77	370.95	346.74	256.86	346.74	427.54
CV	3	261.68	354.20	288.71			
	5	276.18	368.27	296.82			
	7	278.20	421.71	302.22			
	10	282.71	396.57	308.38			
	20	293.36	449.92	320.47			
	Average	278.43	398.13	303.32			
CH	3	394.27	474.40	436.88			
	5	401.11	496.32	446.97			
	7	406.13	511.37	454.52			
	10	408.63	700.98	562.97			
	20	430.84	544.41	471.62			
	Average	408.20	545.50	474.59			
CA	3	506.74	800.00	690.00			
	5	NA	NA				
	7	NA	NA				
	10	586.17	800.00	754.91			
	20	NA	NA				
	Average	575.45	800.00	722.46			

* NAP: Not Appreciable Peak; NA: Not Appreciable.

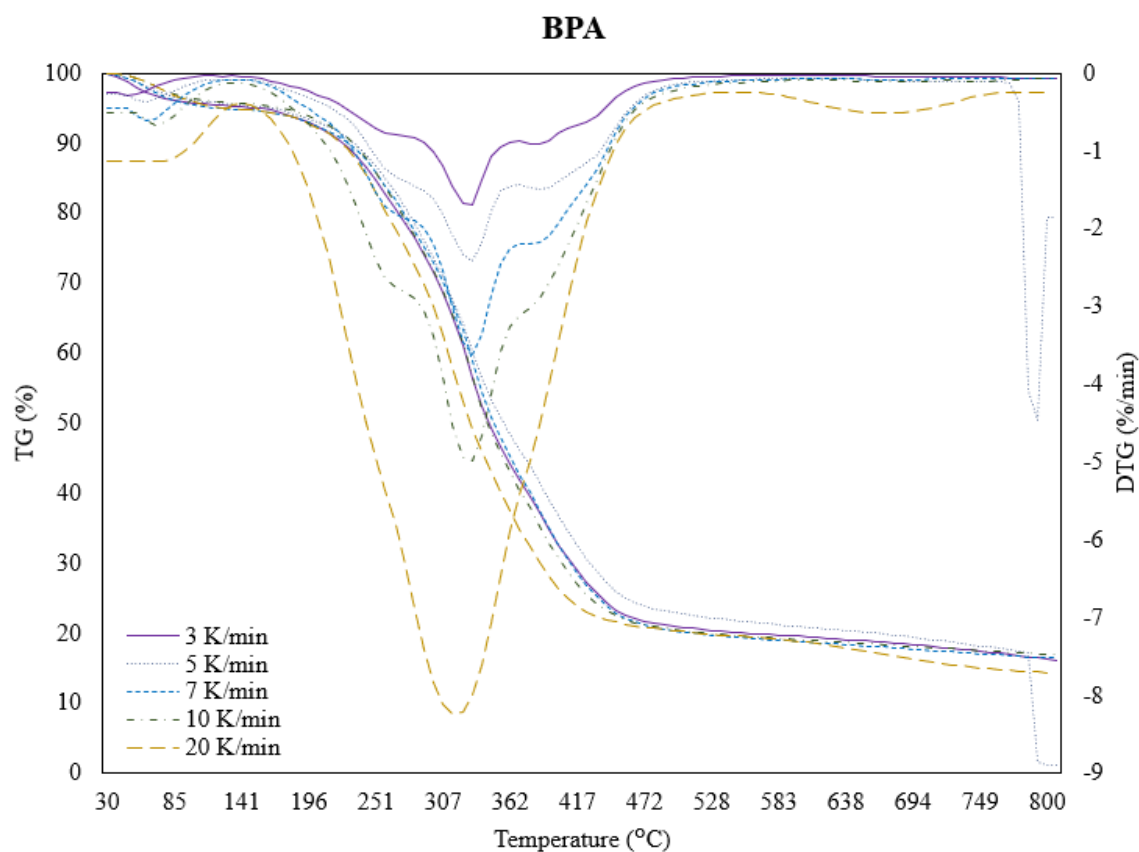


Figure AP 1.1. BPA TG-DTG curves for each heating rate

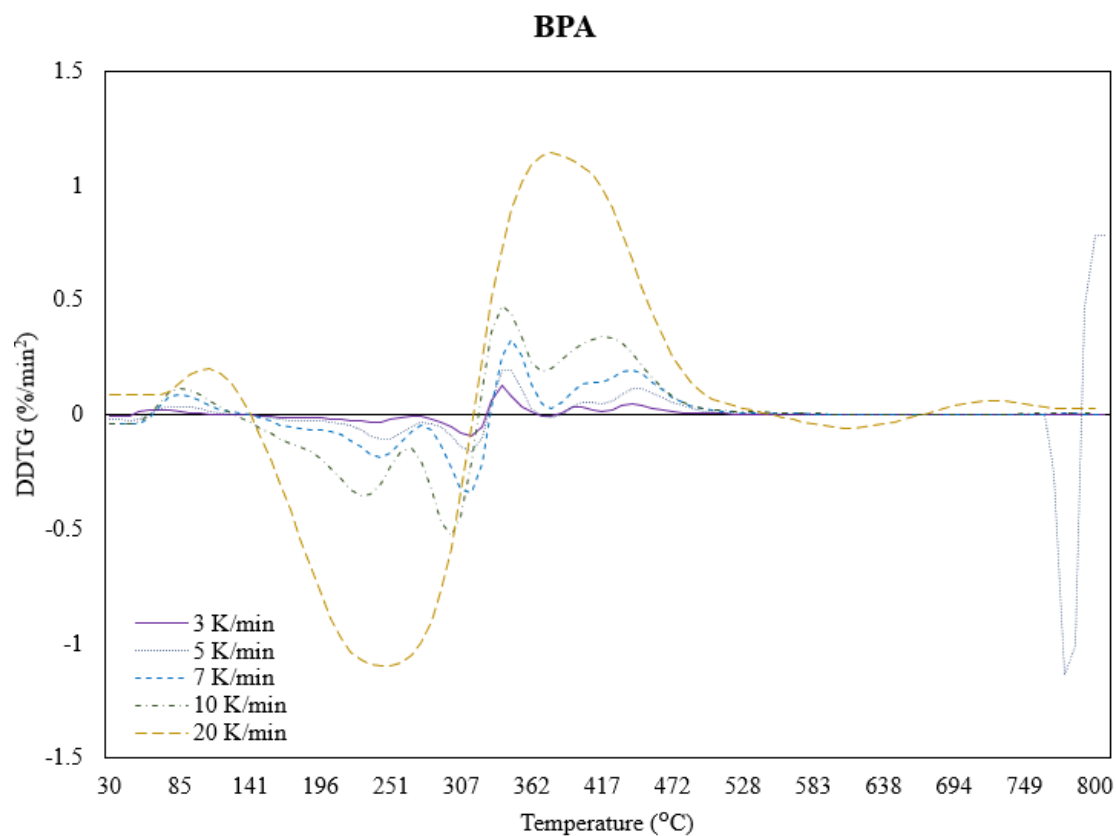


Figure AP 1.2. BPA DDTG curves for each heating rate

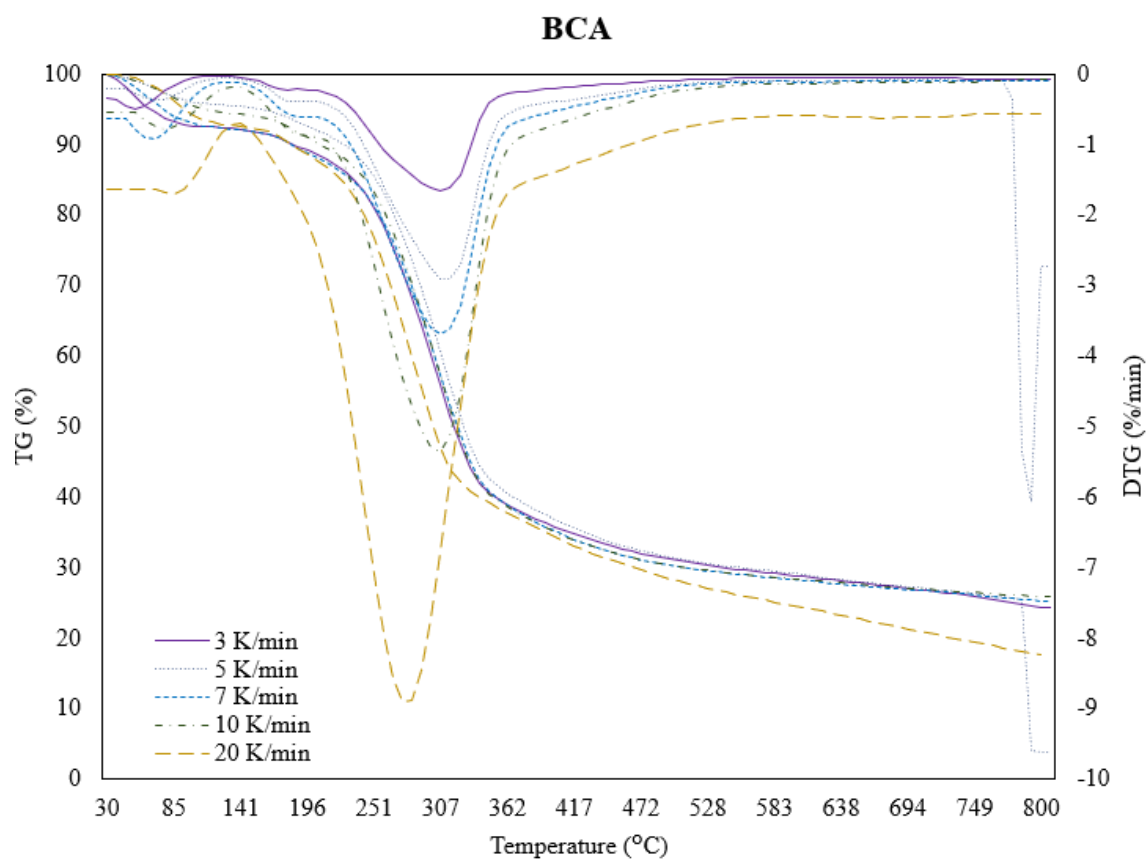


Figure AP 1.3. BCA TG-DTG curves for each heating rate

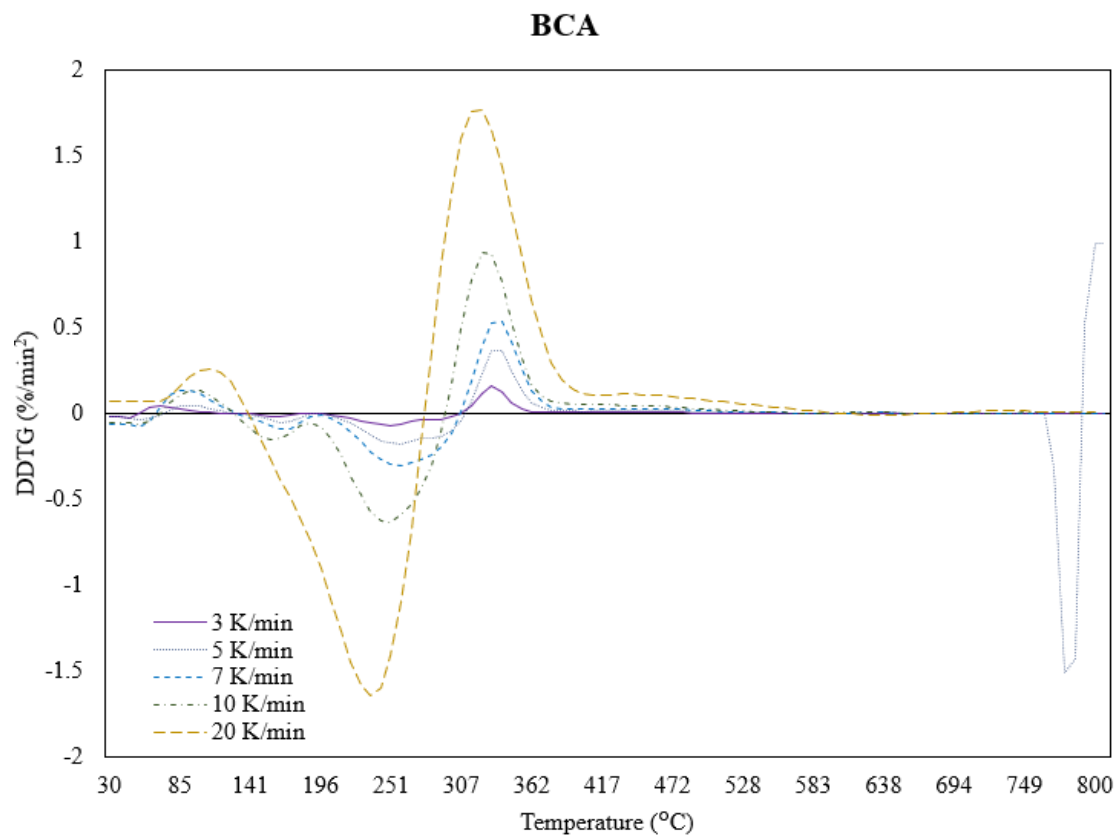


Figure AP 1.4. BCA DDTG curves for each heating rate

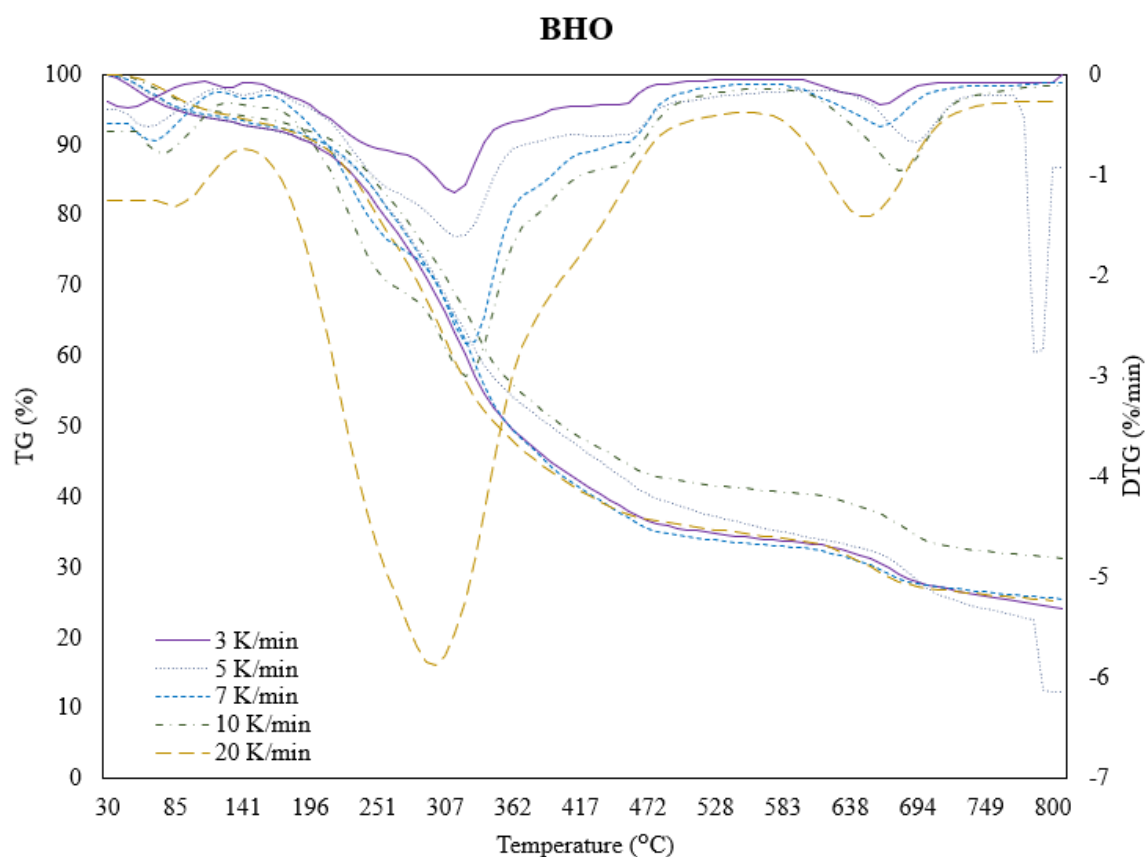


Figure AP 1.5. BHO TG-DTG curves for each heating rate

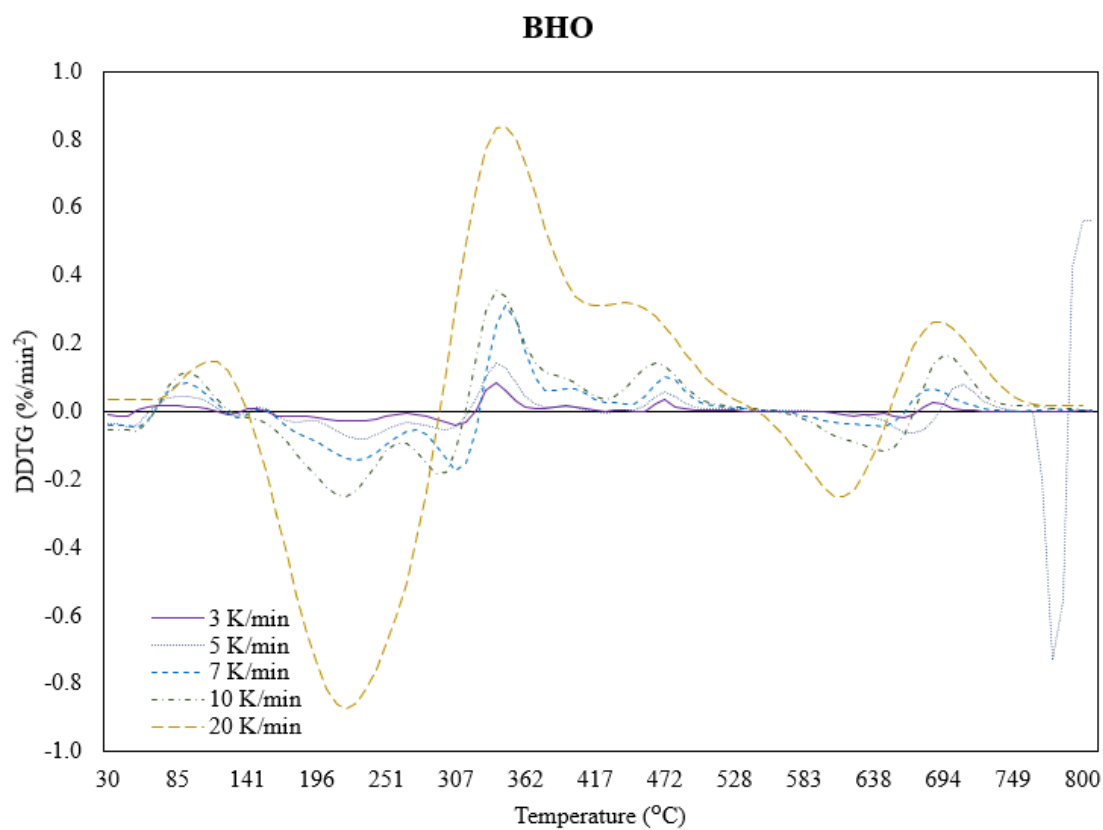


Figure AP 1.6. BHO DDTG curves for each heating rate

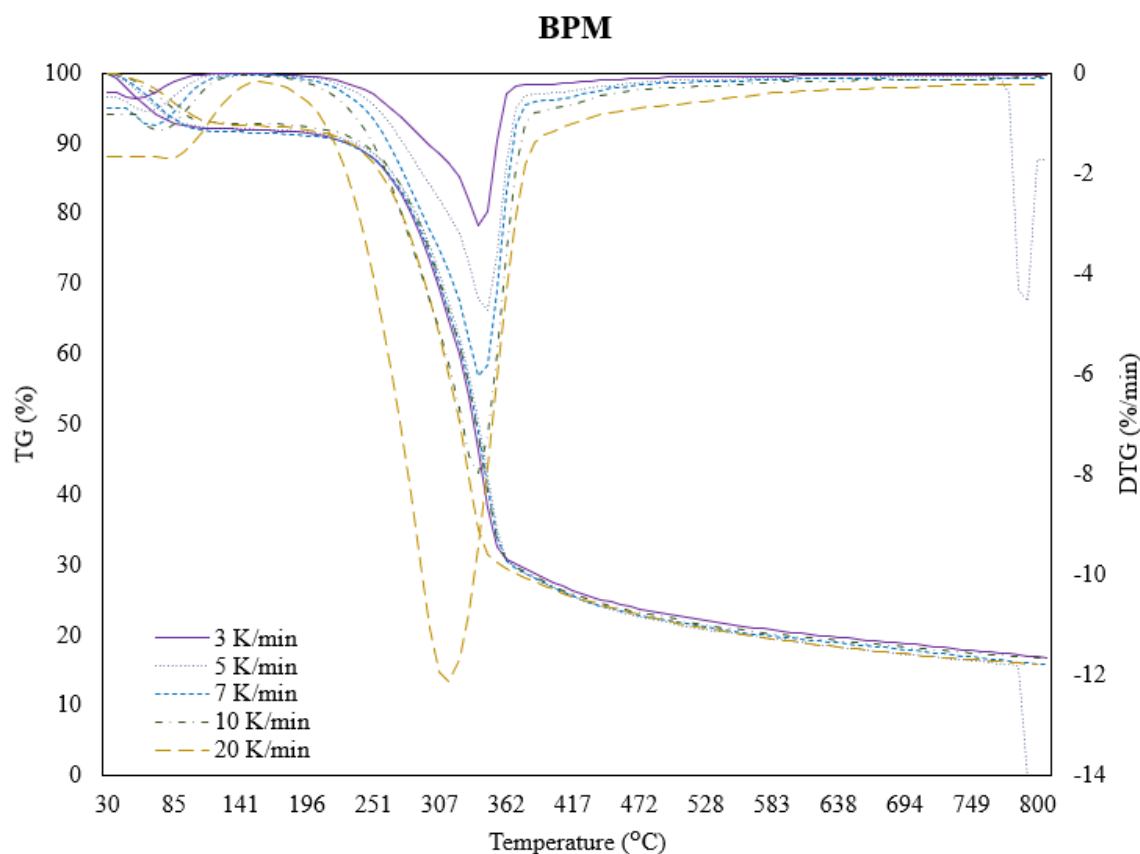


Figure AP 1.7. BPM TG-DTG curves for each heating rate

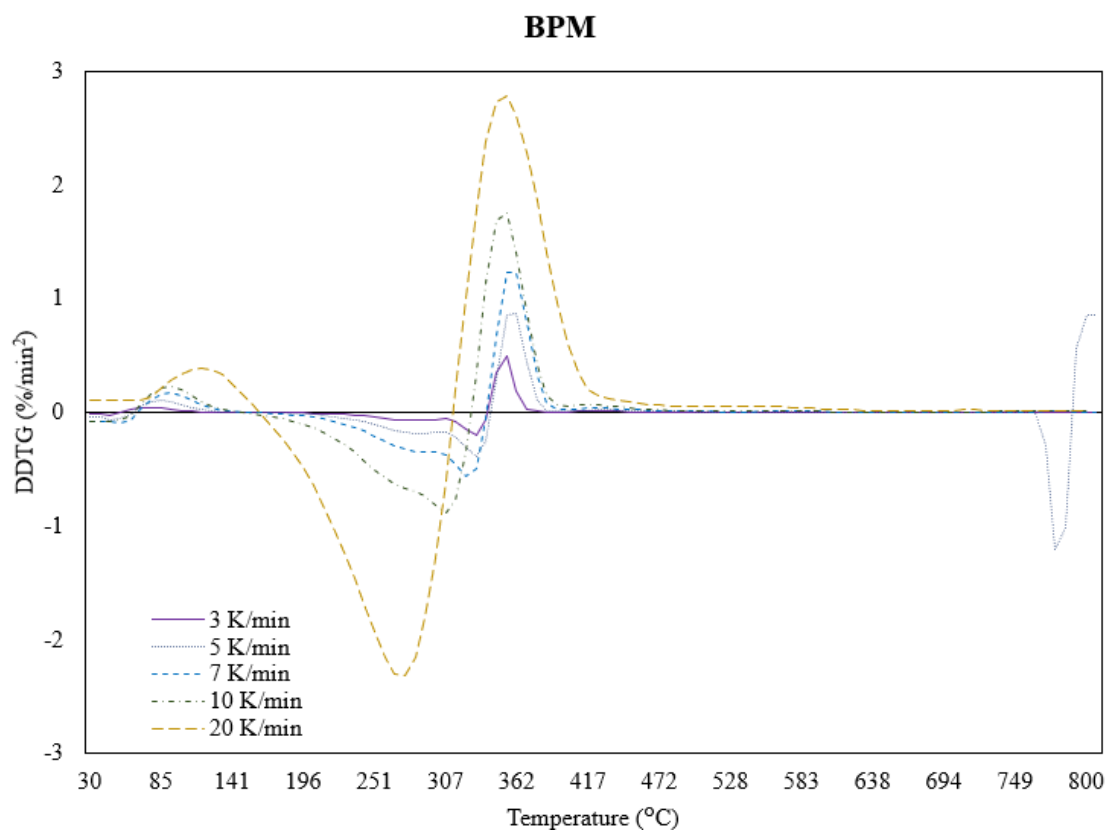


Figure AP 1.8. BPM DDTG curves for each heating rate

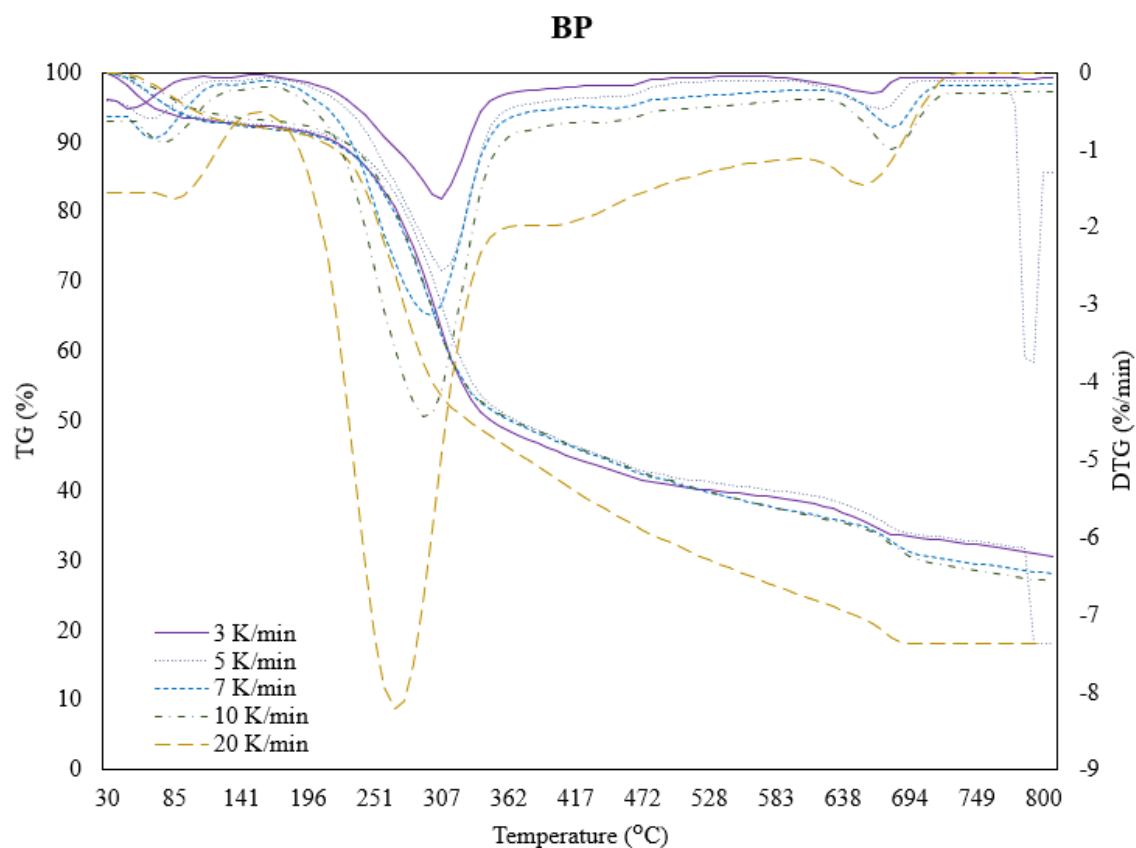


Figure AP 1.9. BP TG-DTG curves for each heating rate

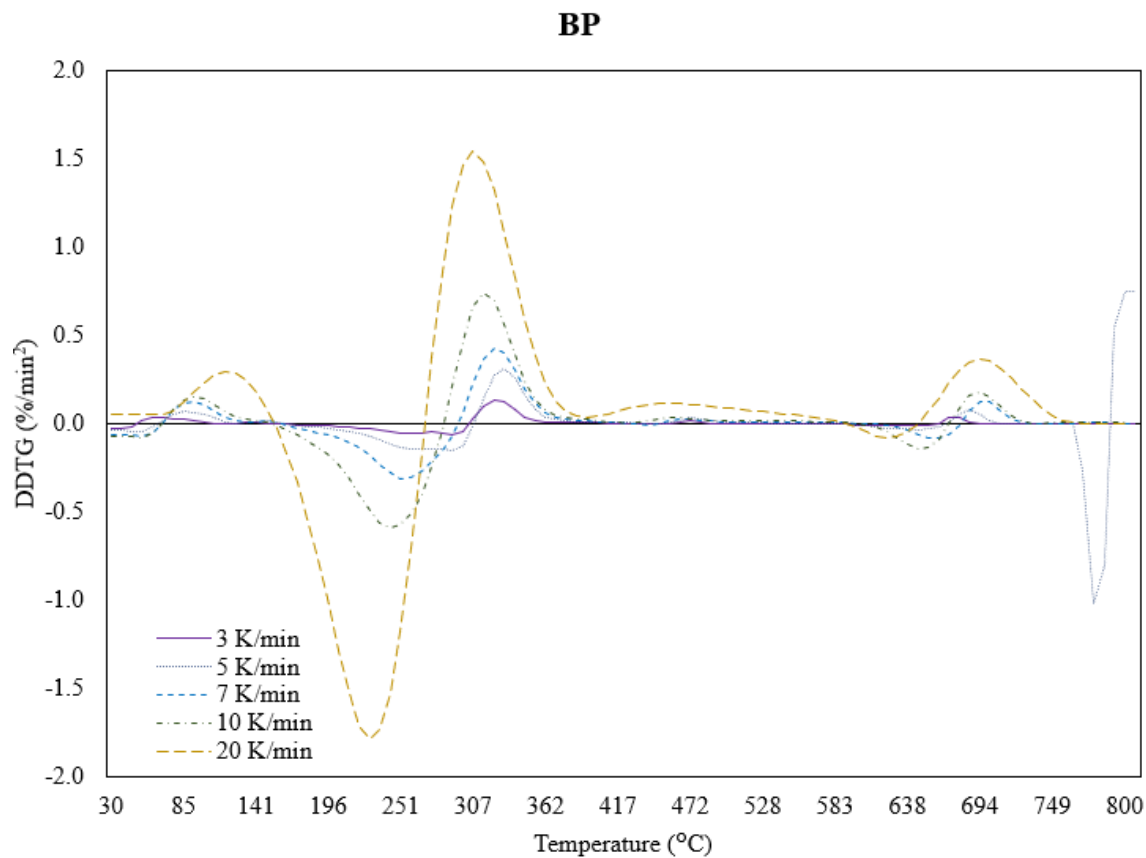


Figure AP 1.10. BP DDTG curves for each heating rate

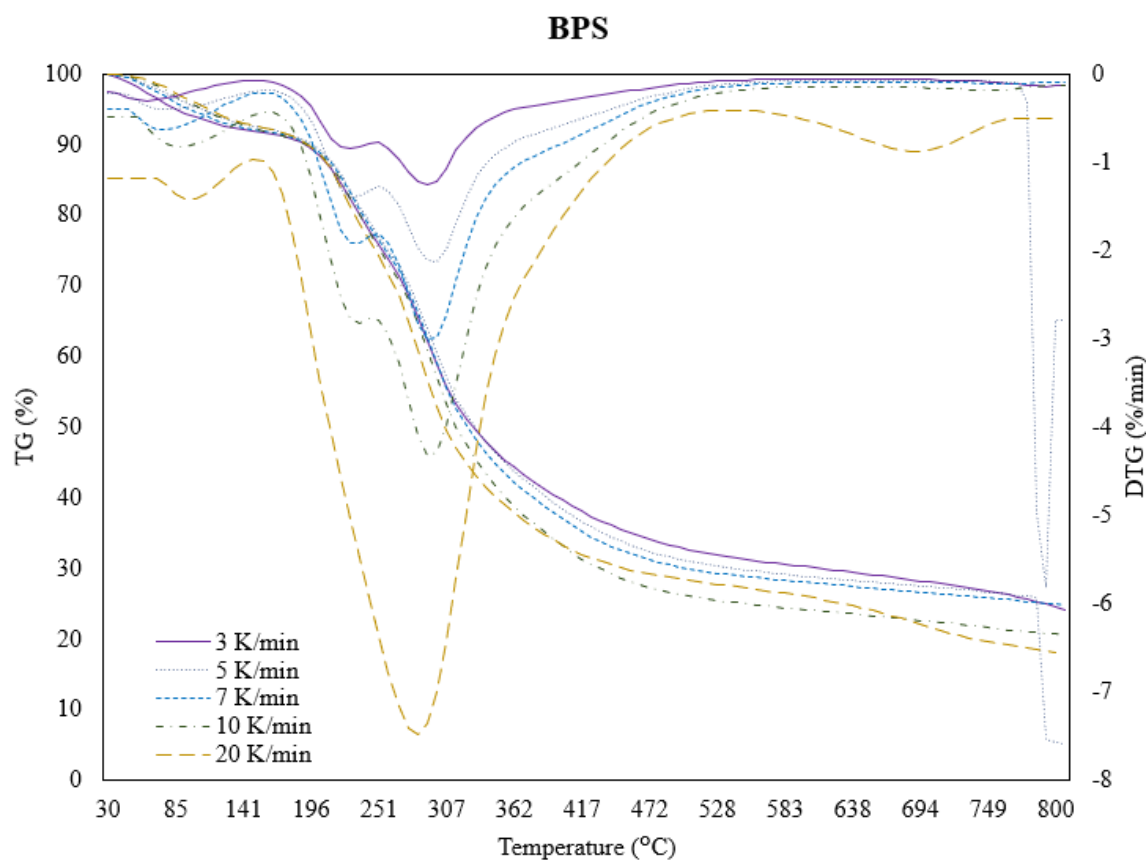


Figure AP 1.11. BPS TG-DTG curves for each heating rate

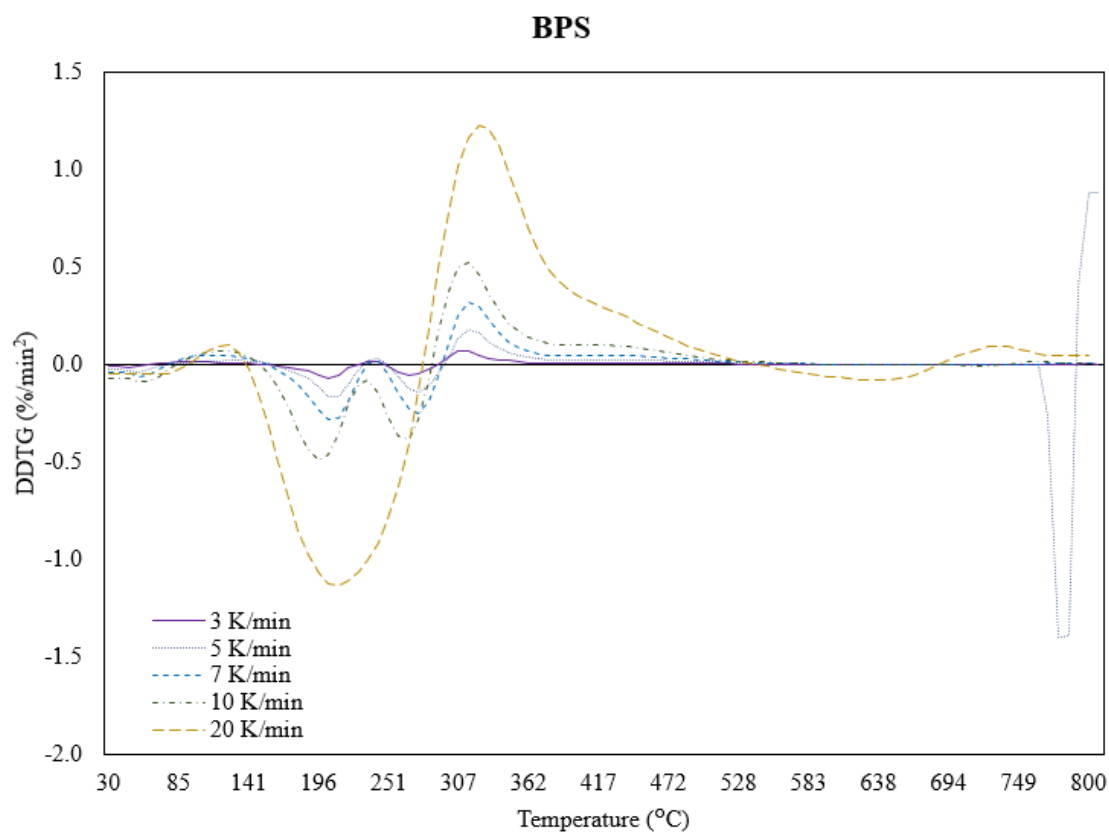


Figure AP 1.12. BPS DDTG curves for each heating rate

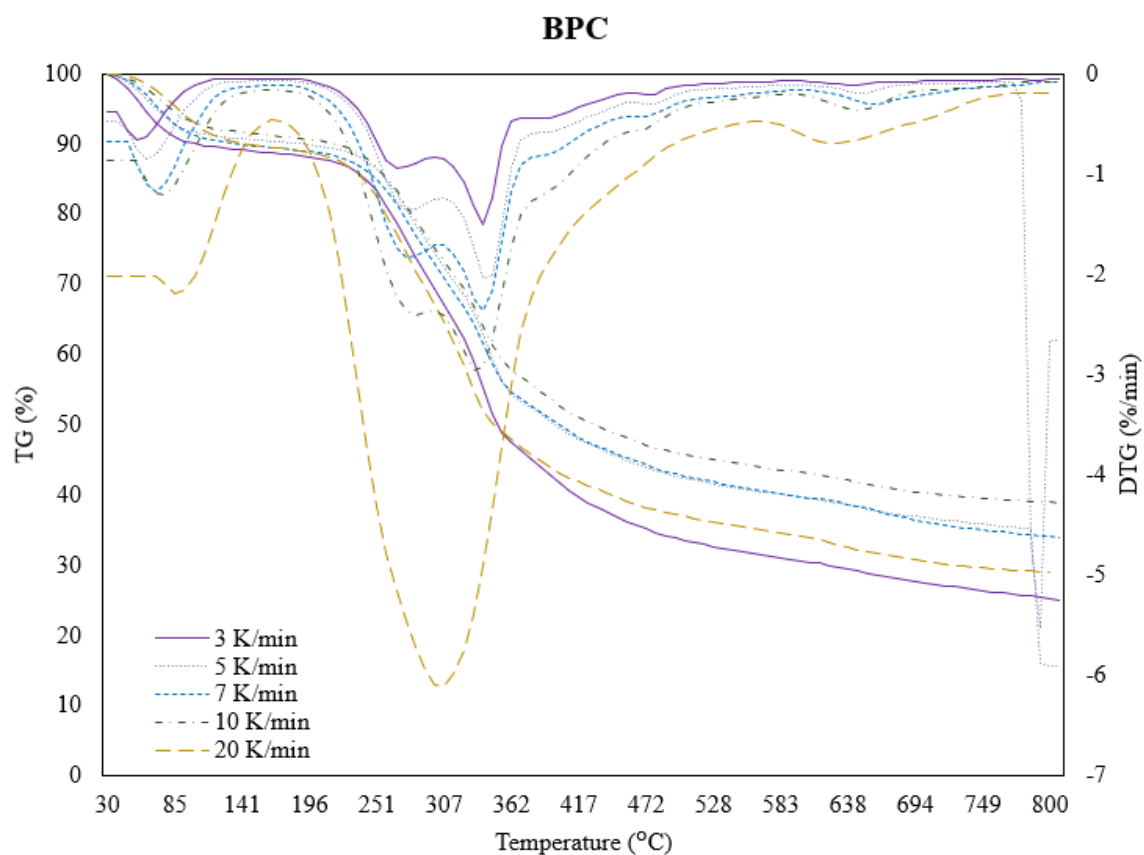


Figure AP 1.13. BPC TG-DTG curves for each heating rate

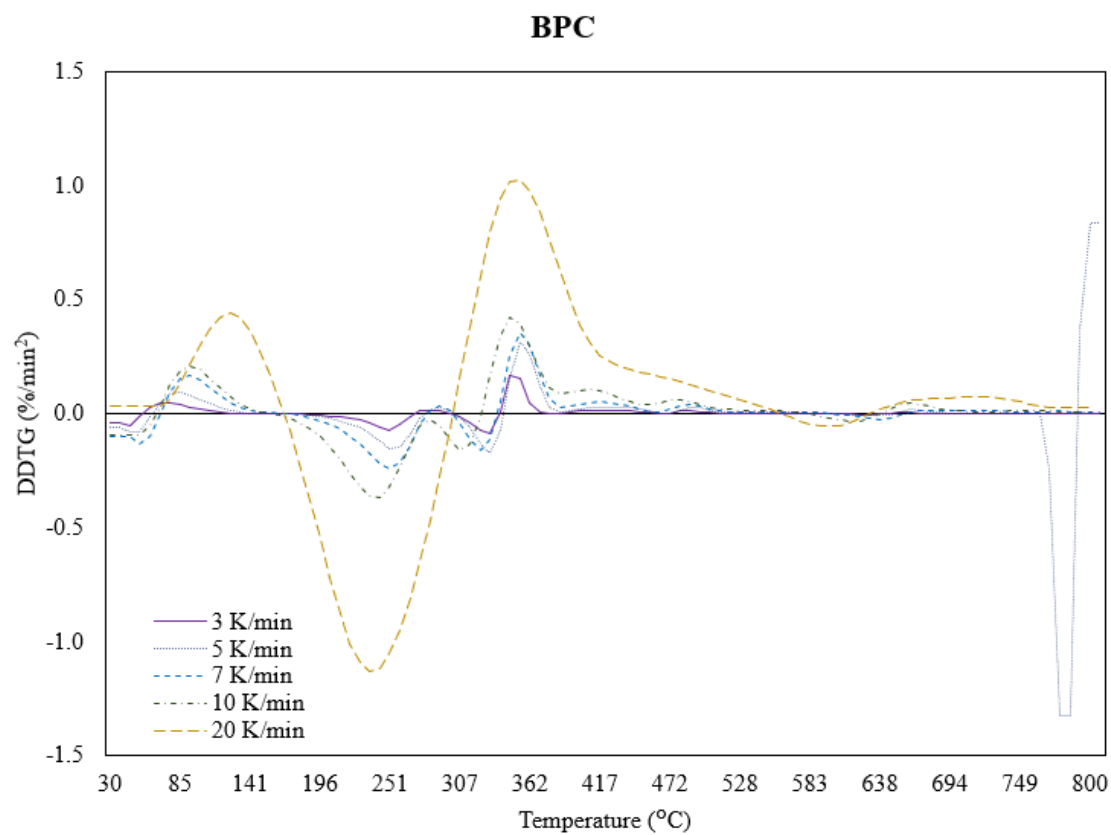


Figure AP 1.14. BPC DDTG curves for each heating rate

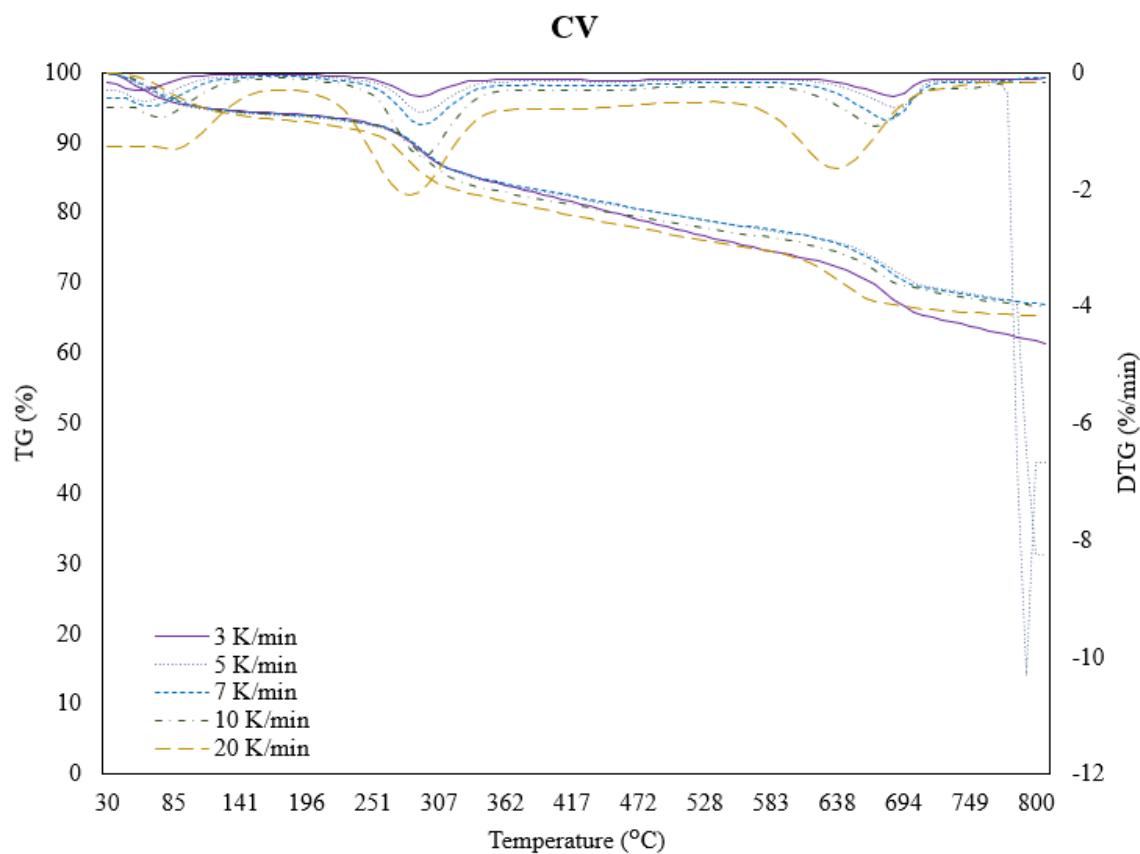


Figure AP 1.15. CV TG-DTG curves for each heating rate

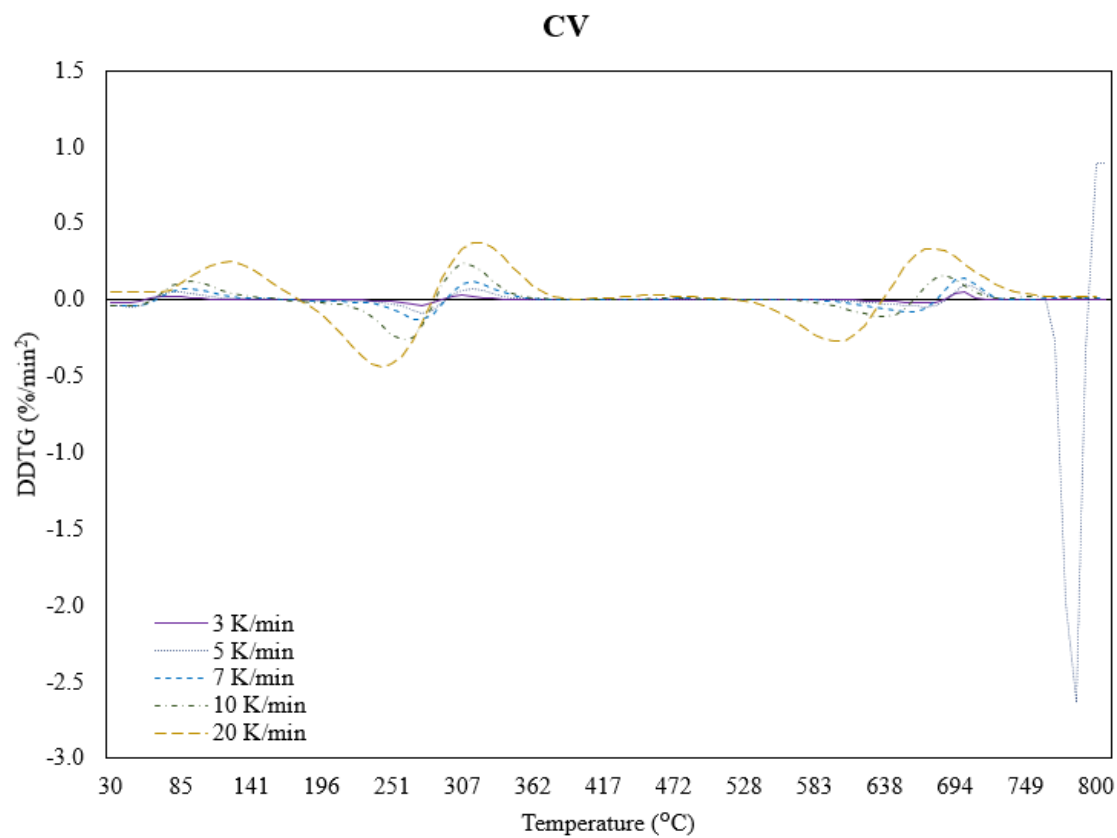


Figure AP 1.16. CV DDTG curves for each heating rate

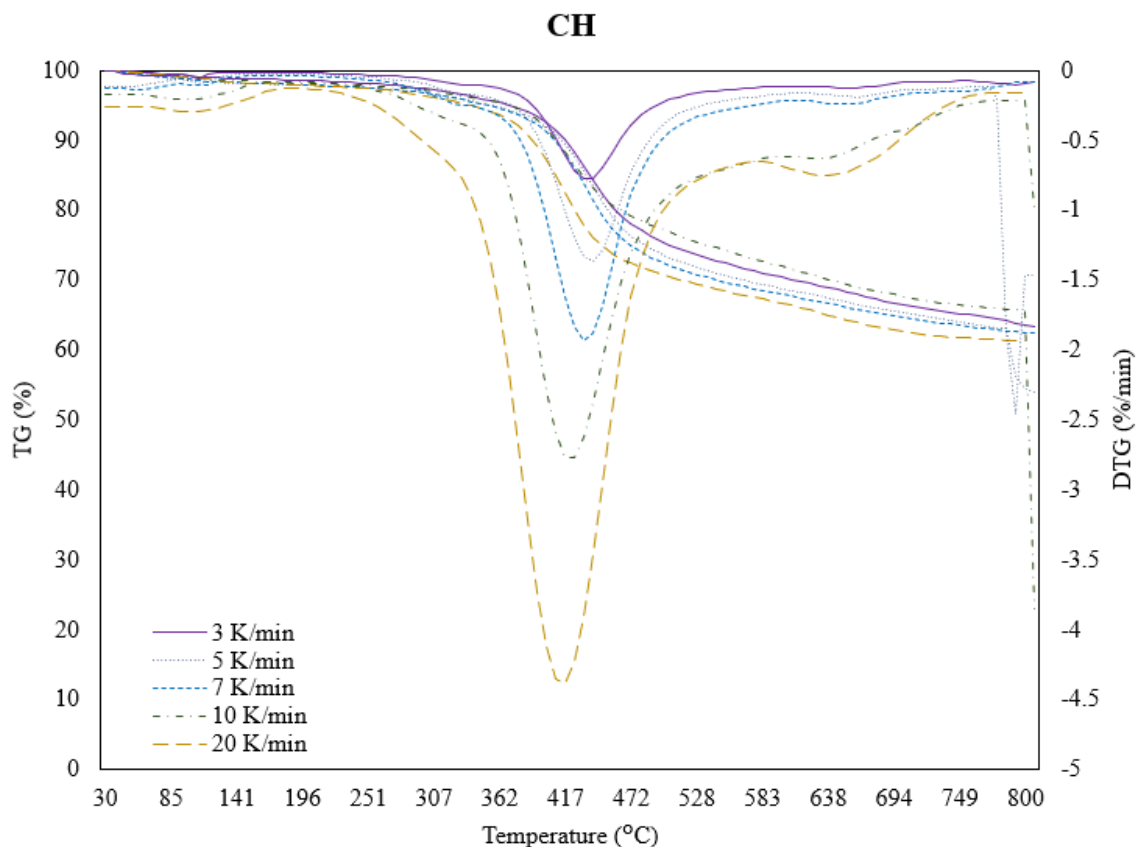


Figure AP 1.17. CH TG-DTG curves for each heating rate

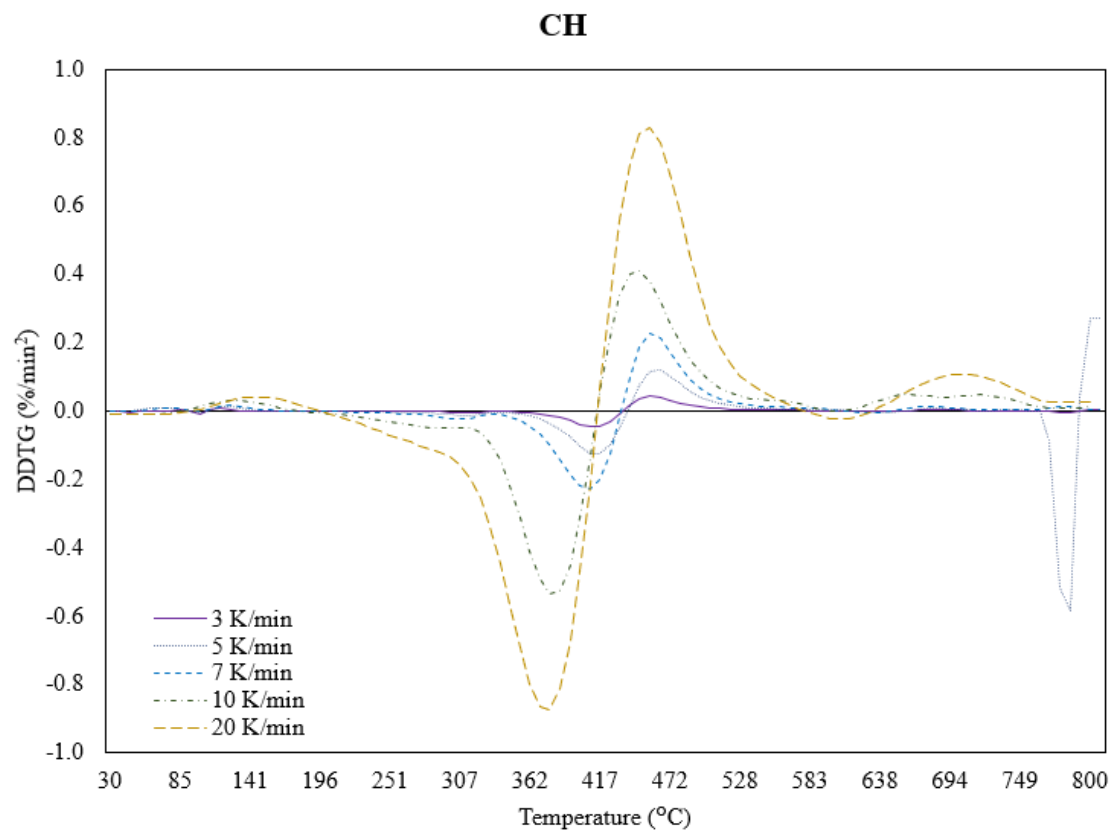


Figure AP 1.18. CH DDTG curves for each heating rate

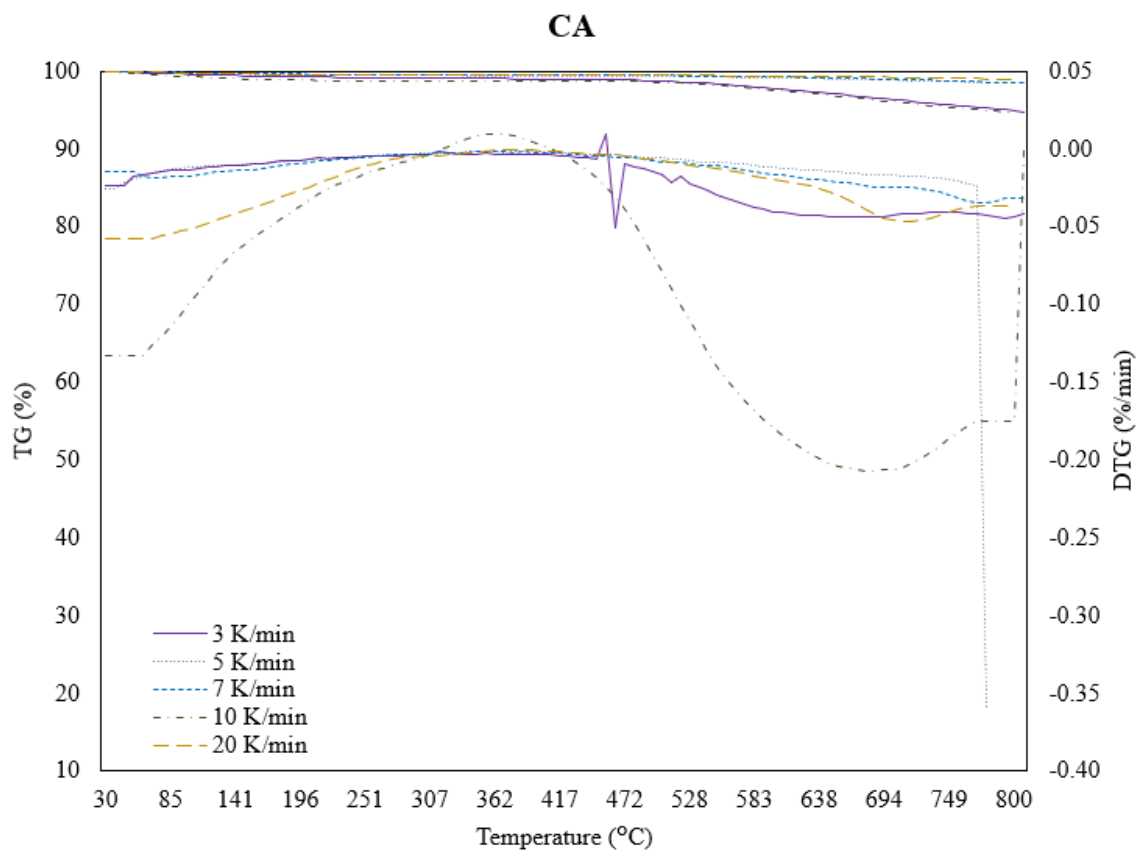


Figure AP 1.19. CA TG-DTG curves for each heating rate

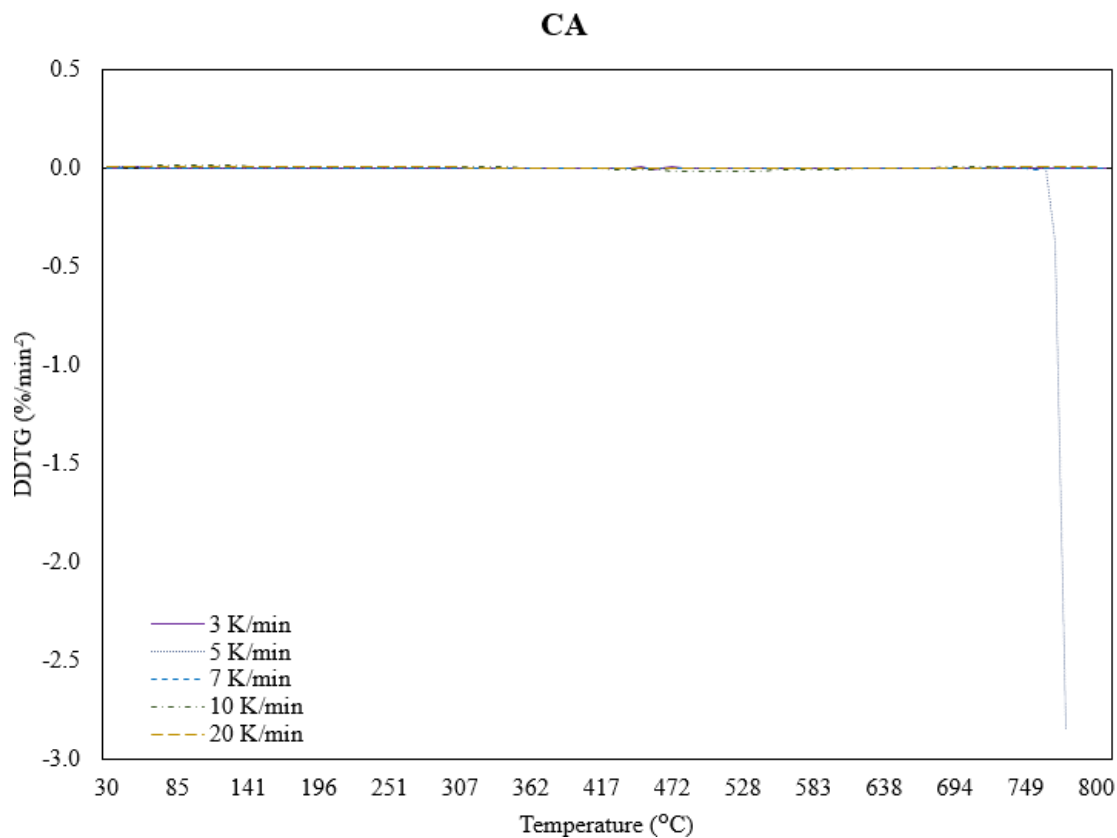


Figure AP 1.20. CA DDTG curves for each heating rate

Appendix 2

Thermogravimetric Approach Graphs for Proximate Analysis

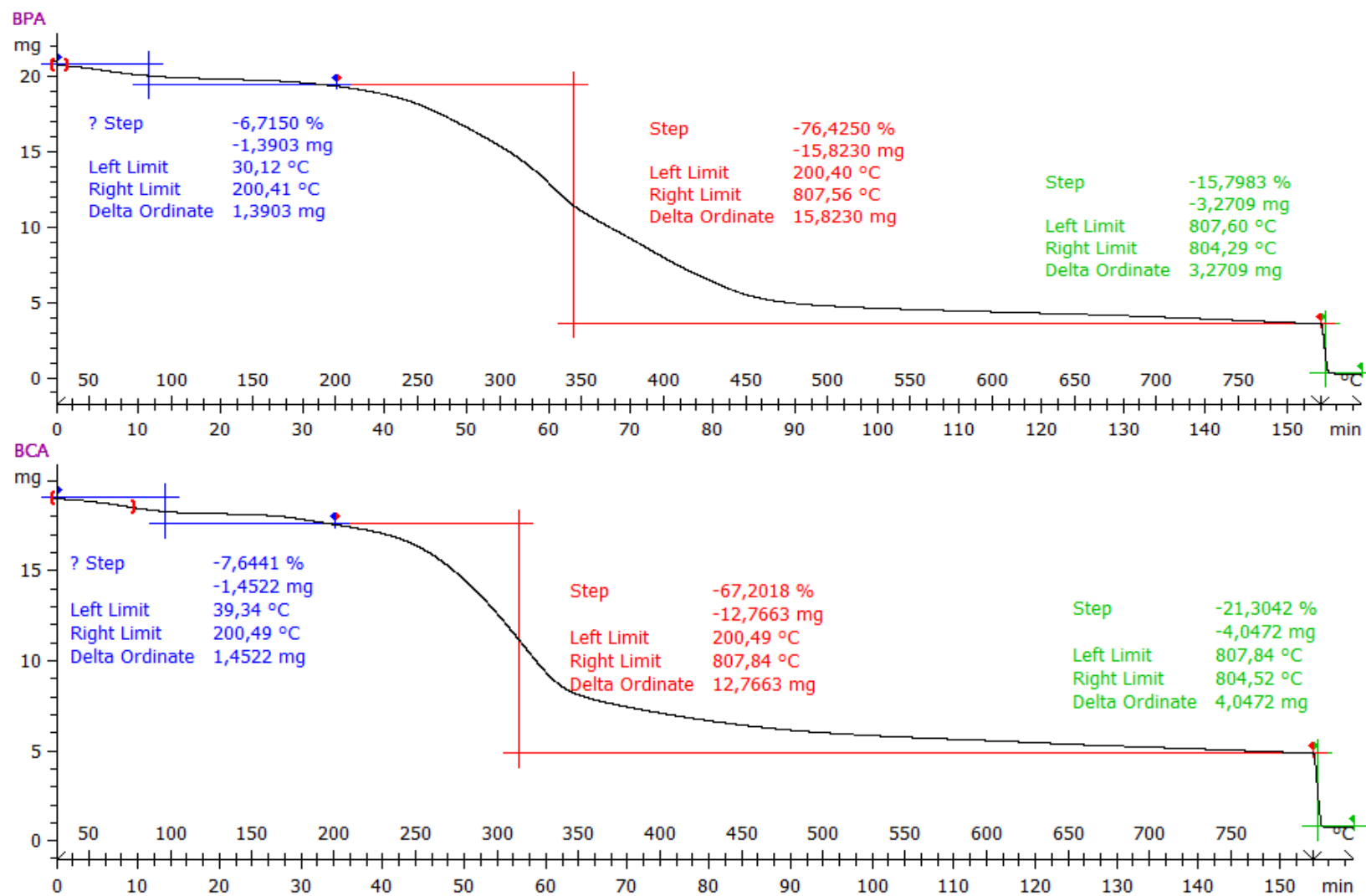


Figure AP 2.1. BPA and BCA thermogravimetric approach graphs for proximate analysis

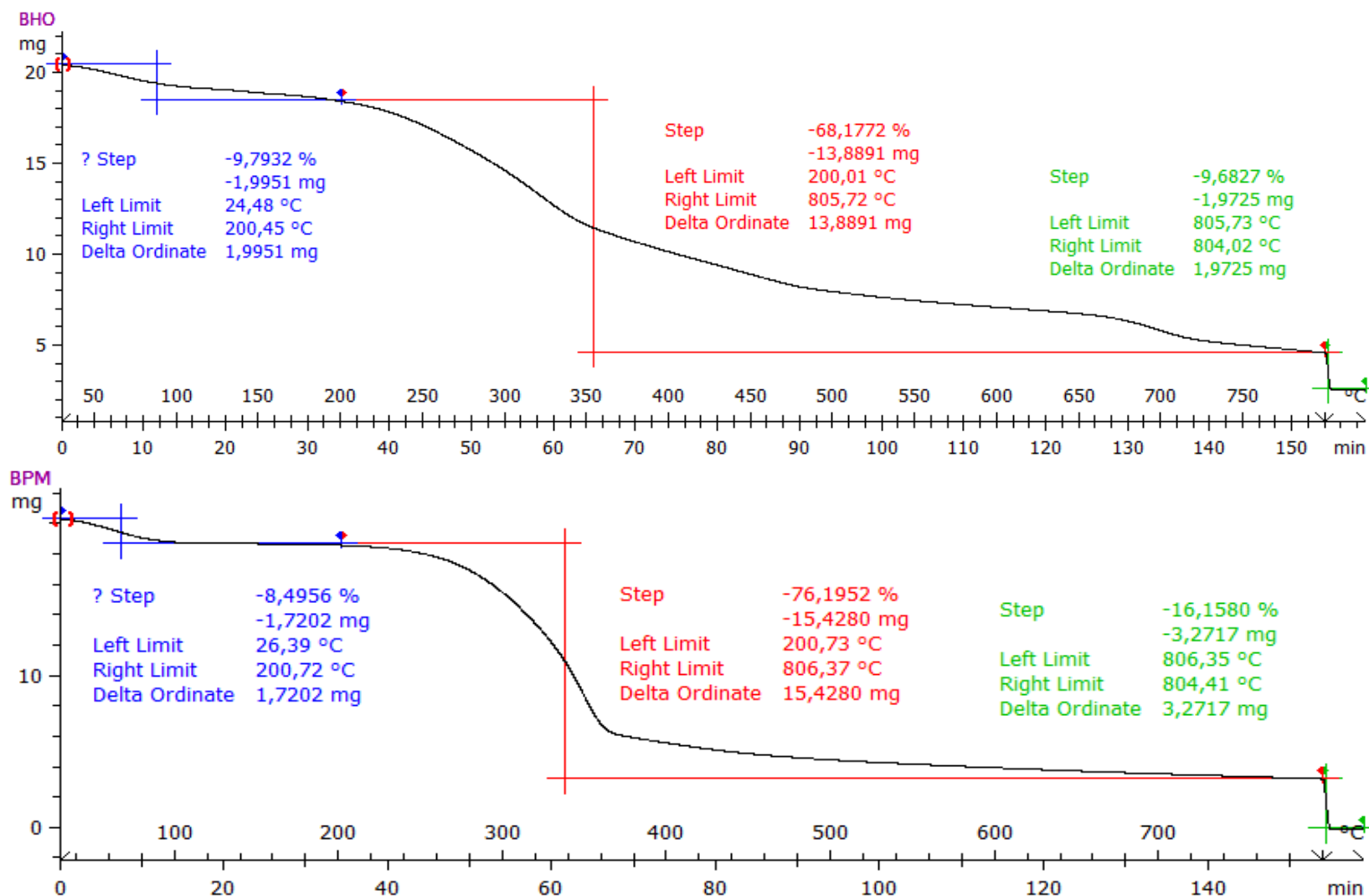


Figure AP 2.2. BHO and BPM thermogravimetric approach graphs for proximate analysis

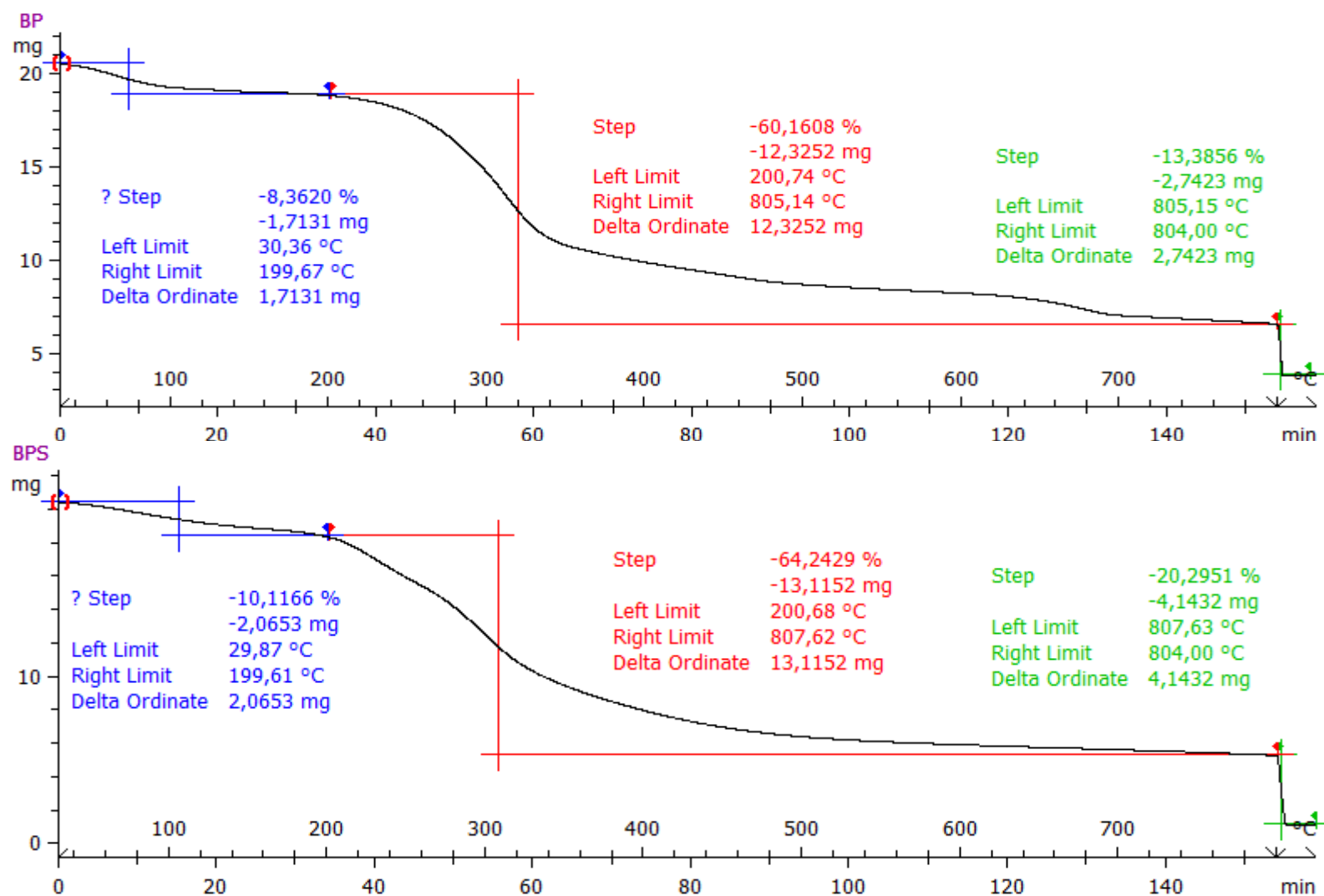


Figure AP 2.3. BP and BPS thermogravimetric approach graphs for proximate analysis

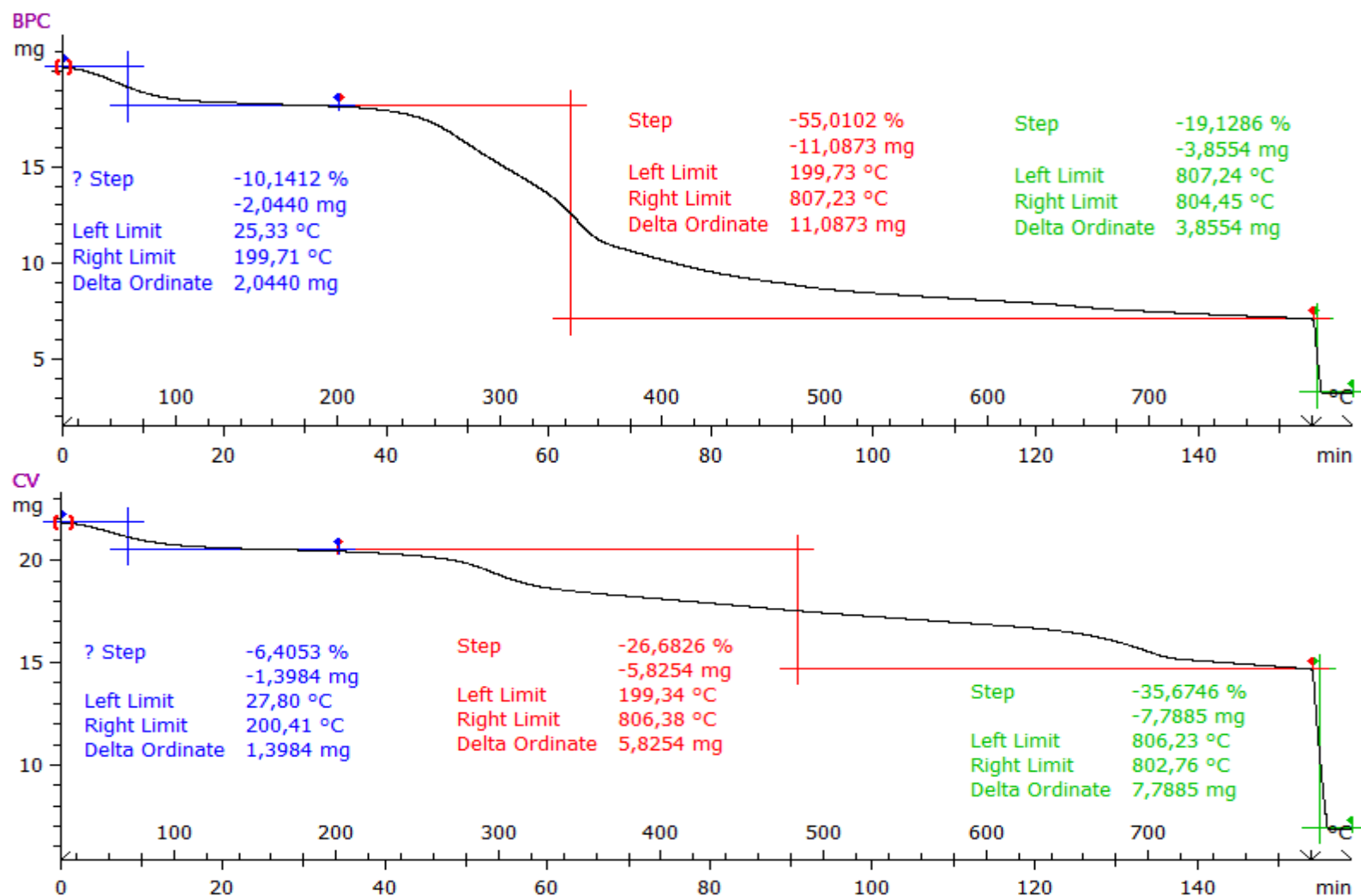


Figure AP 2.4. BPC and CV thermogravimetric approach graphs for proximate analysis

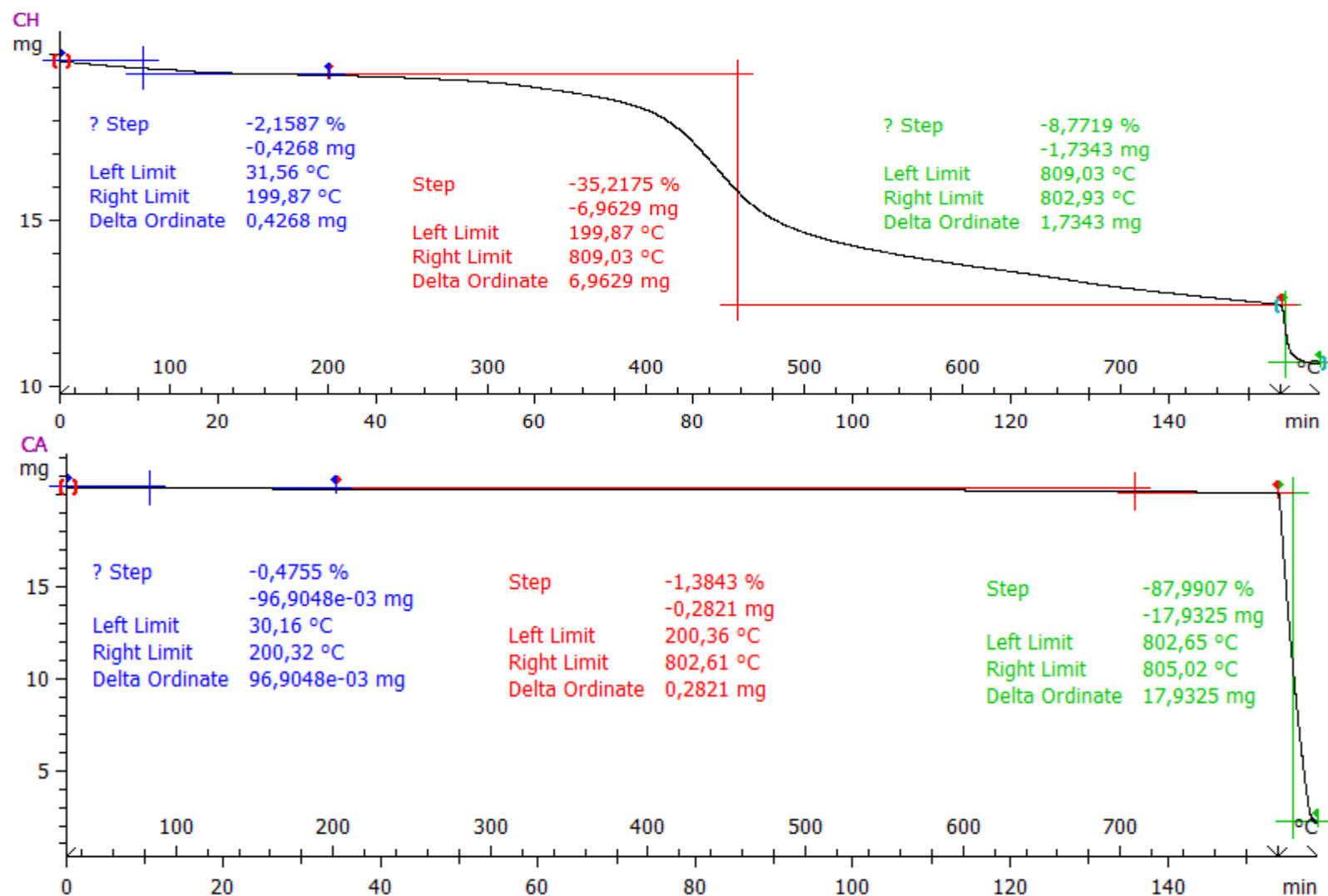
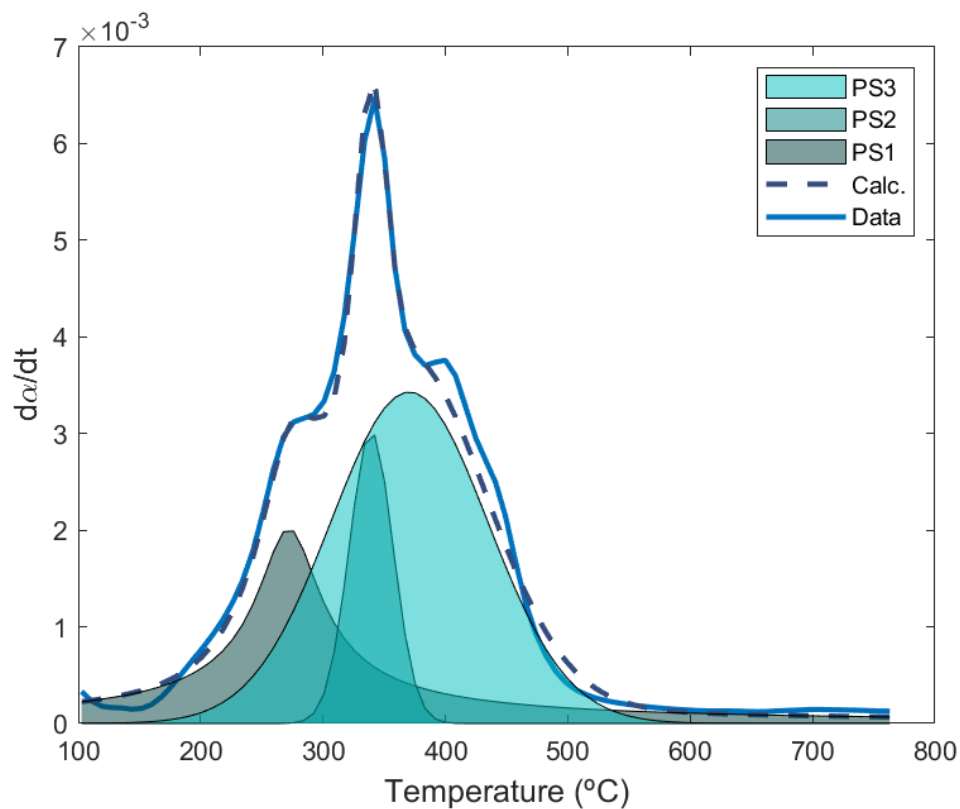
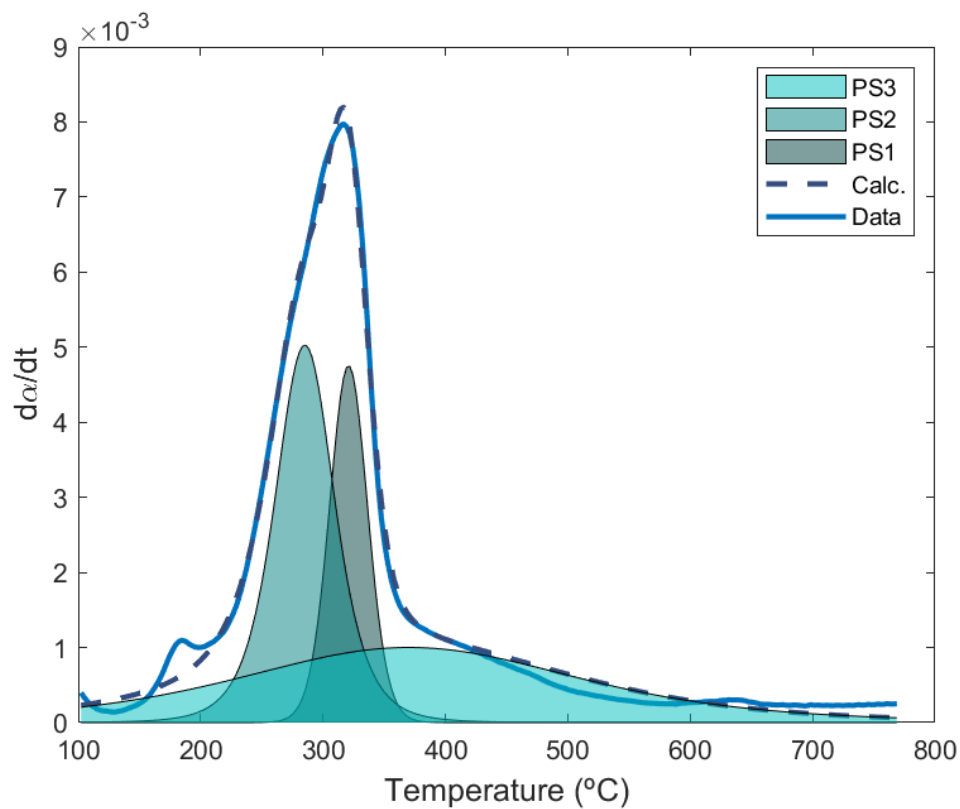
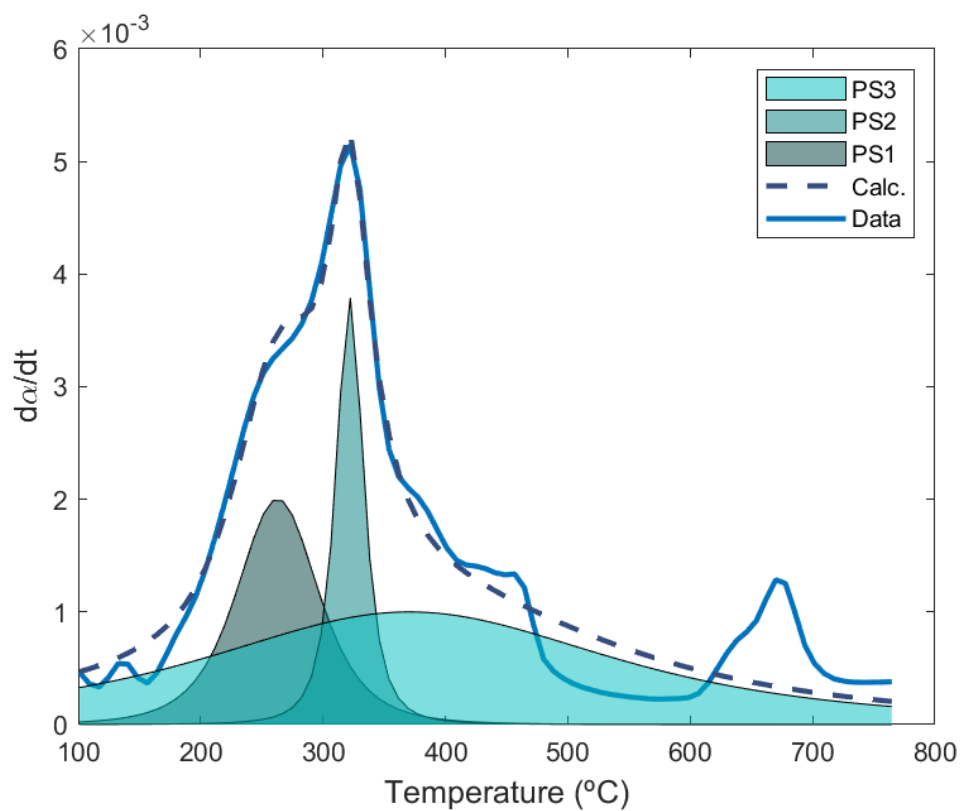
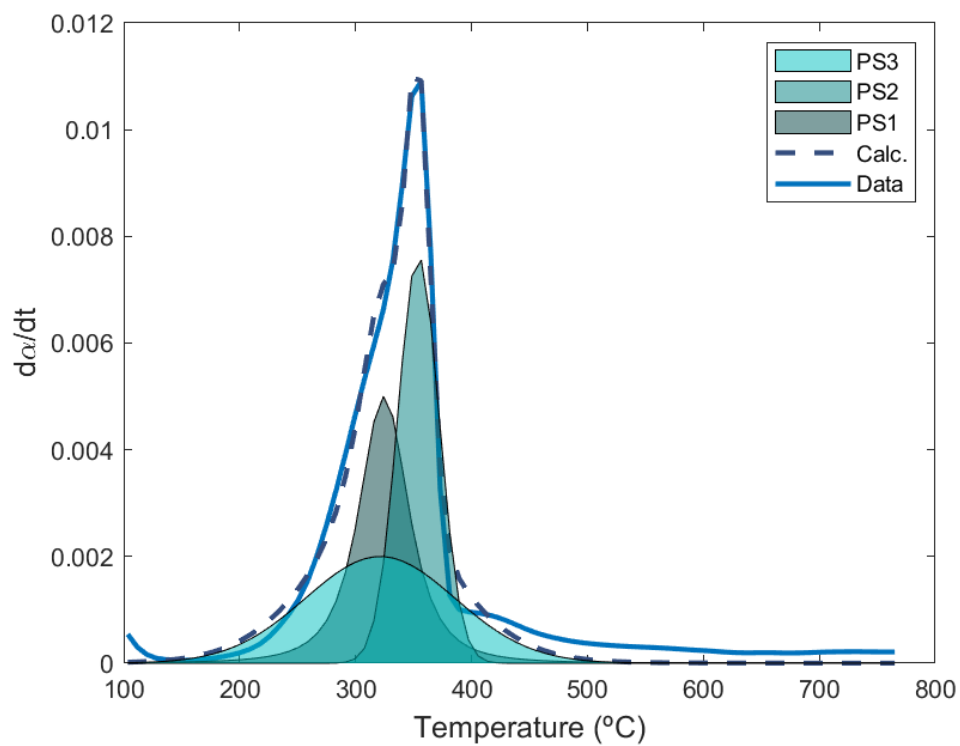


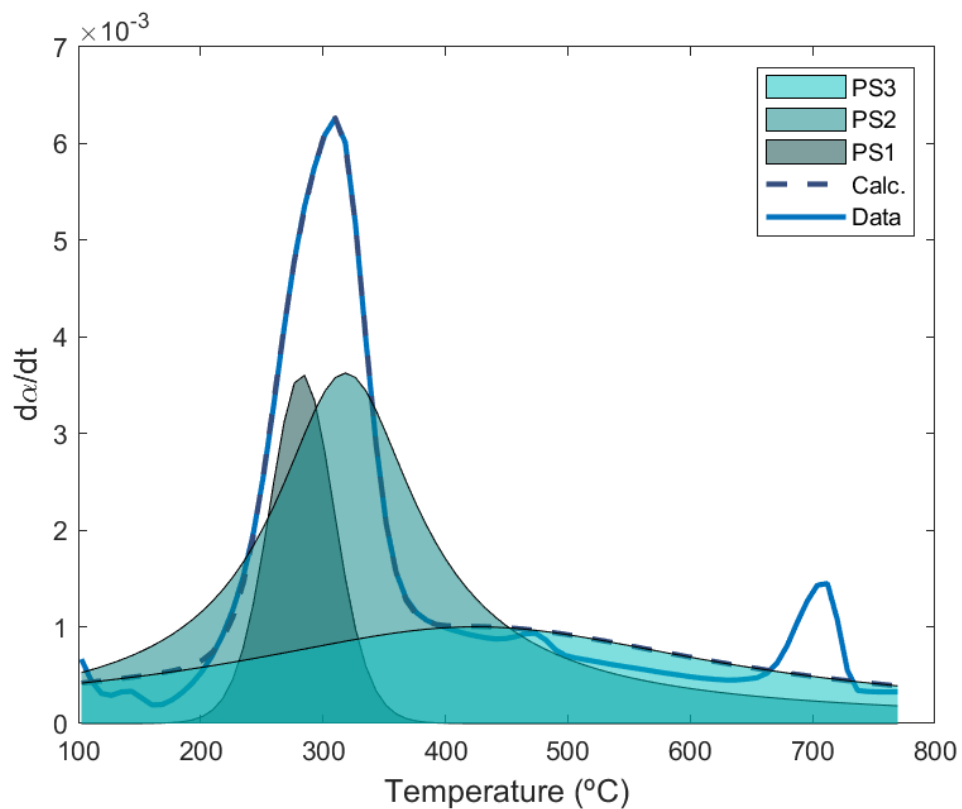
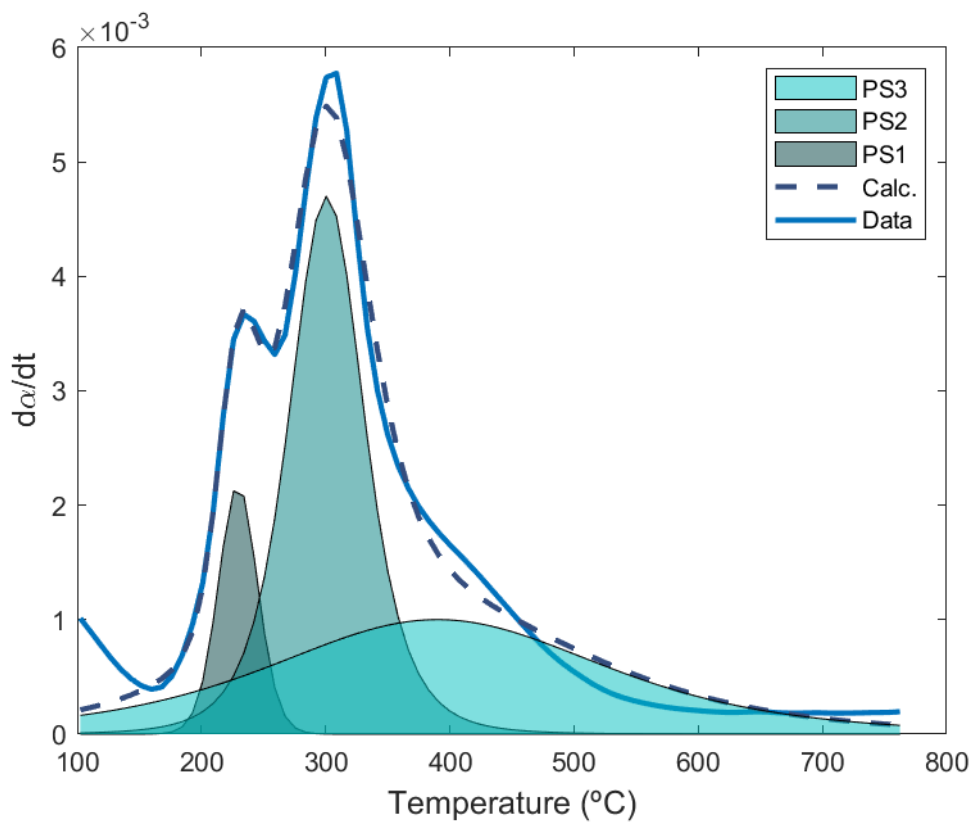
Figure AP 2.5 CH and CA thermogravimetric approach graphs for proximate analysis

Appendix 3

Fraser Suzuki Graphs

**Figure AP 3.1.** BPA Fraser Suzuki graph**Figure AP 3.2.** BCA Fraser Suzuki graph

**Figure AP 3.3.** BHO Fraser Suzuki graph**Figure AP 3.4.** BPM Fraser Suzuki graph

**Figure AP 3.5.** BP Fraser Suzuki graph**Figure AP 3.6.** BPS Fraser Suzuki graph

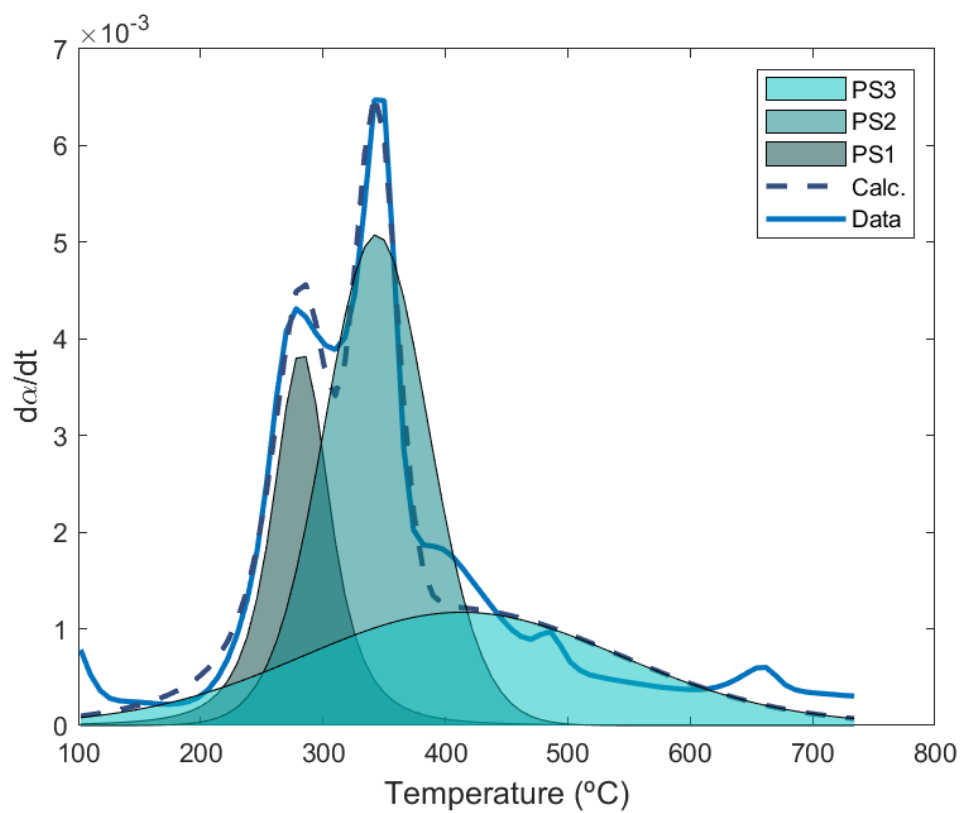


Figure AP 3.7. BPC Fraser Suzuki graph

Appendix 4

Thermogravimetric Index of Spontaneous Ignition

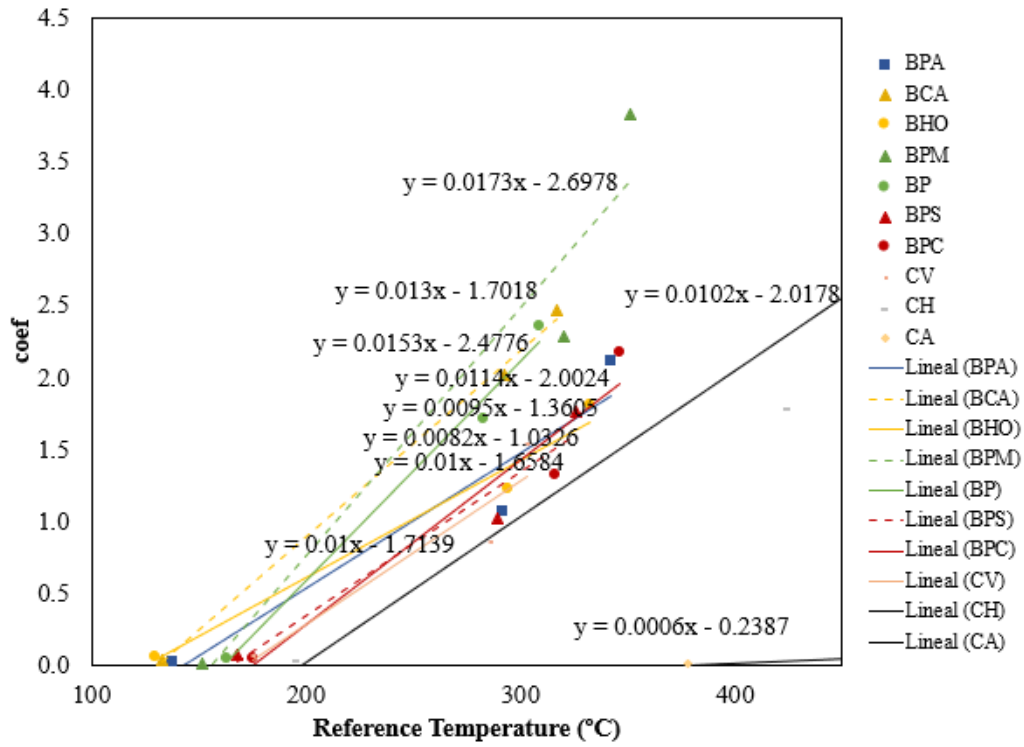


Figure AP 4.1. Coef vs. Reference temperature

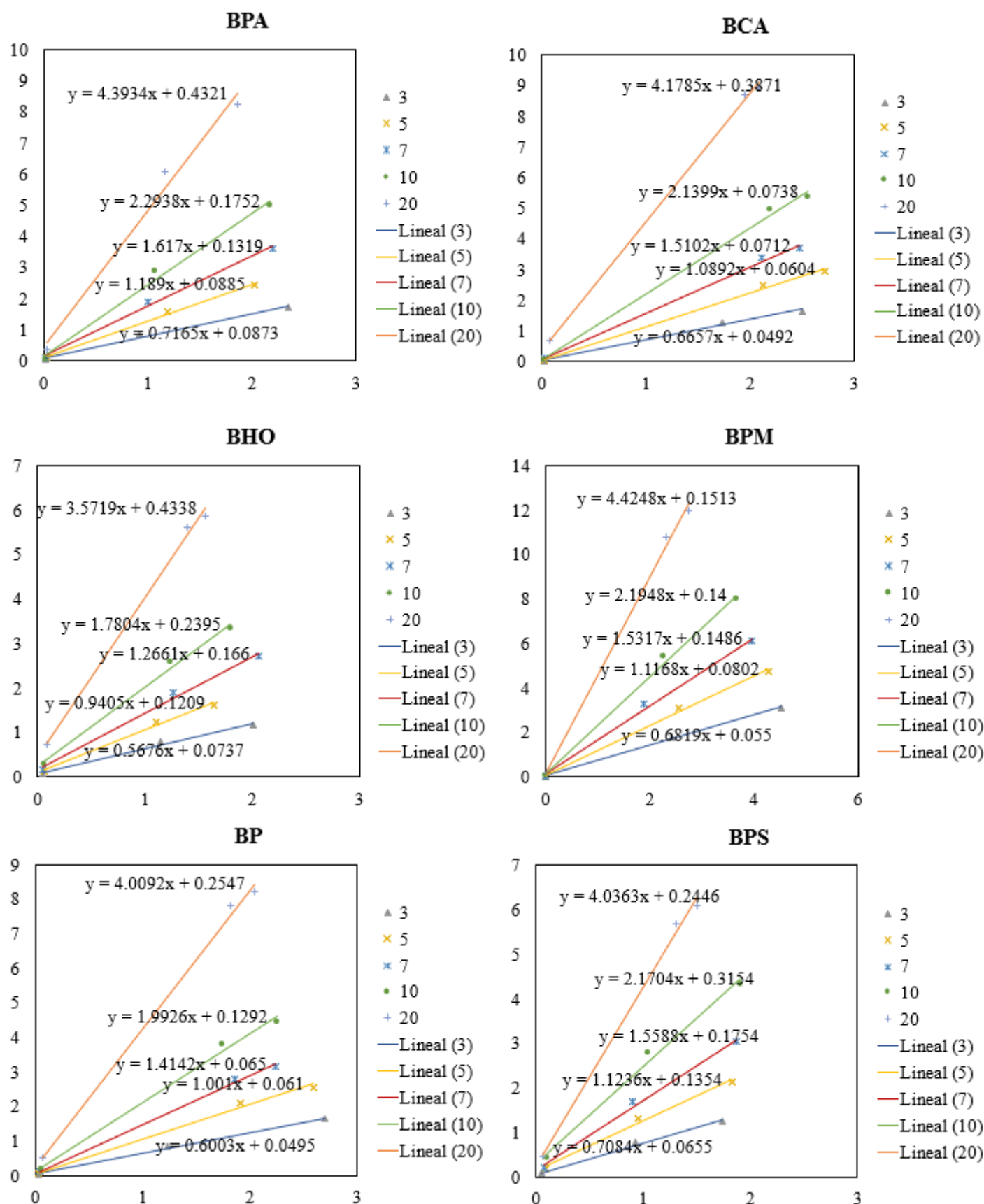


Figure AP 4.2. Linear regression for each sample and heating rate

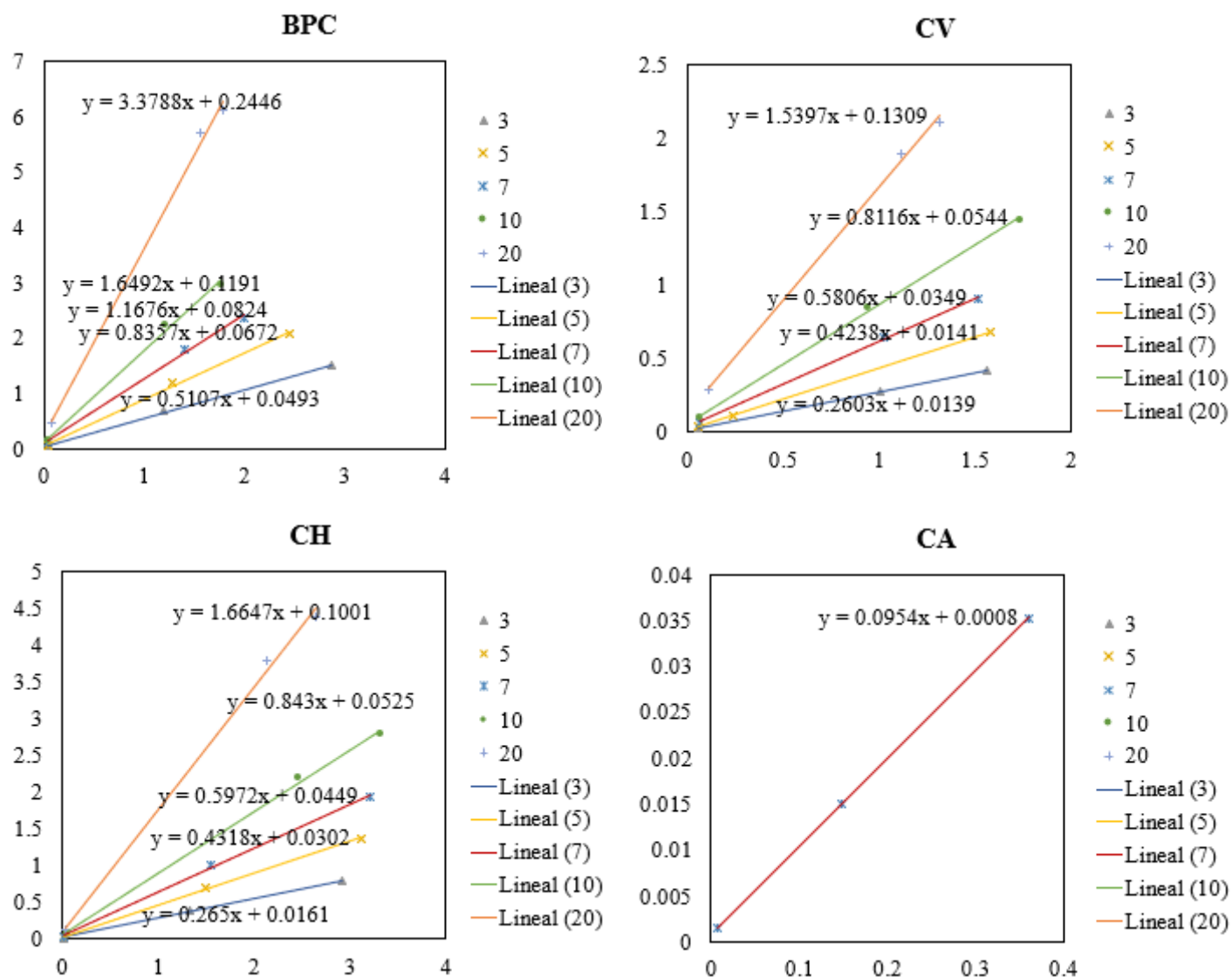


Figure AP 4.3. Linear regression for each sample and heating rate

Appendix 5

Thermal Degradation Kinetic and Thermodynamic Graphs

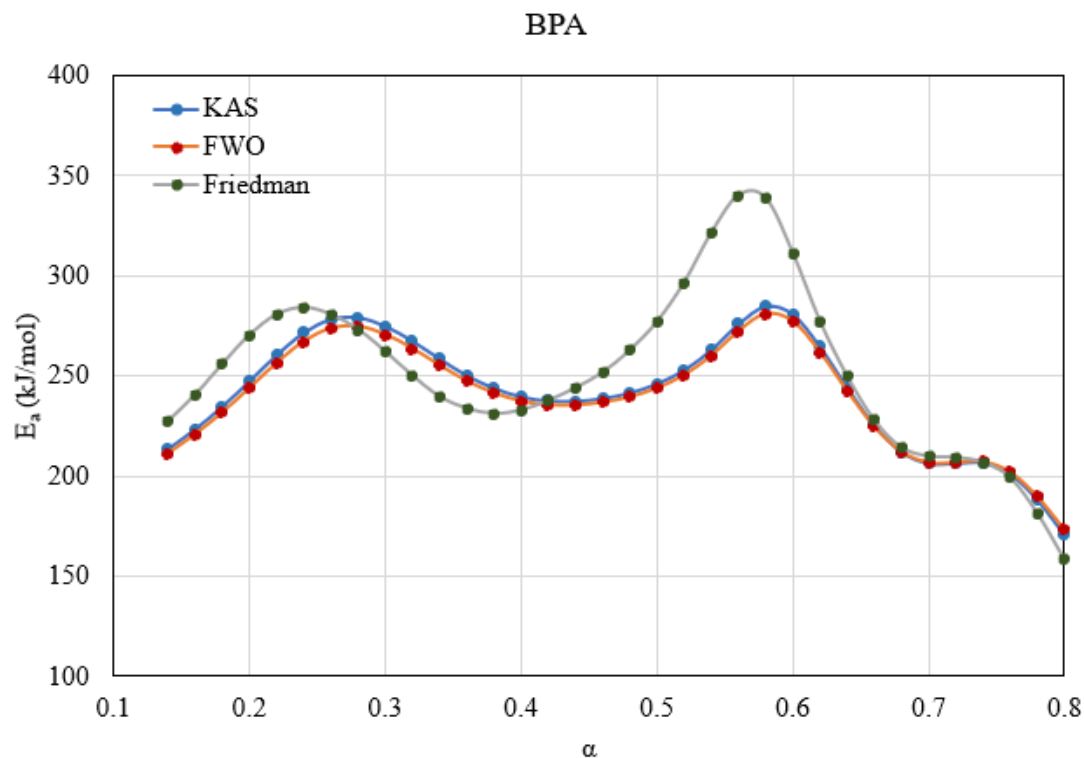


Figure AP 5.1. BPA E_a curves for each method

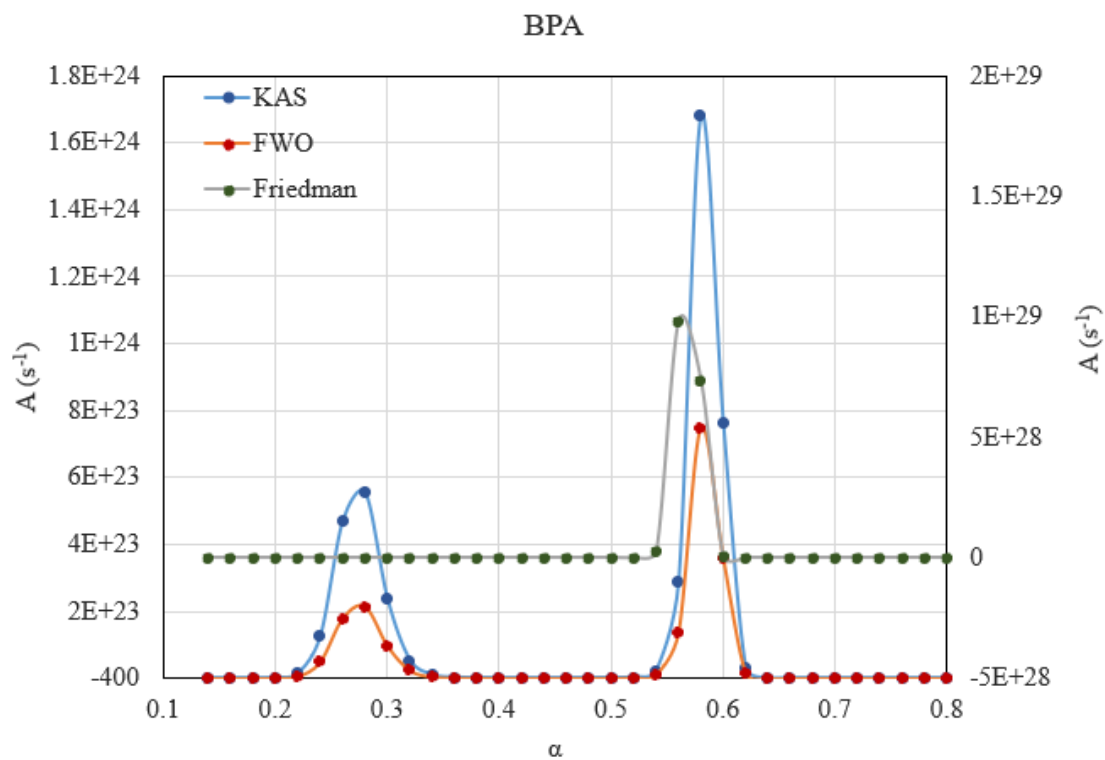


Figure AP 5.2. BPA pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

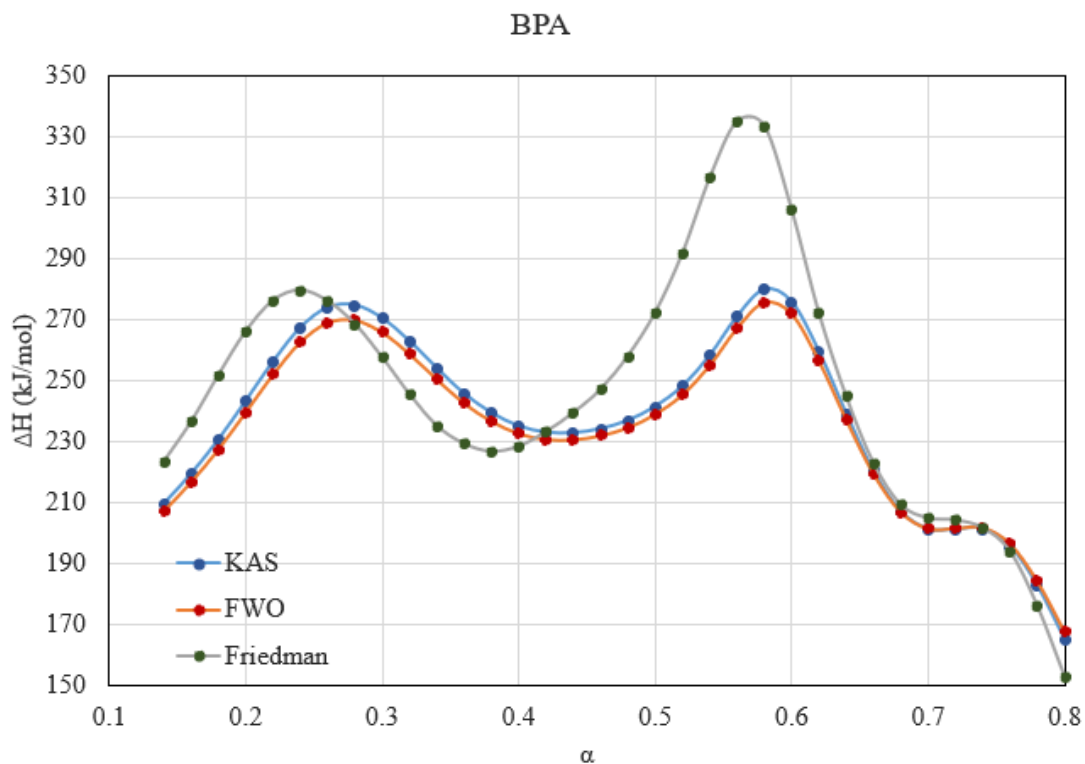


Figure AP 5.3. BPA ΔH curves for each method

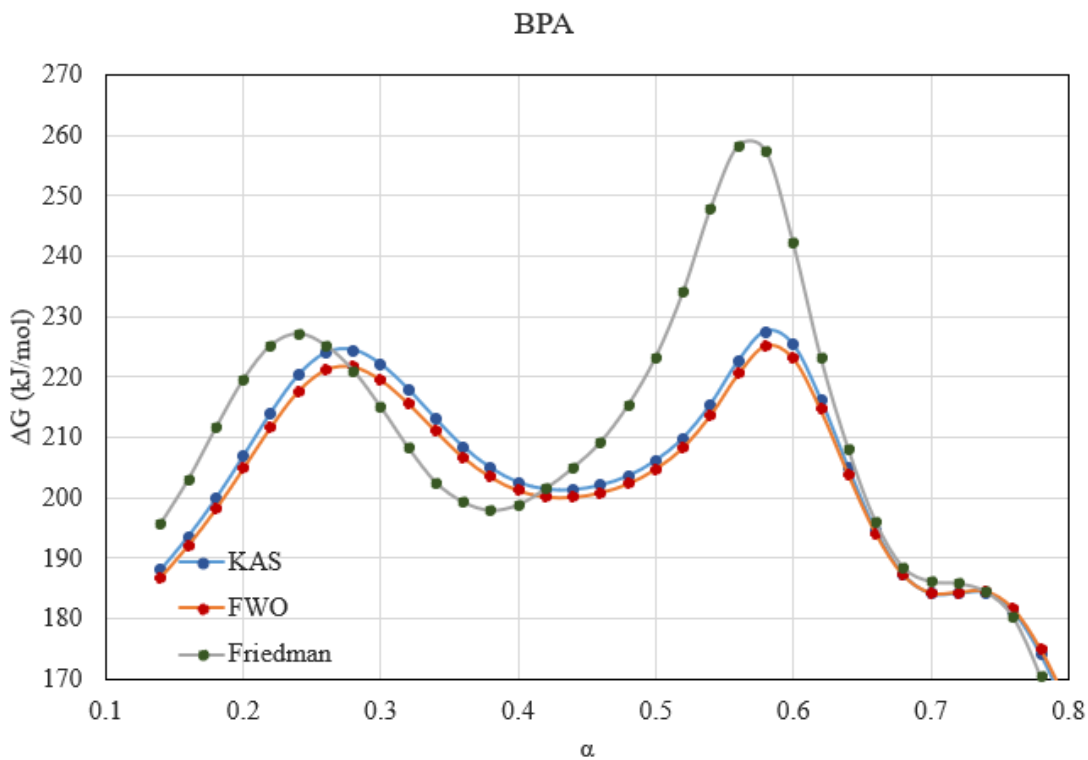


Figure AP 5.4. BPA ΔG curves for each method

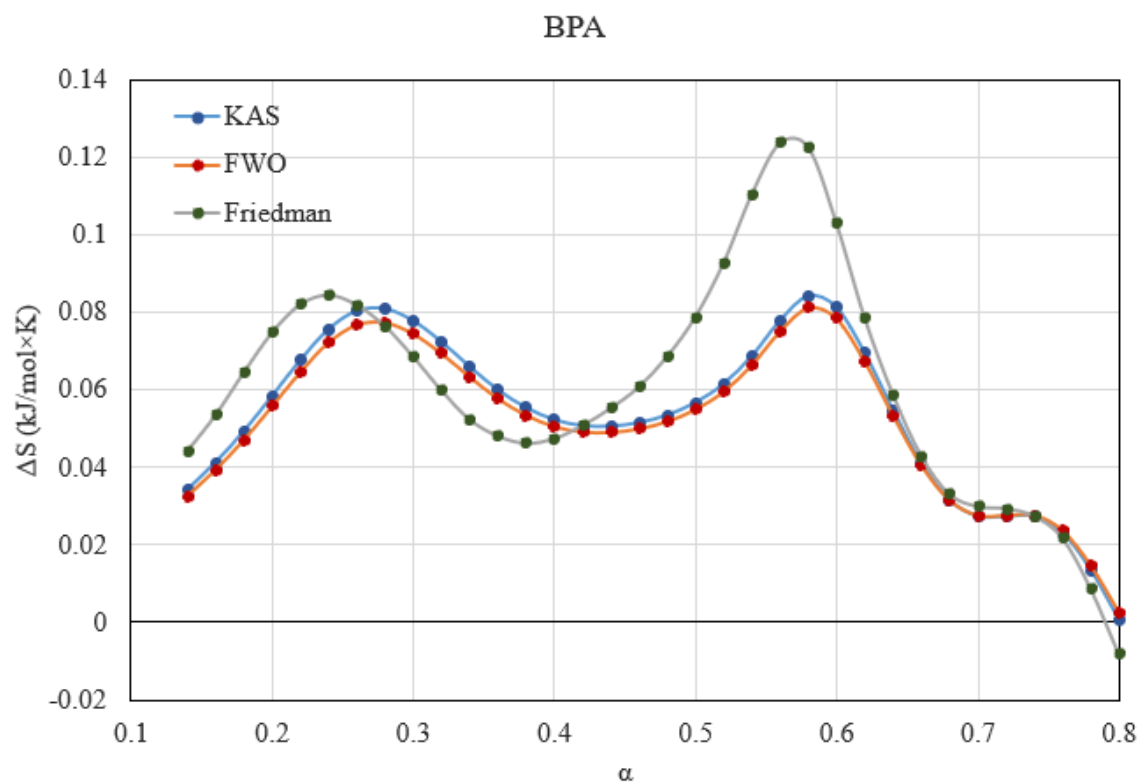


Figure AP 5.5. BPA ΔS curves for each method

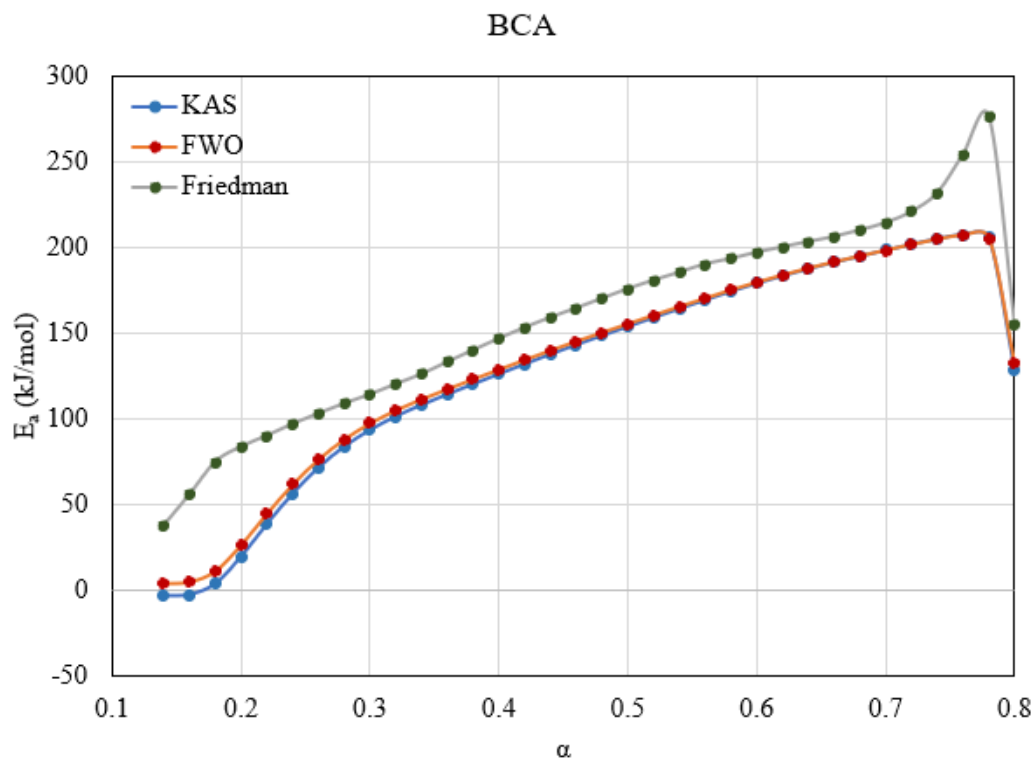


Figure AP 5.6. BCA E_a curves for each method

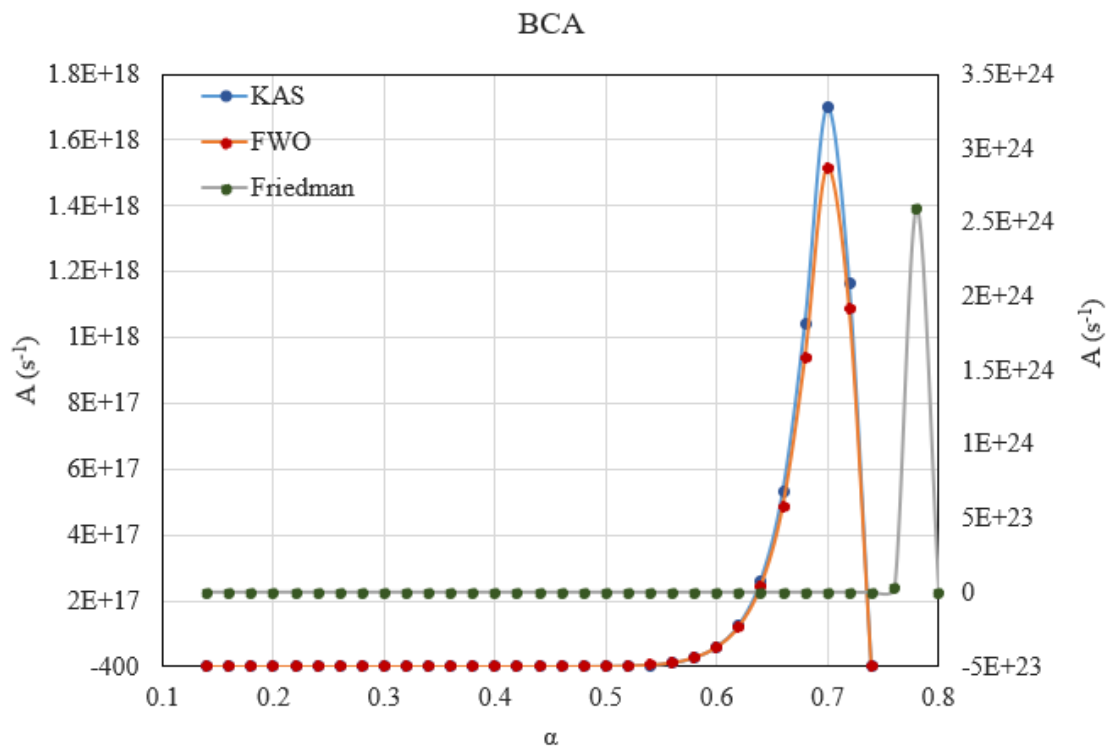


Figure AP 5.7. BCA pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

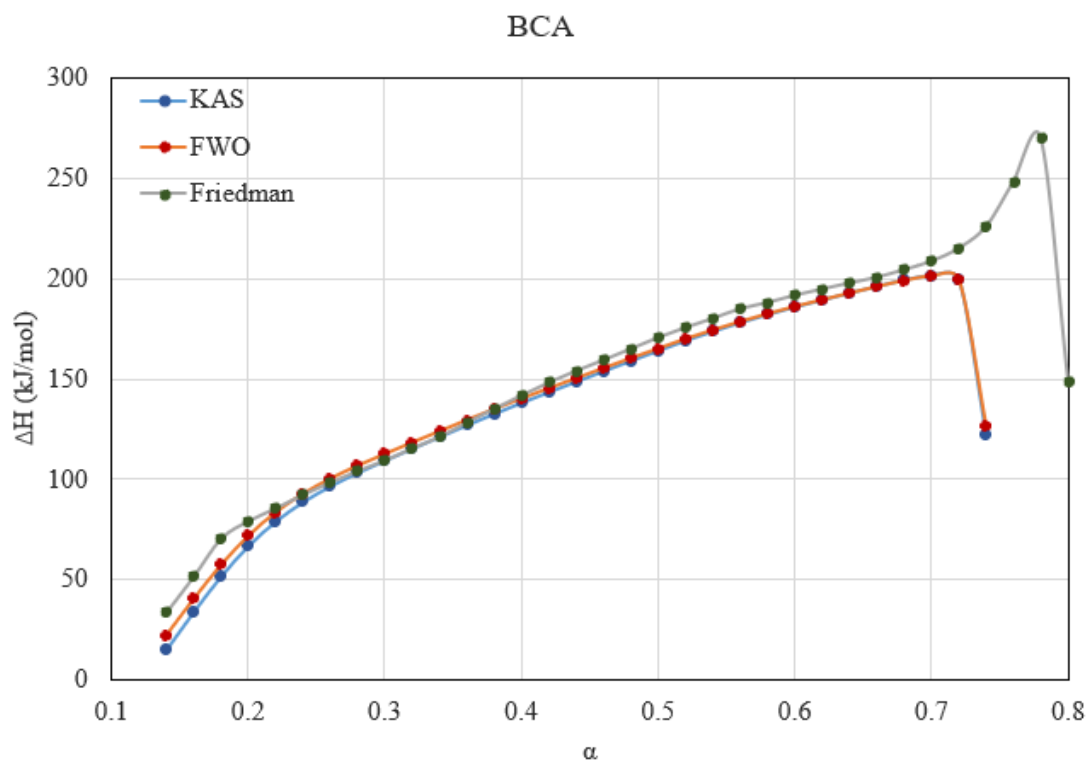


Figure AP 5.8. BCA ΔH curves for each method

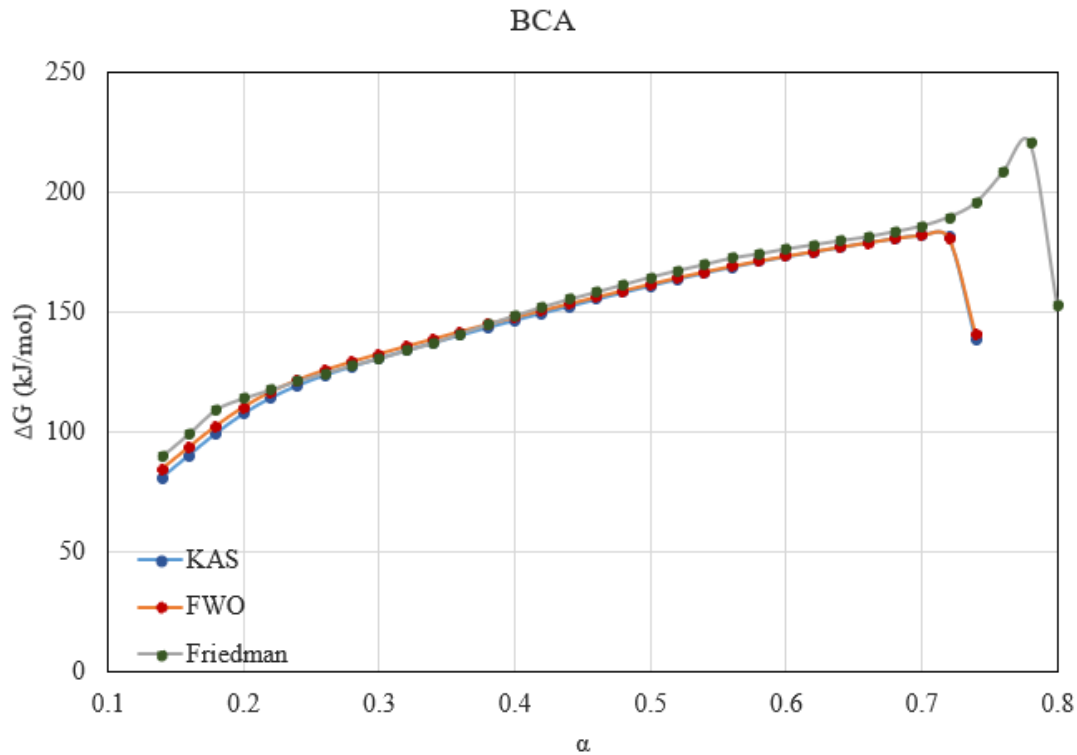


Figure AP 5.9. BCA ΔG curves for each method

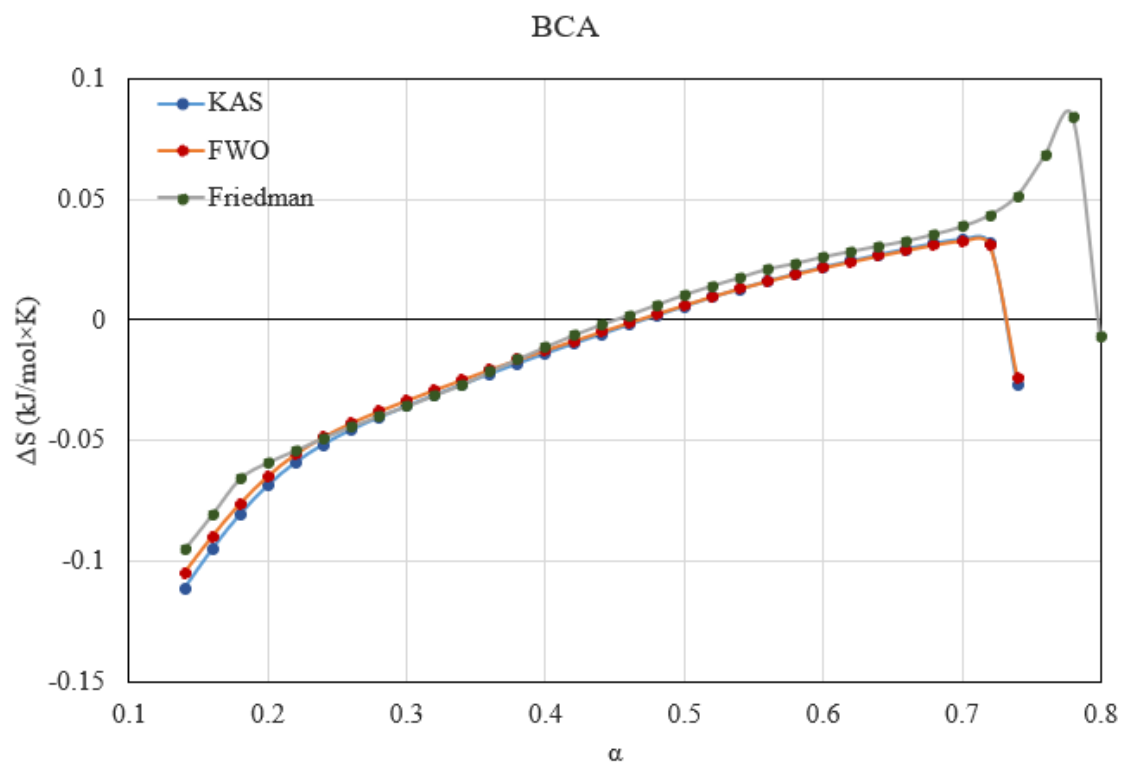


Figure AP 5.10. BCA ΔS curves for each method

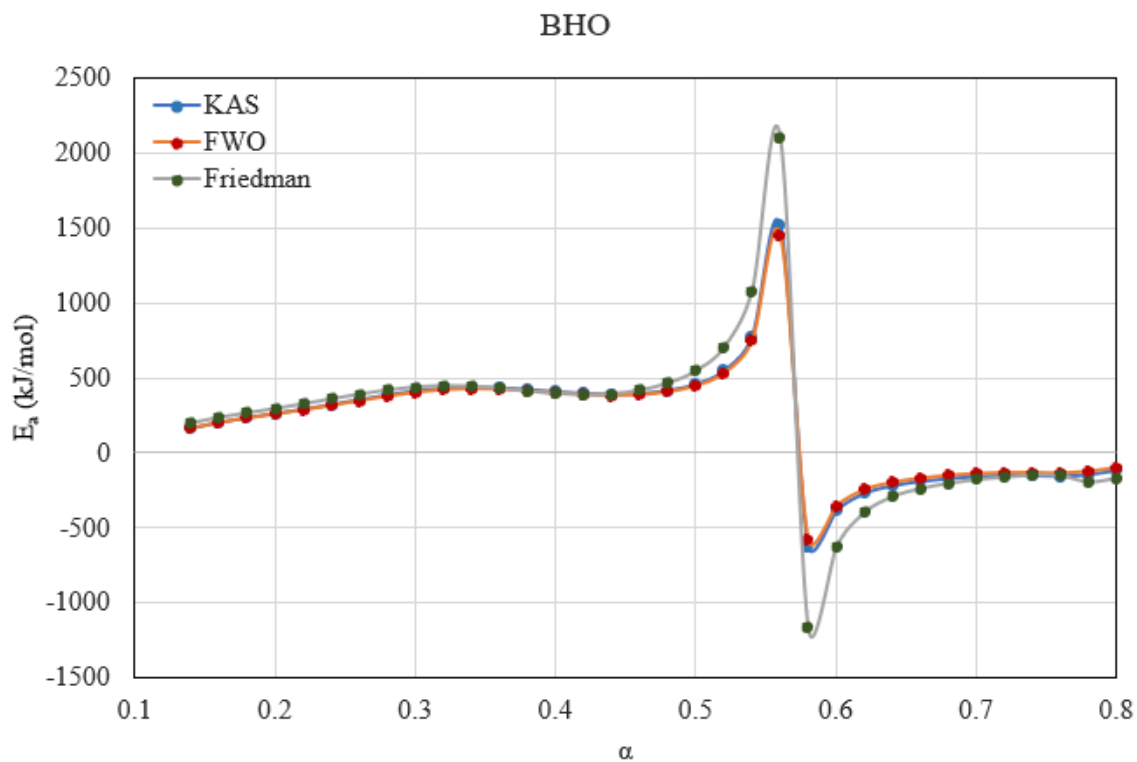


Figure AP 5.11. BHO E_a curves for each method

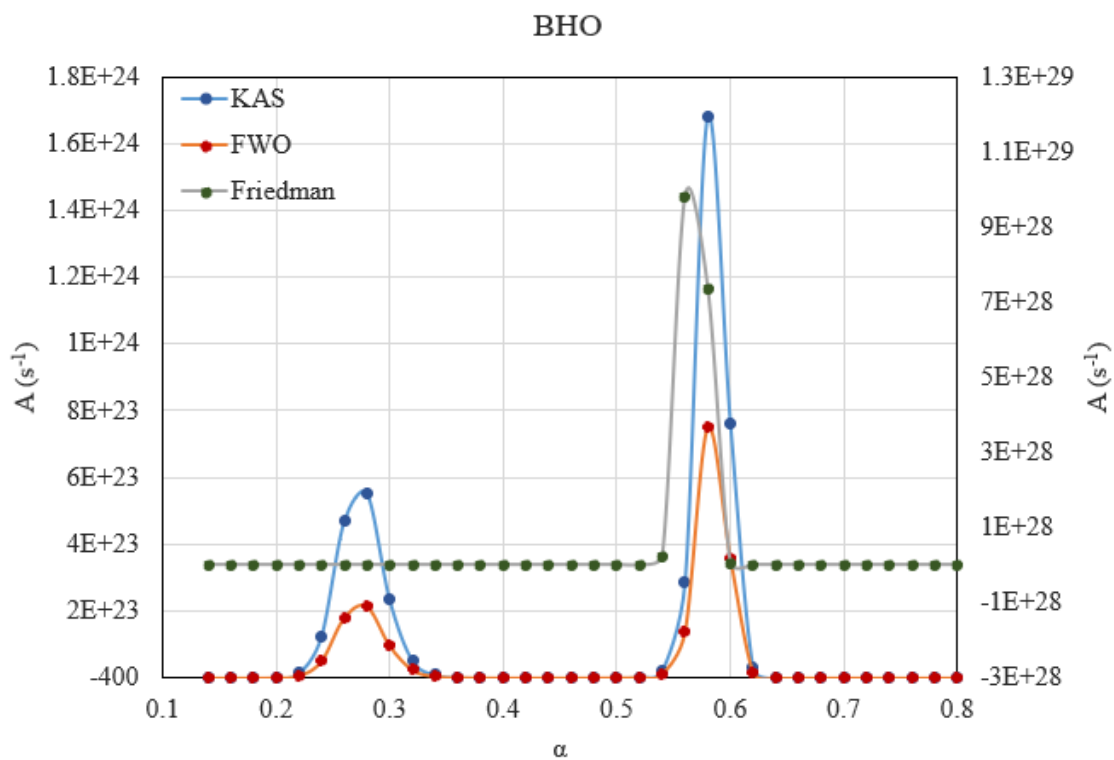


Figure AP 5.12. BHO pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

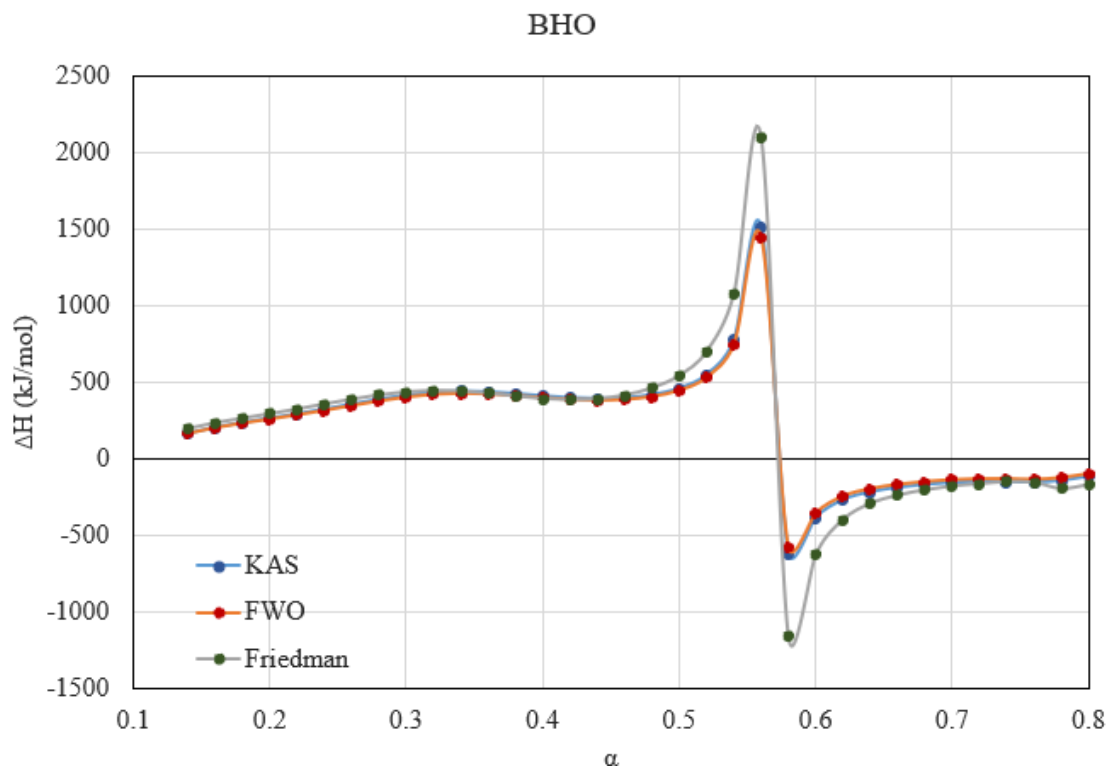


Figure AP 5.13. BHO ΔH curves for each method

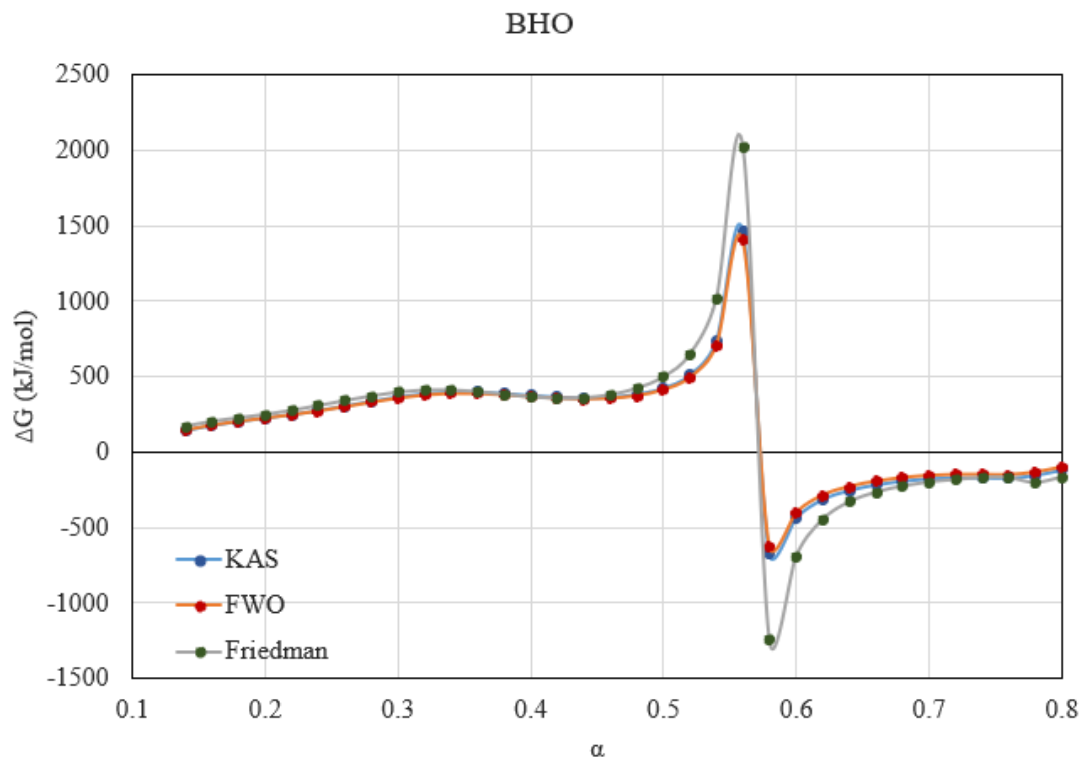


Figure AP 5.14. BHO ΔG curves for each method

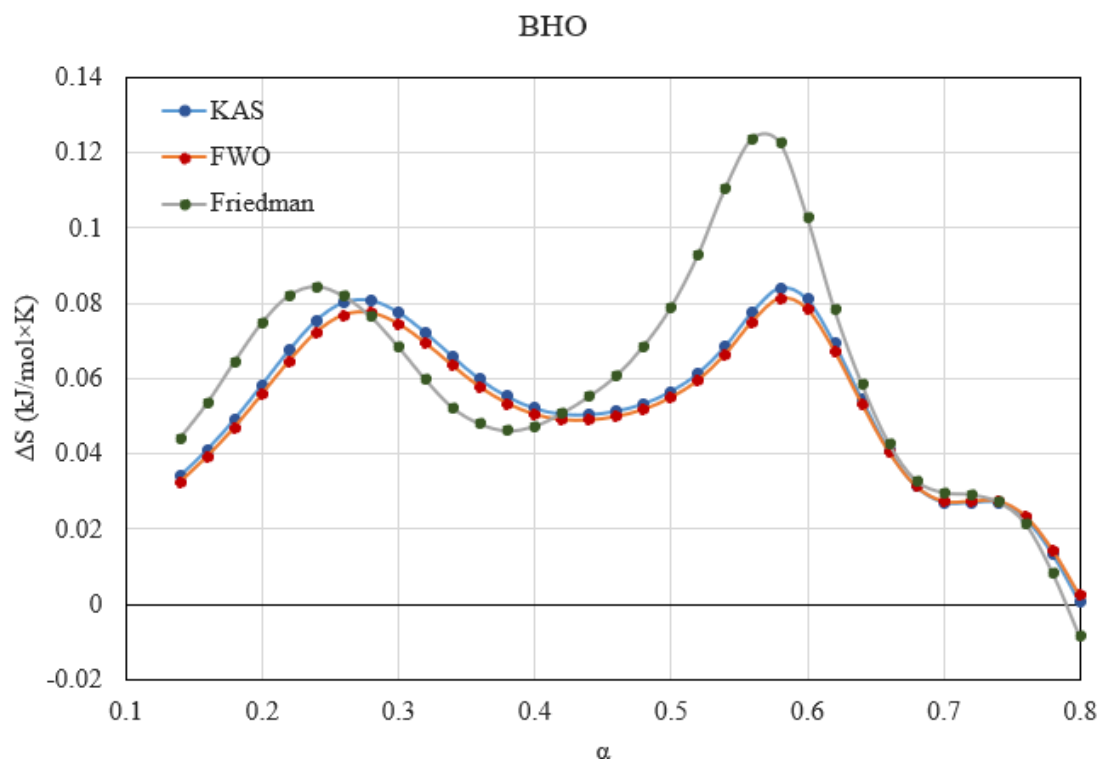


Figure AP 5.15. BHO ΔS curves for each method

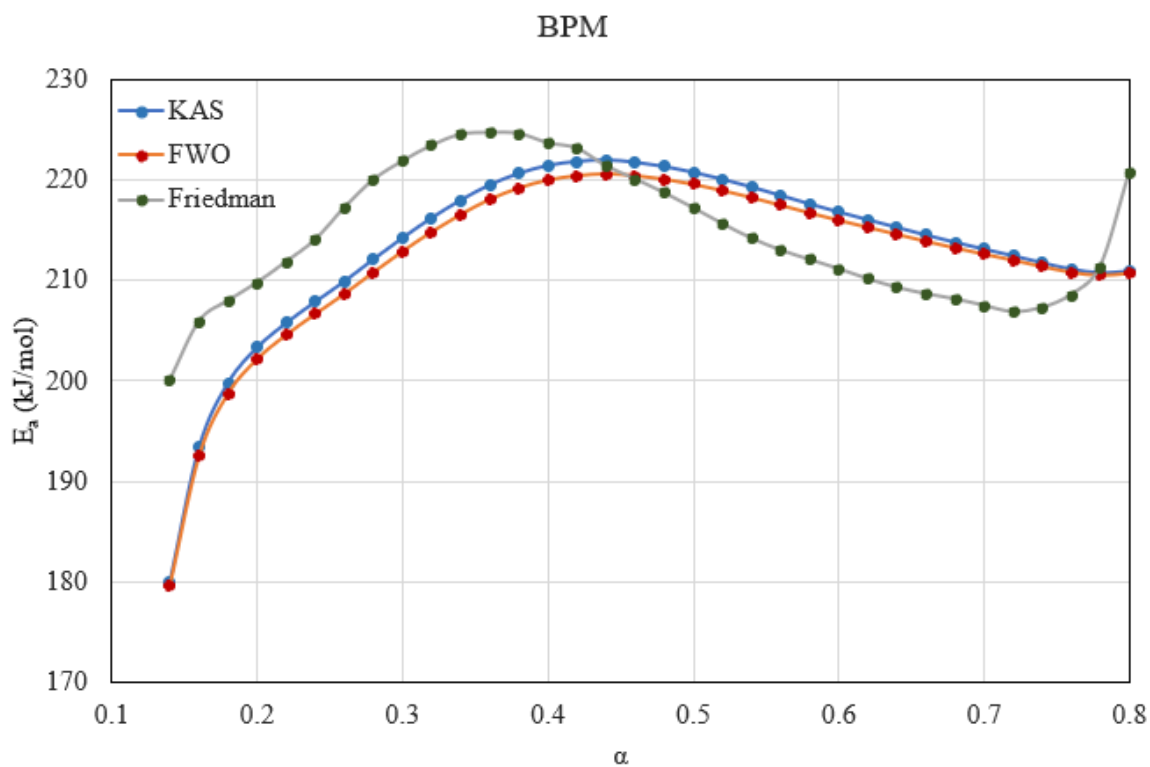


Figure AP 5.16. BPM E_a curves for each method

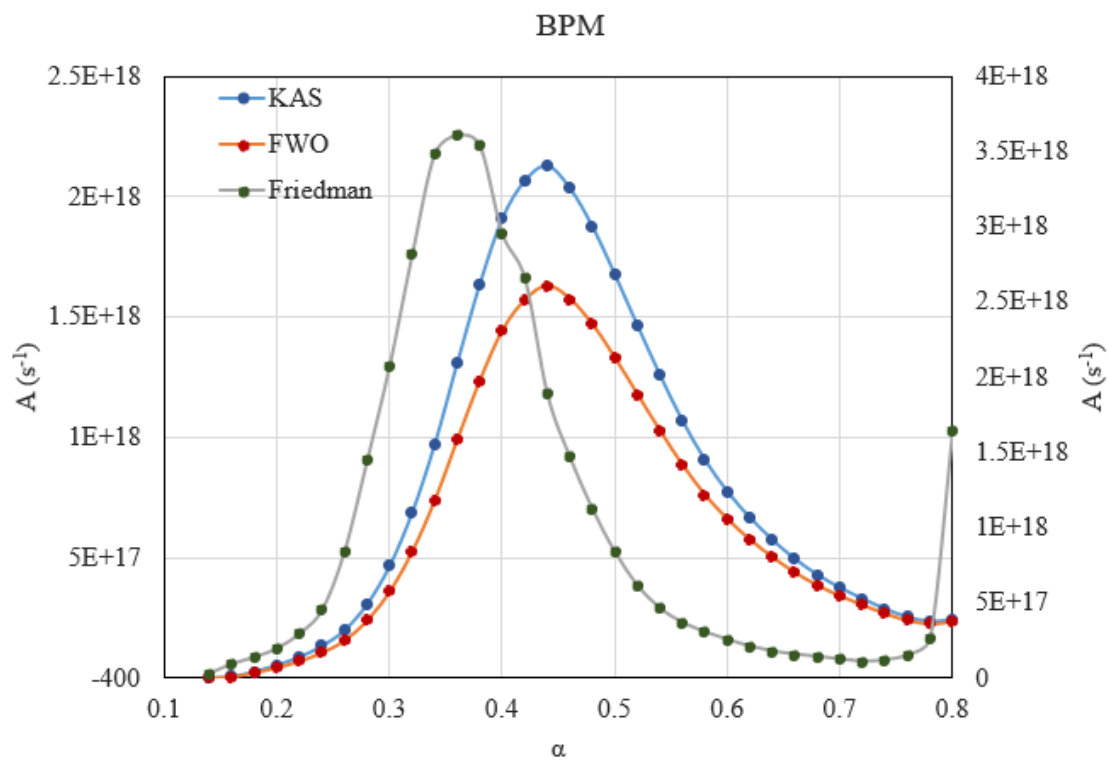


Figure AP 5.17. BPM pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

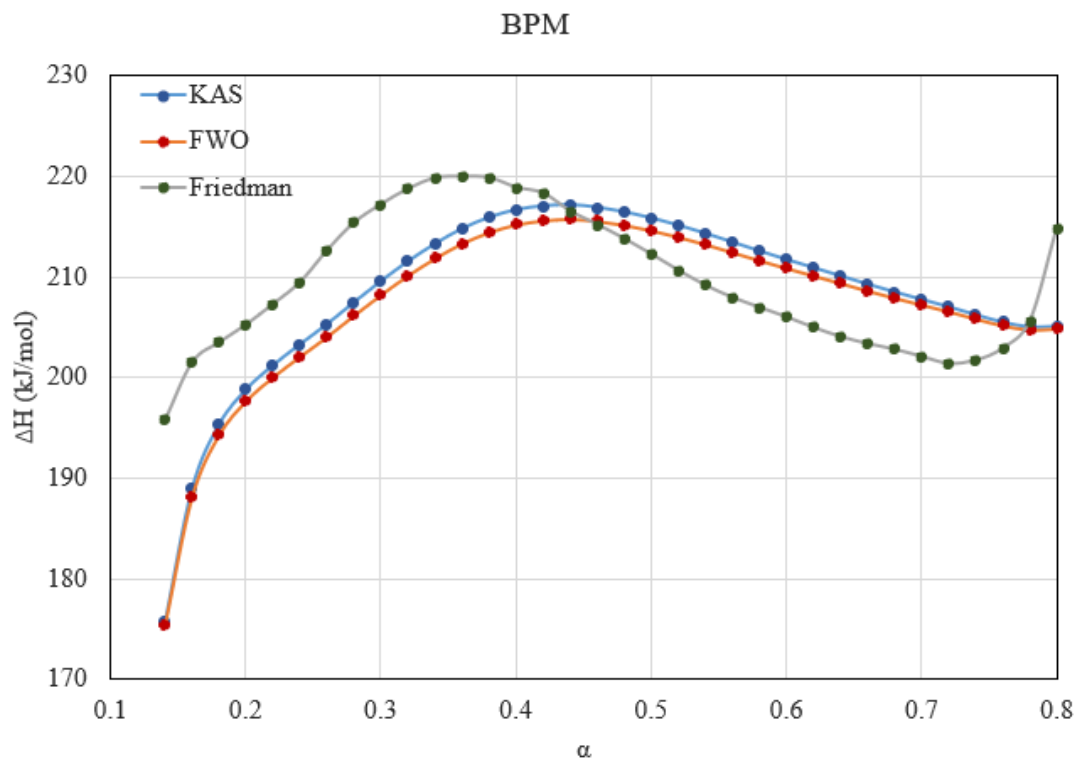


Figure AP 5.18. BPM ΔH curves for each method

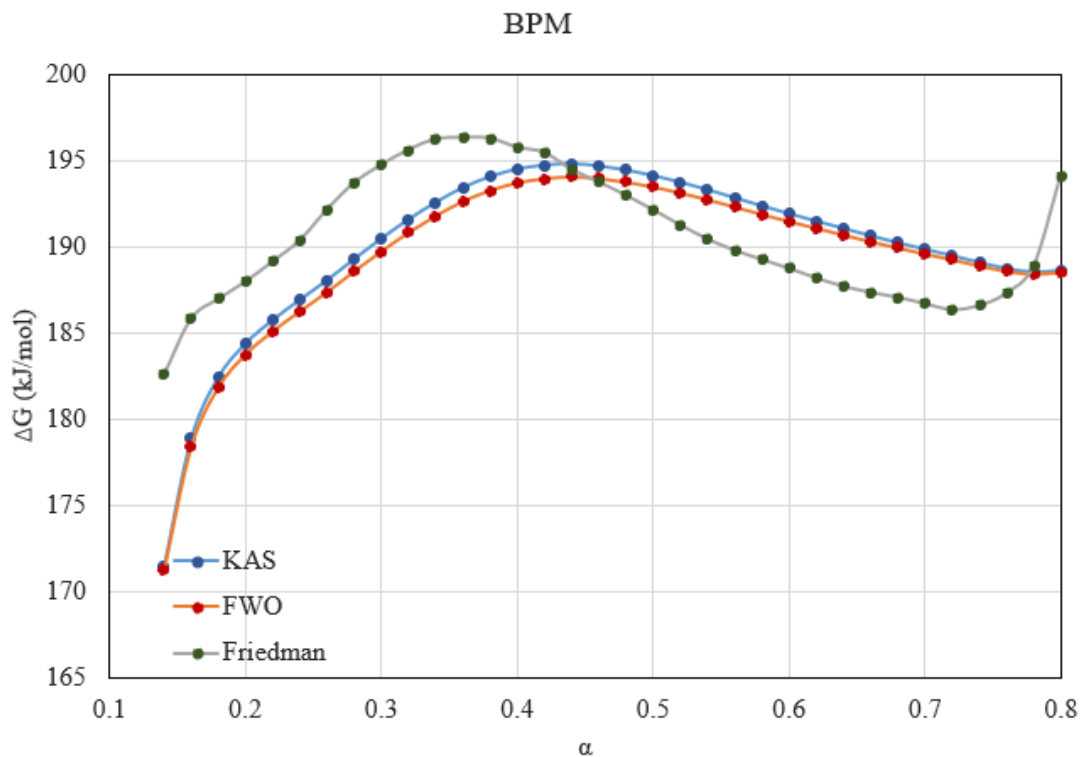


Figure AP 5.19. BPM ΔG curves for each method

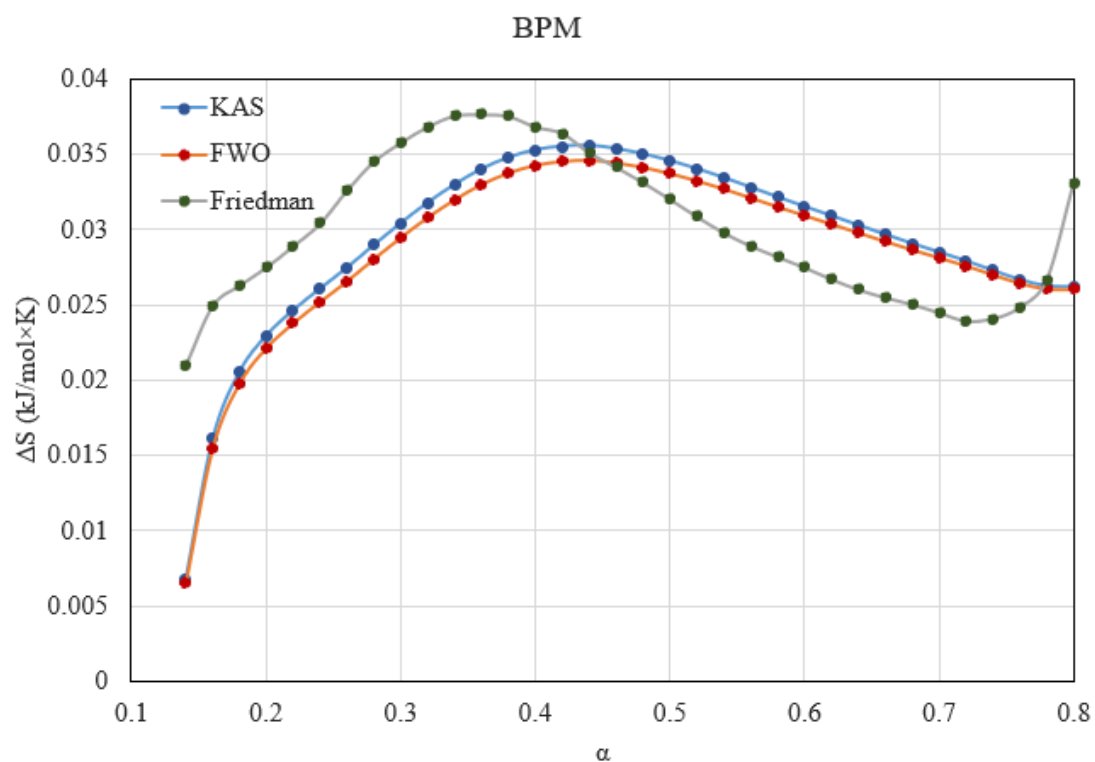


Figure AP 5.20. BPM ΔS curves for each method

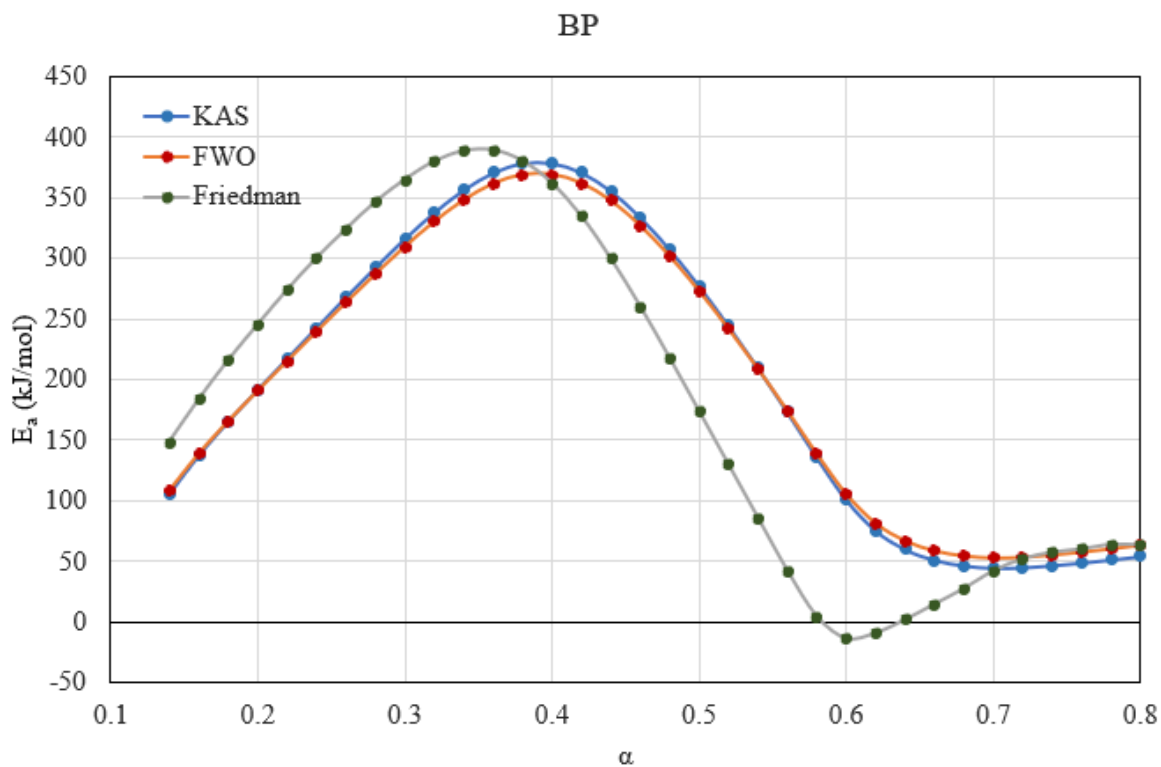


Figure AP 5.21. BP E_a curves for each method

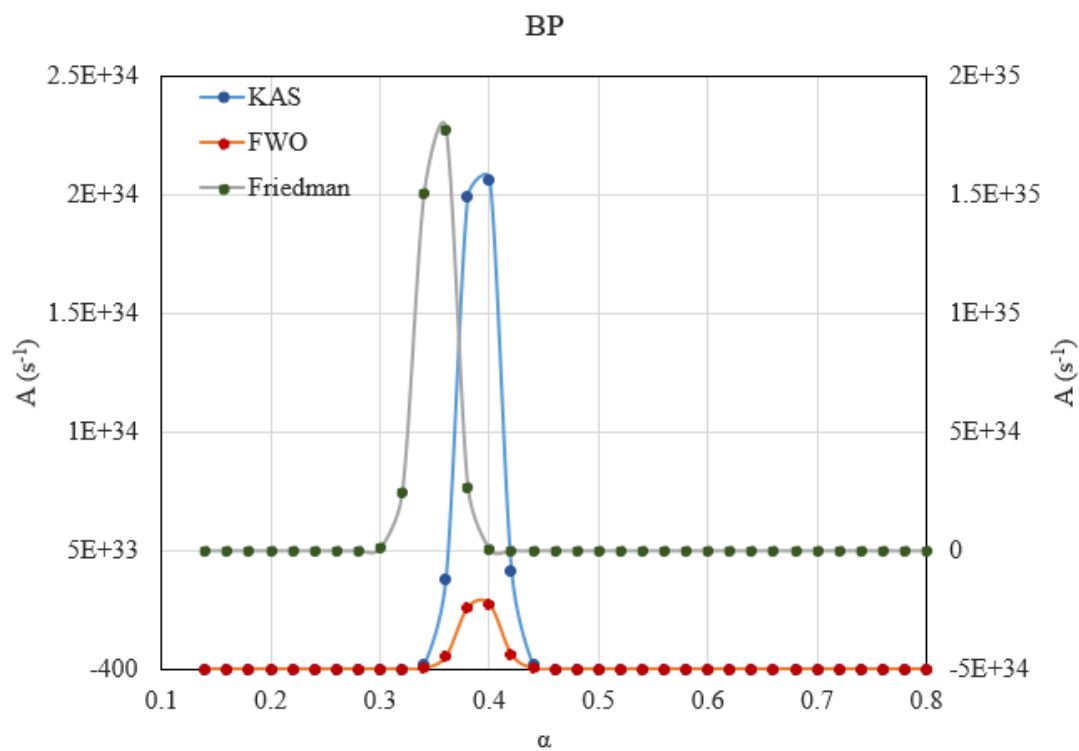


Figure AP 5.22. BP pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

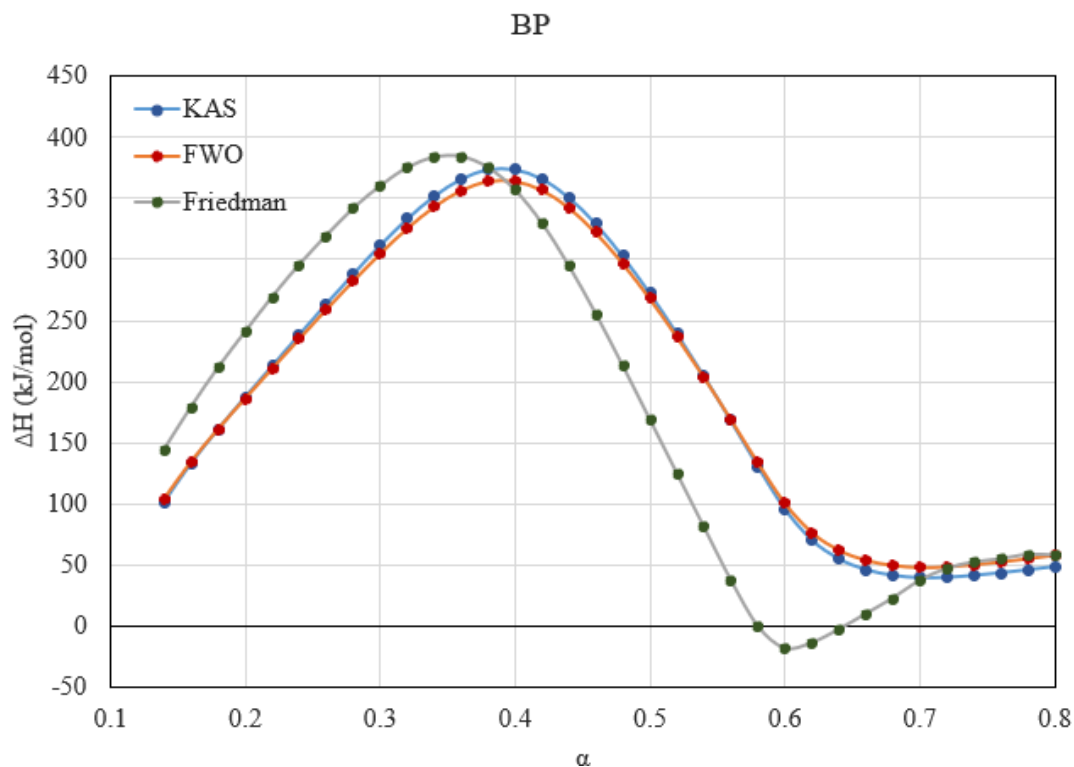


Figure AP 5.23. BP ΔH curves for each method

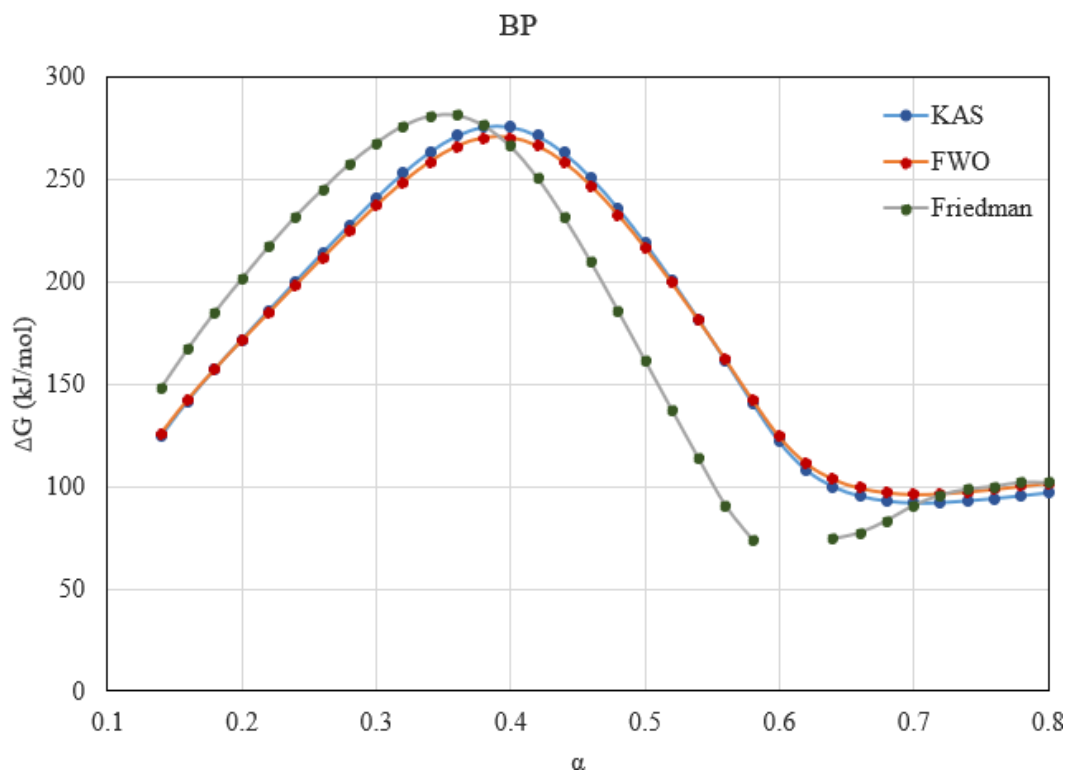


Figure AP 5.24. BP ΔG curves for each method

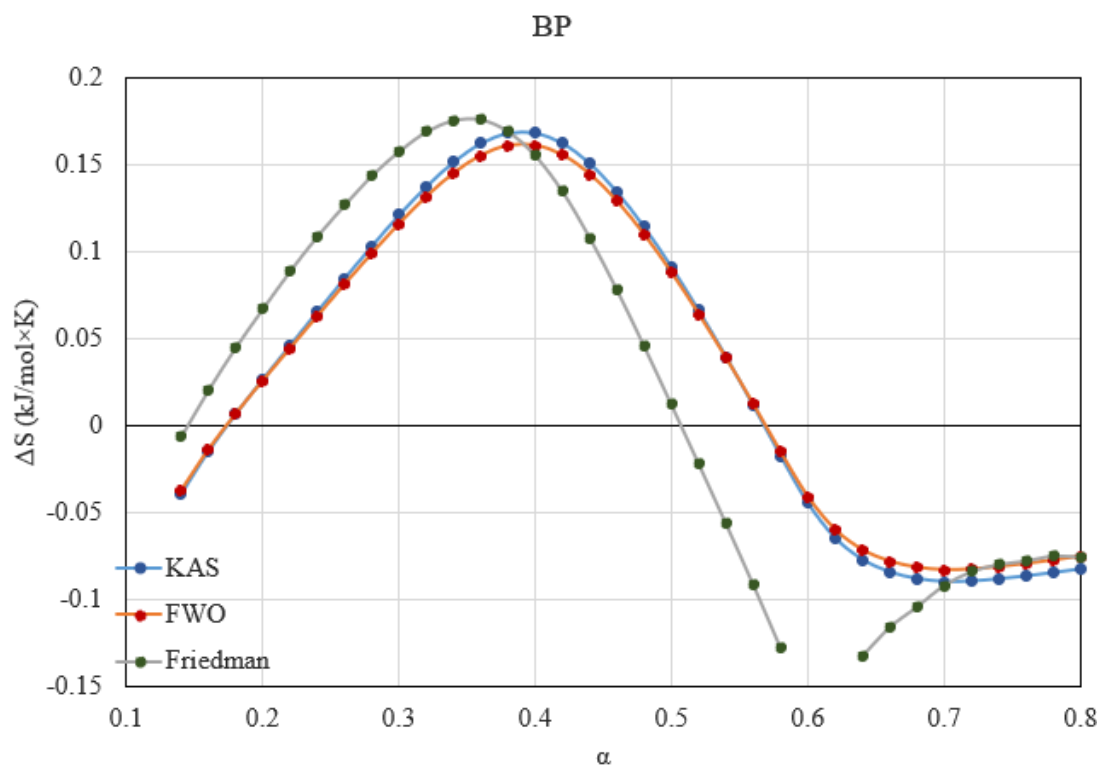


Figure AP 5.25. BP ΔS curves for each method

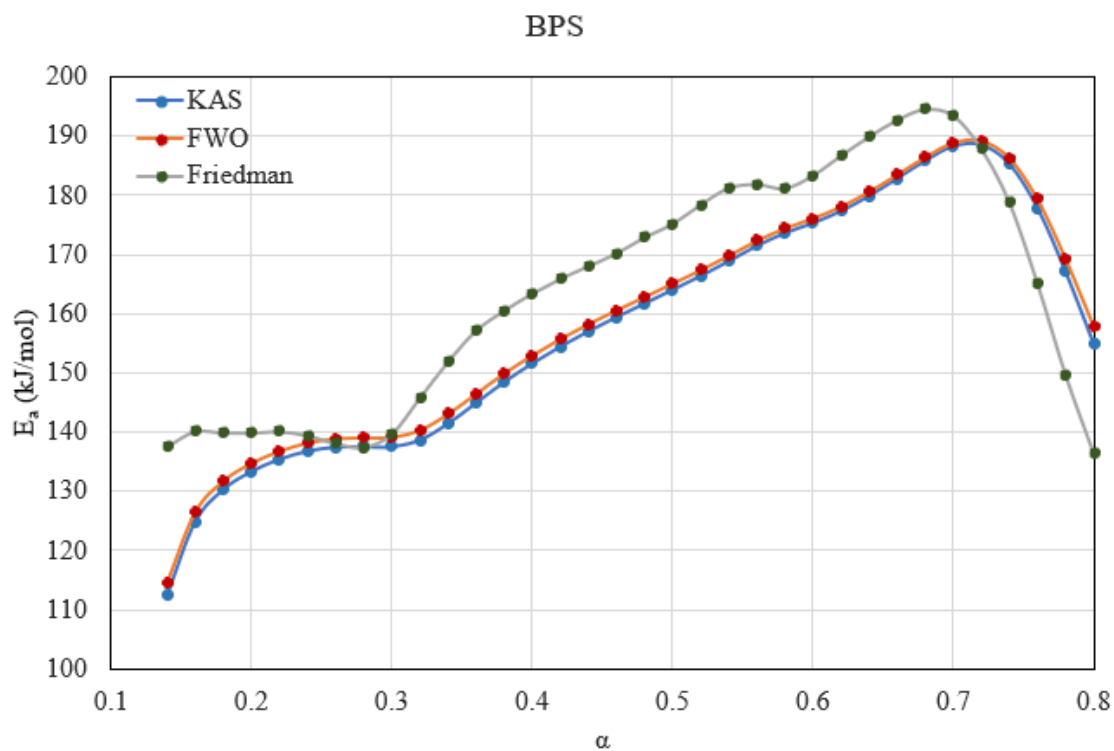


Figure AP 5.26. BPS E_a curves for each method

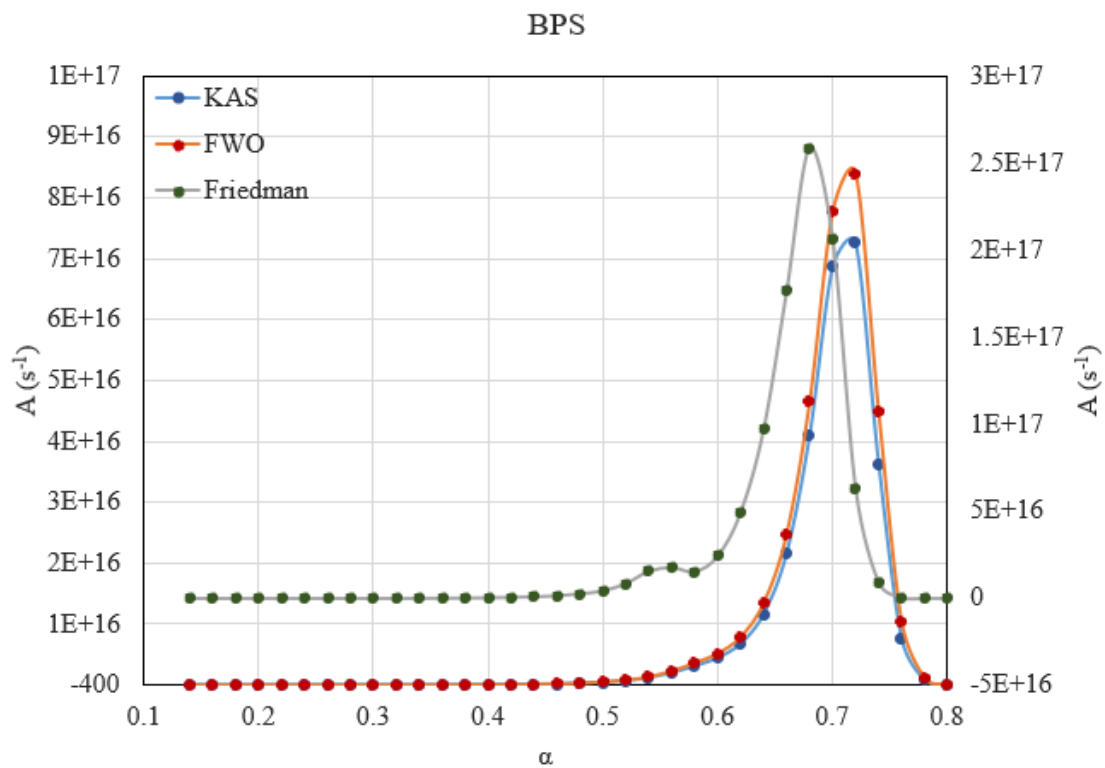


Figure AP 5.27. BPS pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

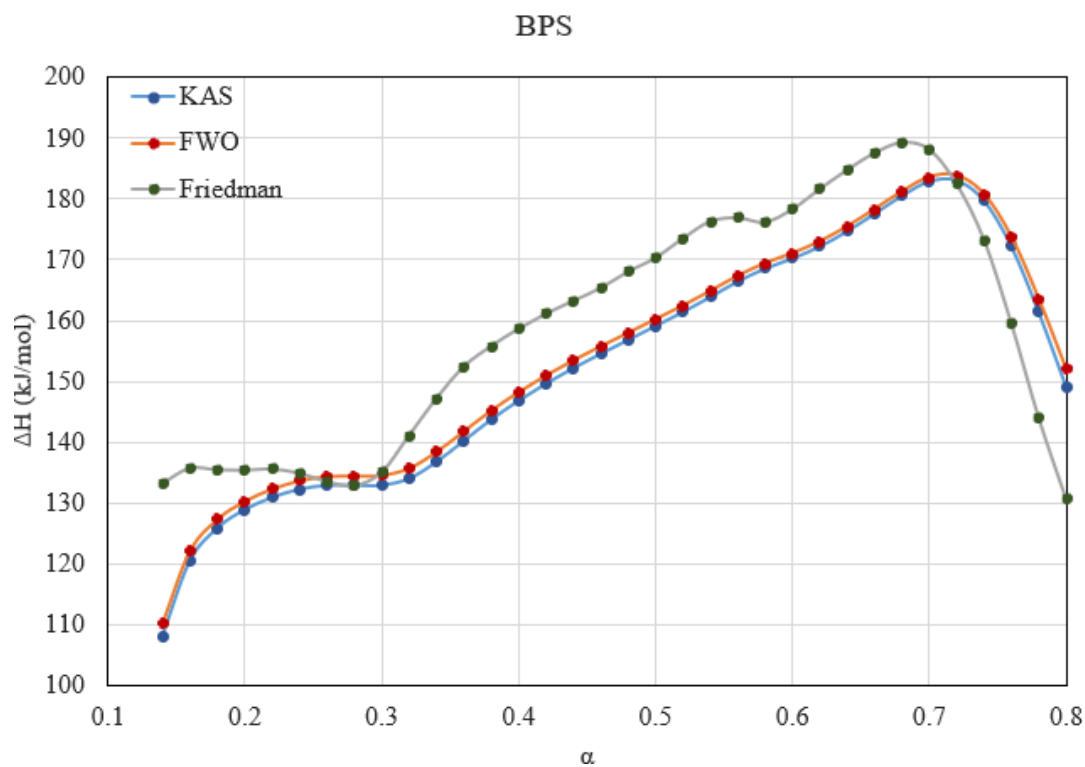


Figure AP 5.28. BPS ΔH curves for each method

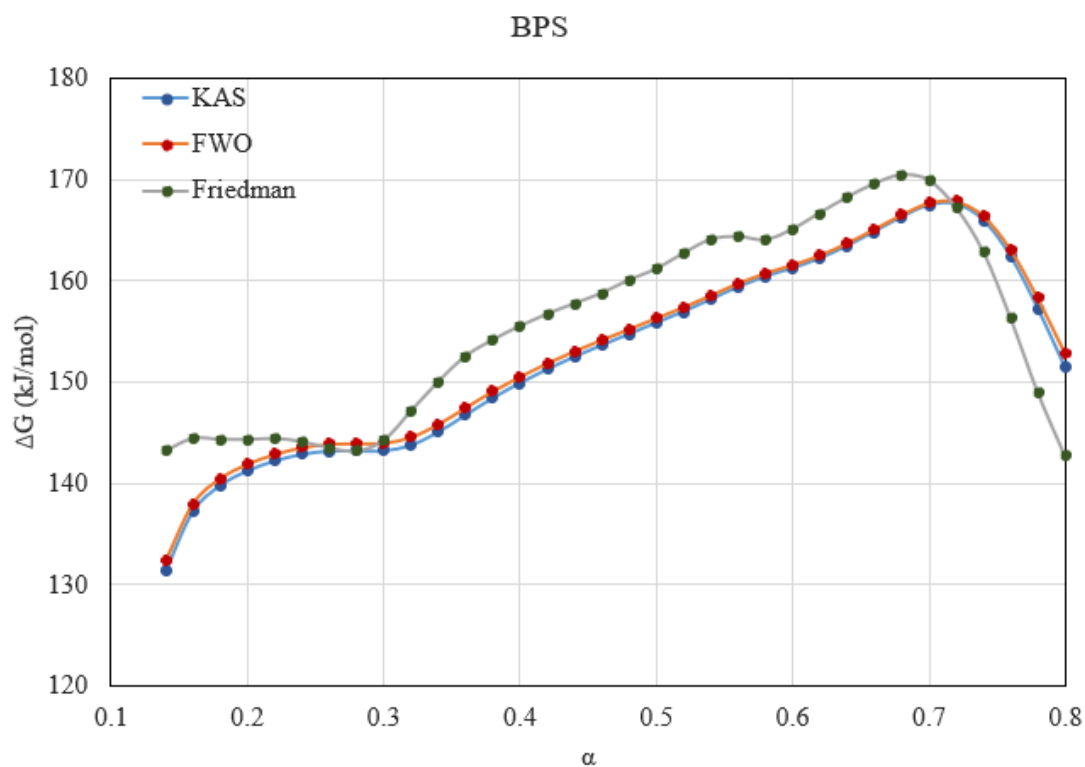


Figure AP 5.29. BPS ΔG curves for each method

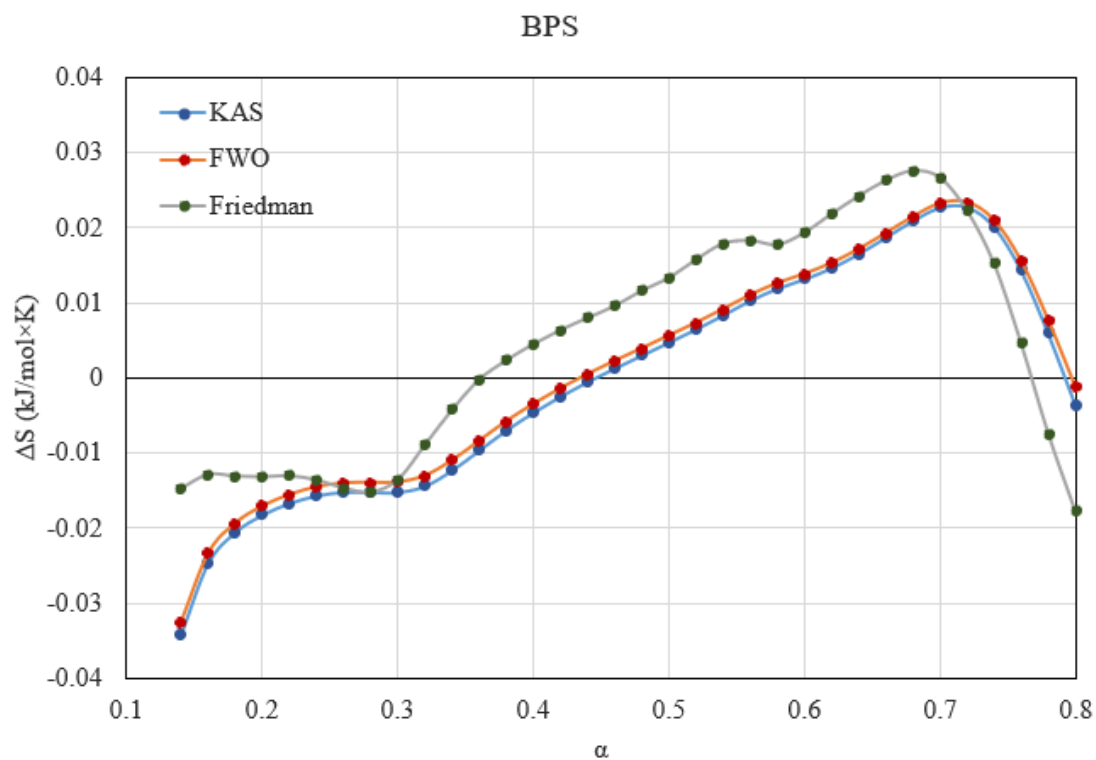


Figure AP 5.30. BPS ΔS curves for each method

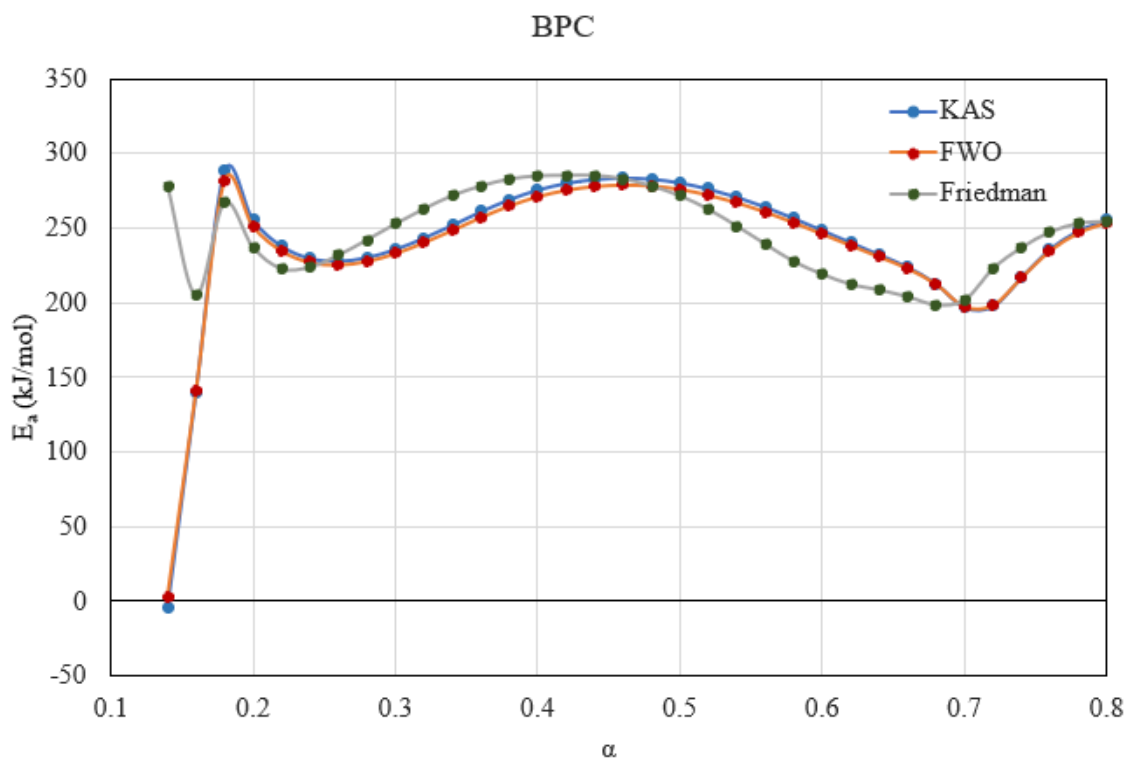


Figure AP 5.31. BPC E_a curves for each method

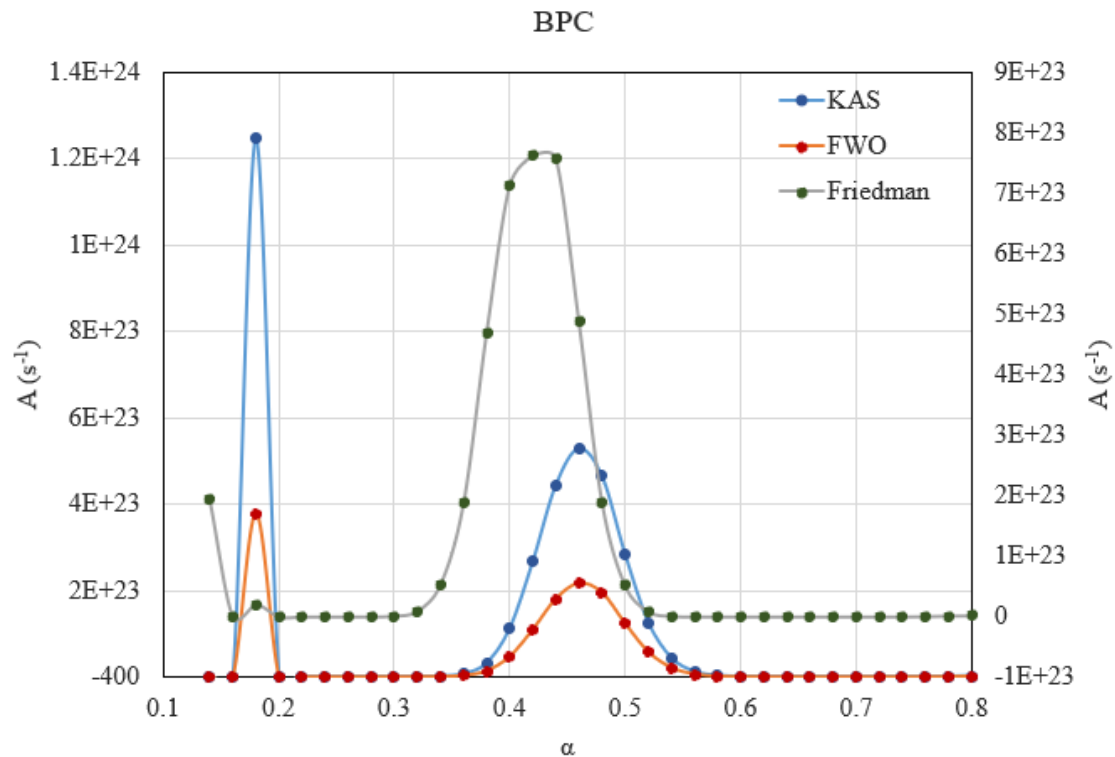


Figure AP 5.32. BPC pre-exponential factor curves for each method (Friedman: right-hand Y-axis)

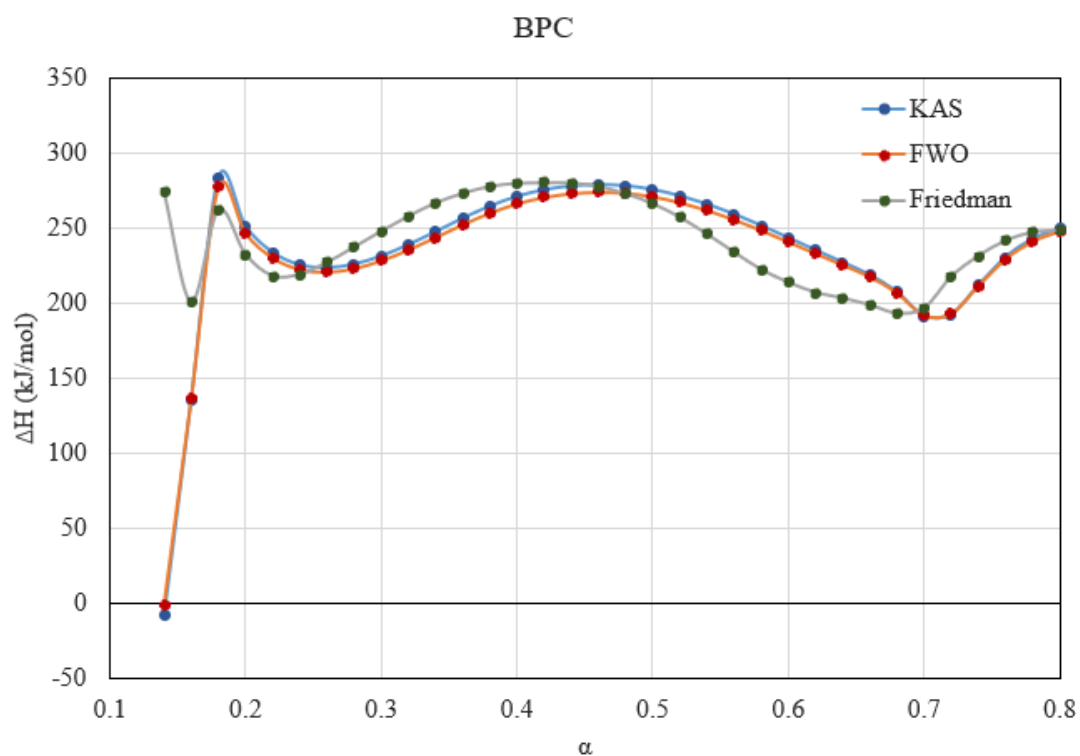


Figure AP 5.33. BPC ΔH curves for each method

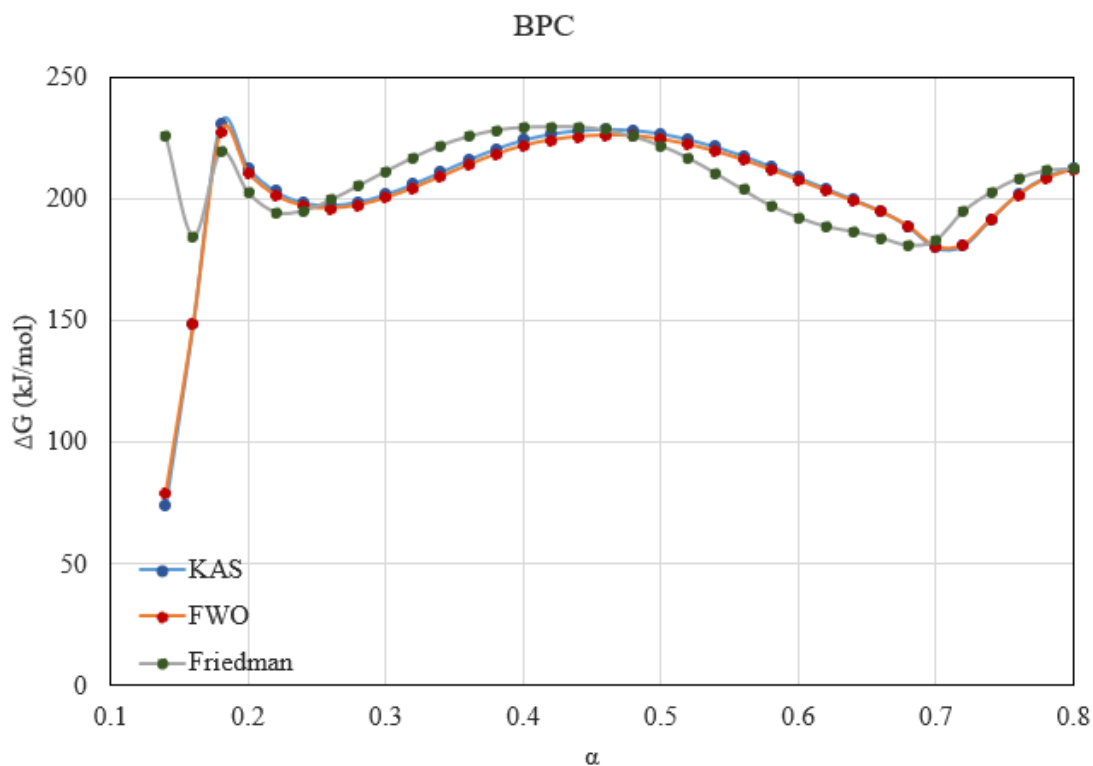


Figure AP 5.34. BPC ΔG curves for each method

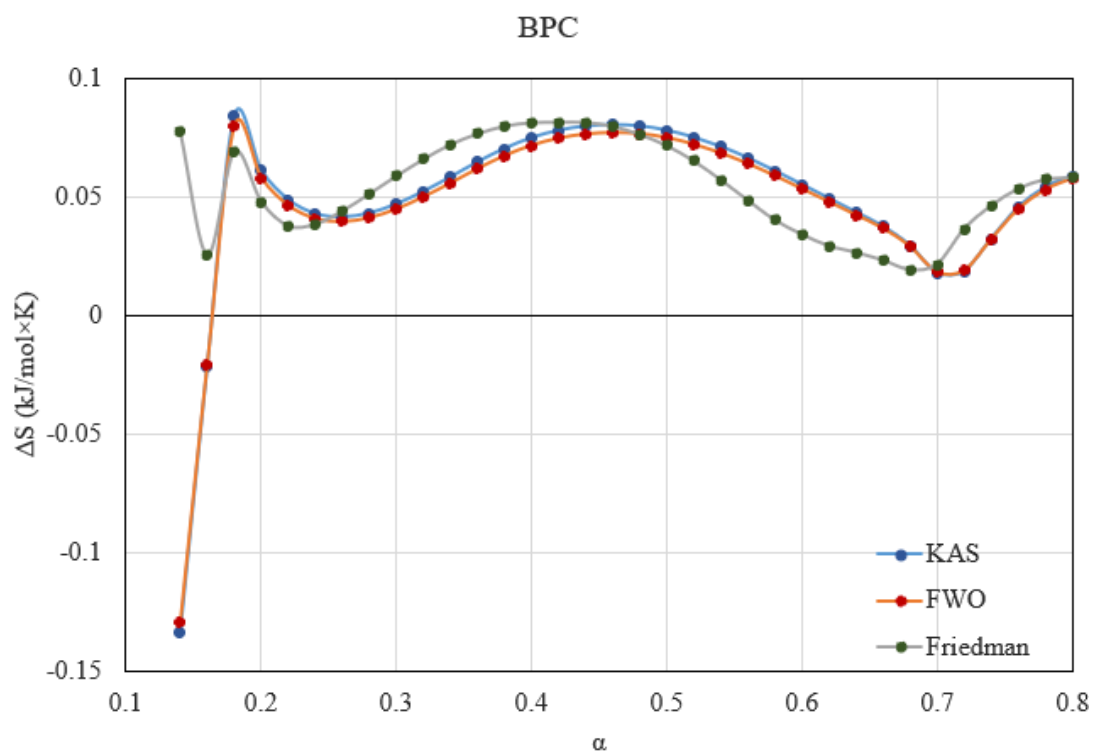


Figure AP 5.35. BPC ΔS curves for each method

Appendix 6

Minimum Ignition Temperature of Dust Layer Approach Results

Table AP 6.1. Minimum ignition temperature of dust layer approach results

Sample	Heating rate (K/min)	MIT _L (°C)	MIT _{Lapproach} (°C)	Error (%)	In range?*
BPA	3	320	313.78	1.94	Yes
	5		318.06	0.61	Yes
	7		322.79	0.87	Yes
	Average		318.21	0.56	Yes
BCA	3	290	286.81	1.10	Yes
	5		289.7	0.10	Yes
	7		NAP	-	-
	Average		288.26	0.60	Yes
BHO	3	310	308.63	0.44	Yes
	5		305.68	1.39	Yes
	7		319.93	3.20	No
	Average		311.41	0.46	Yes
BPM	3	340	331.2	2.59	Yes
	5		335.67	1.27	Yes
	7		336.1	1.15	Yes
	Average		334.32	1.67	Yes
BP	3	290	292.19	0.76	Yes
	5		294.39	1.51	Yes
	7		NAP	-	-
	Average		293.30	1.13	Yes
BPS	3	270	268.69	0.49	Yes
	5		276.76	2.50	No
	7		282.03	4.46	No
	Average		275.83	2.16	No
BPC	3	310	328.94	6.11	No
	5		334.37	7.86	No
	7		334.71	7.97	No
	Average		332.67	7.31	No
CV	3	290	274.01	5.51	Yes
	5		278.95	3.81	Yes
	7		281.29	3.00	Yes
	Average		278.08	4.11	Yes

*In range?: Yes, if $MIT_{Lapproach} < MIT_L + 5 \text{ K}$; No, if $MIT_{Lapproach} > MIT_L + 5 \text{ K}$

Appendix 7

Explosion Severity Experimental And Computational Test Graphs

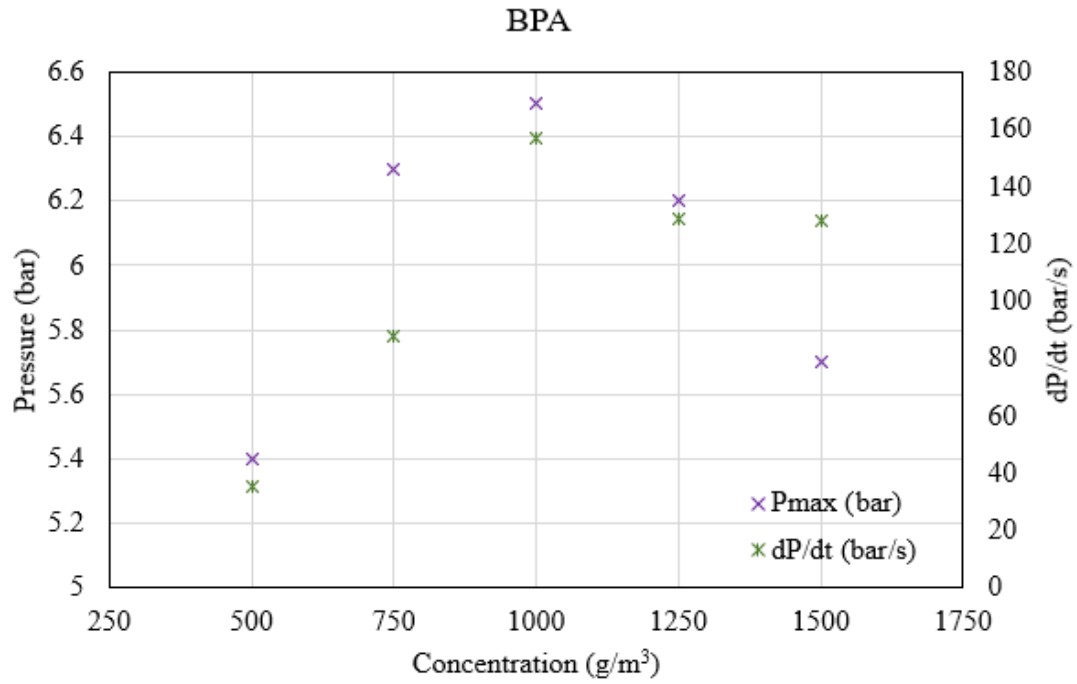


Figure AP 7.1. BPA Explosion severity experimental test results

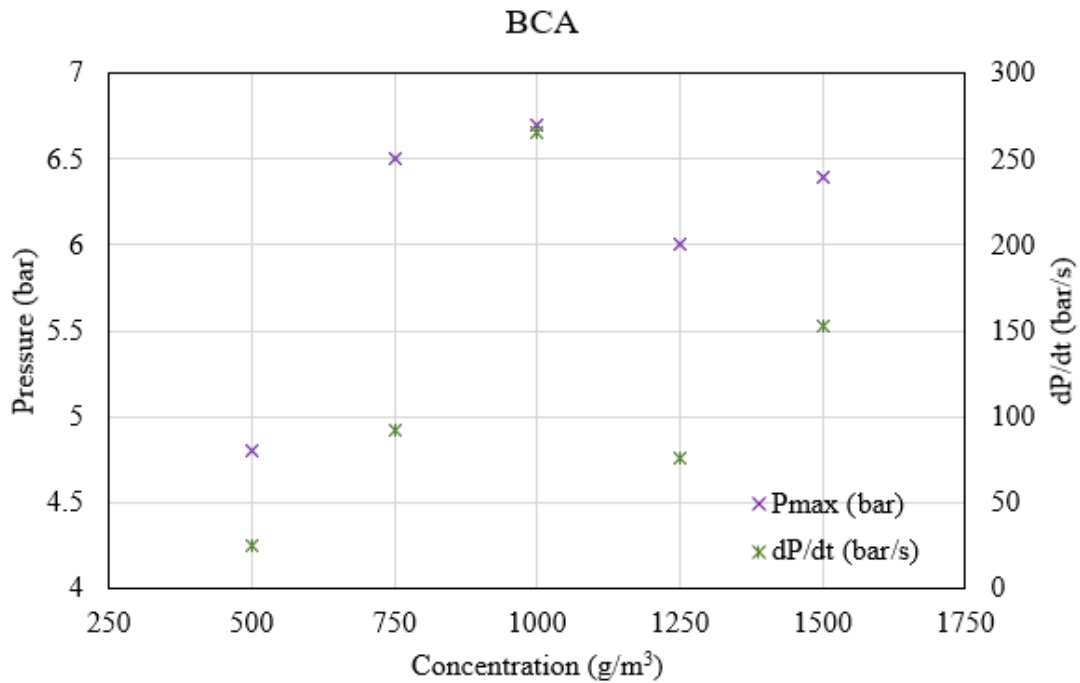


Figure AP 7.2. BCA Explosion severity experimental test results

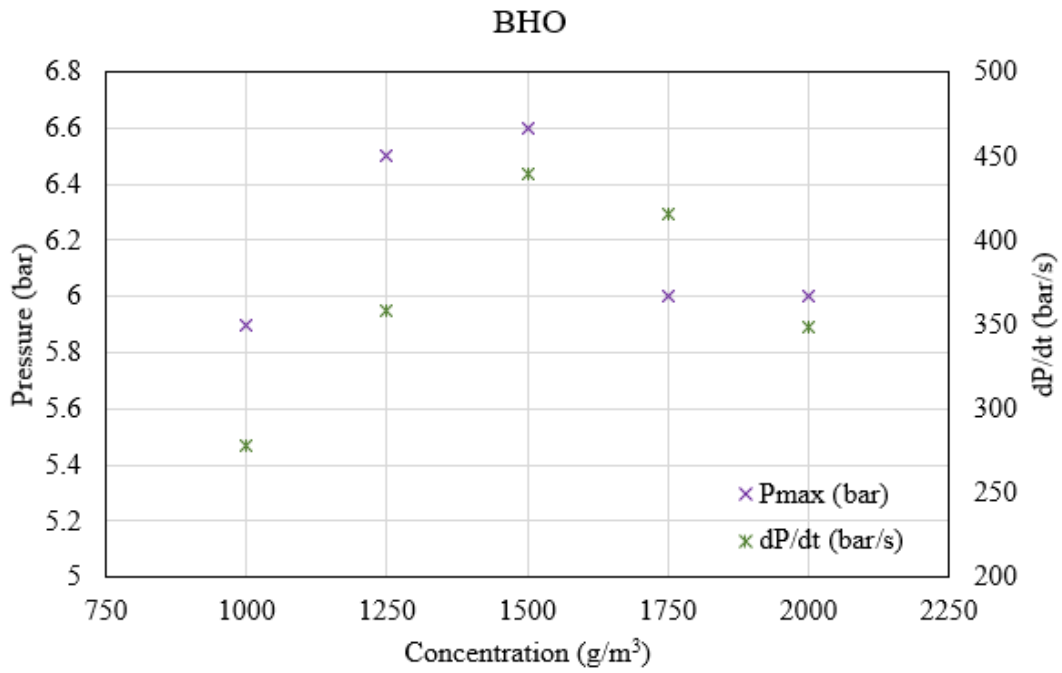


Figure AP 7.3. BHO Explosion severity experimental test results

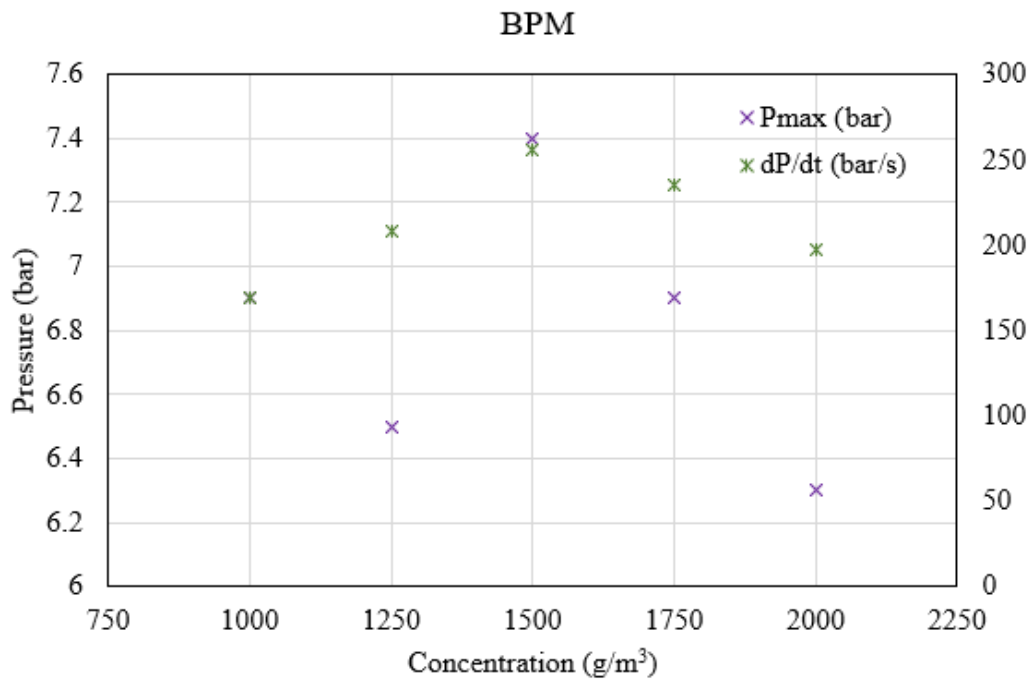


Figure AP 7.4. BPM Explosion severity experimental test results

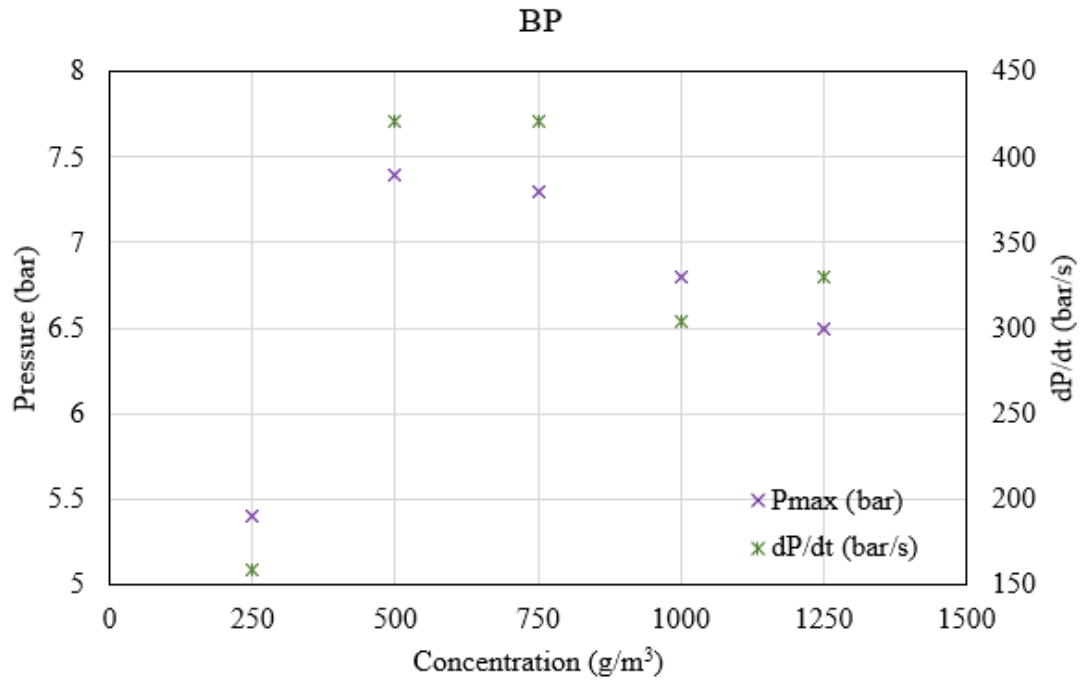


Figure AP 7.5. BP Explosion severity experimental test results

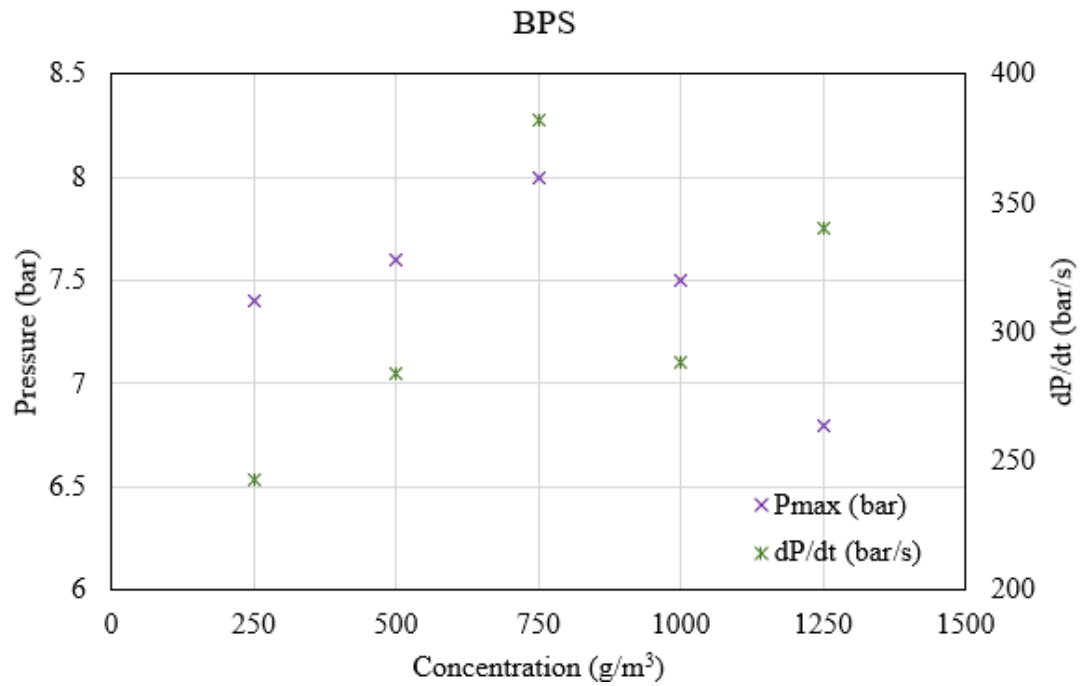


Figure AP 7.6. BPS Explosion severity experimental test results

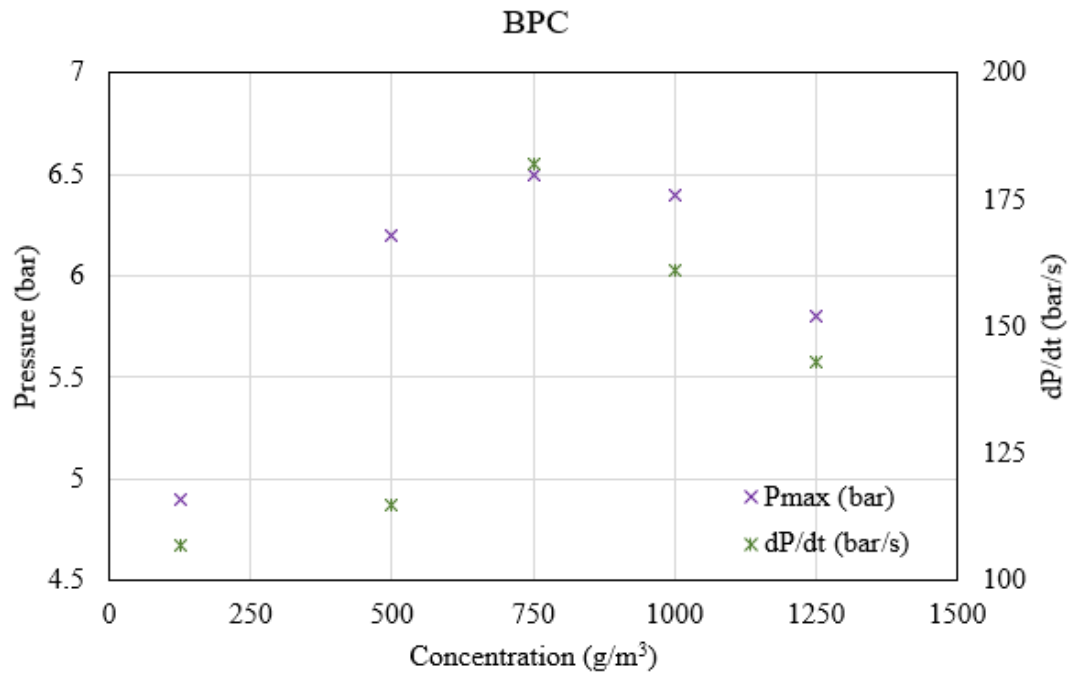


Figure AP 7.7. BPC Explosion severity experimental test results

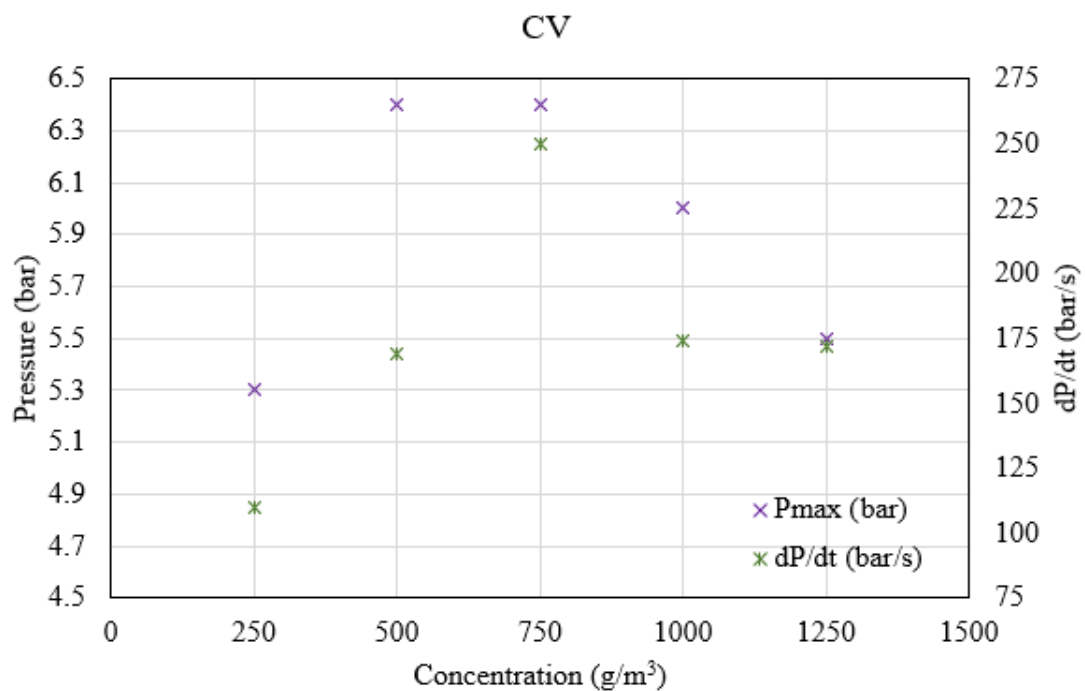


Figure AP 7.8. CV Explosion severity experimental test results

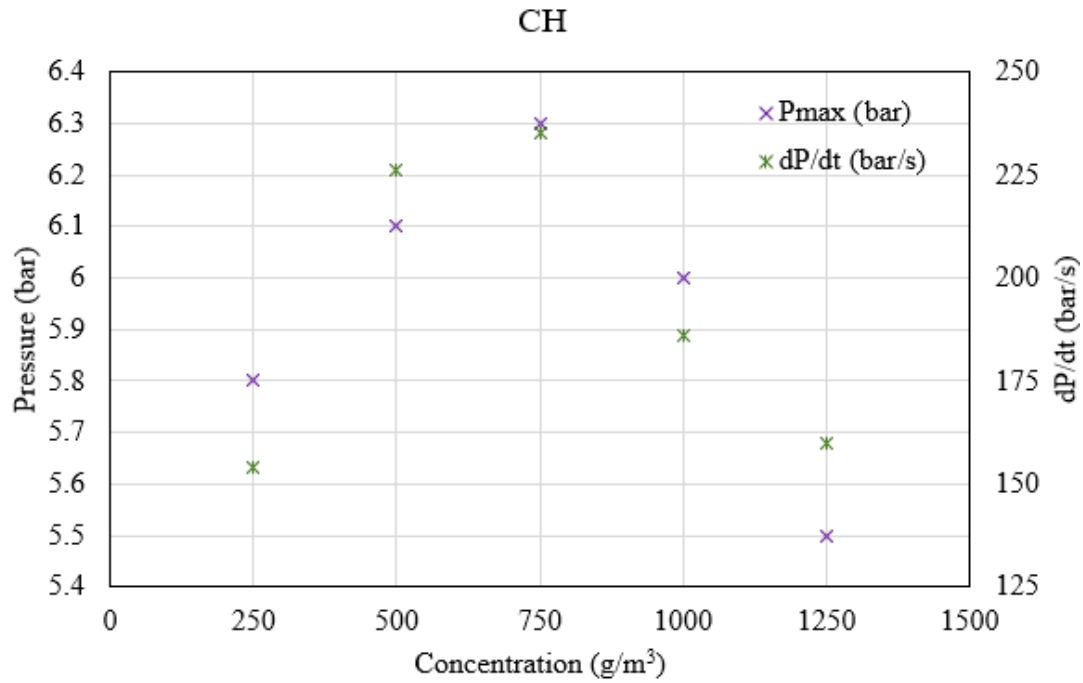


Figure AP 7.9. CH Explosion severity experimental test results

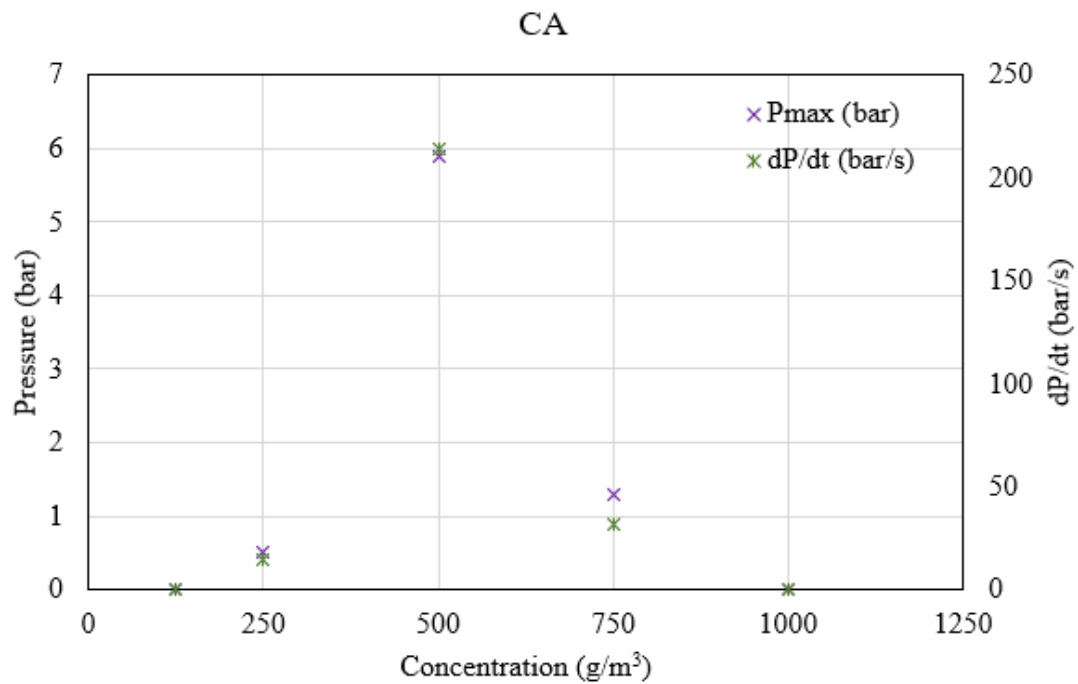


Figure AP 7.10. CA Explosion severity experimental test results

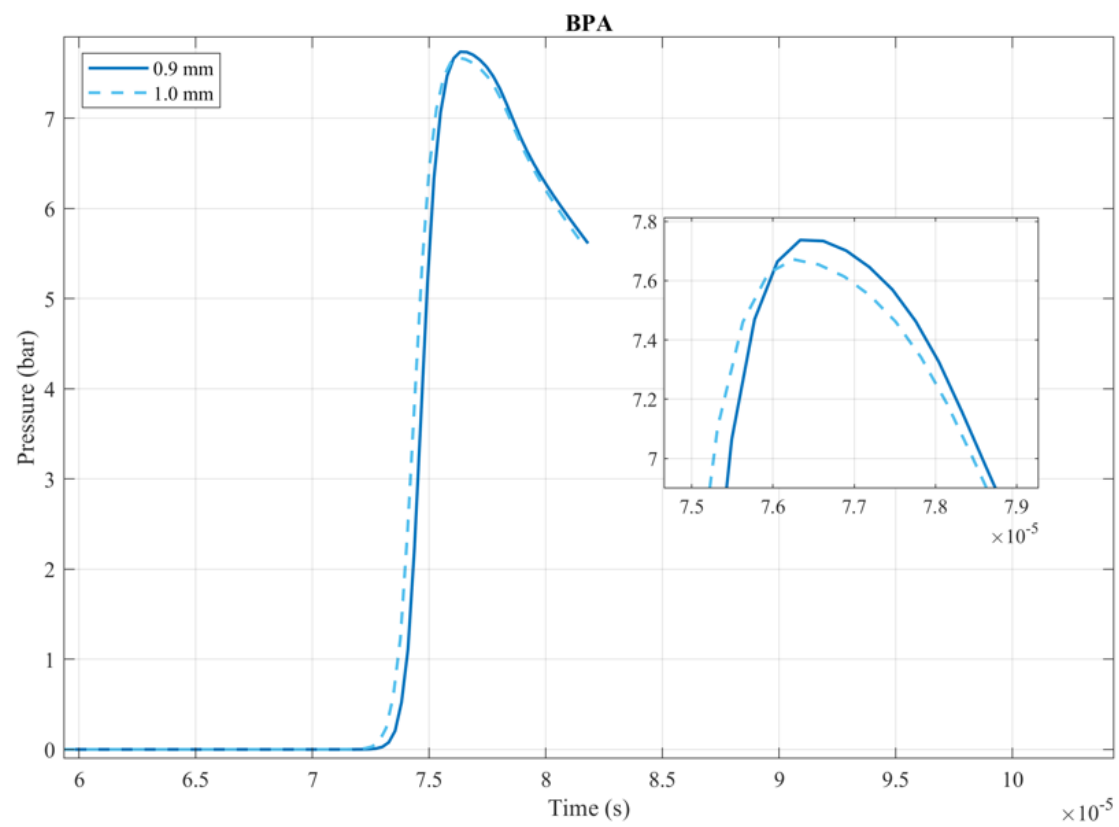


Figure AP 7.11. BPA Explosion severity CFD test results

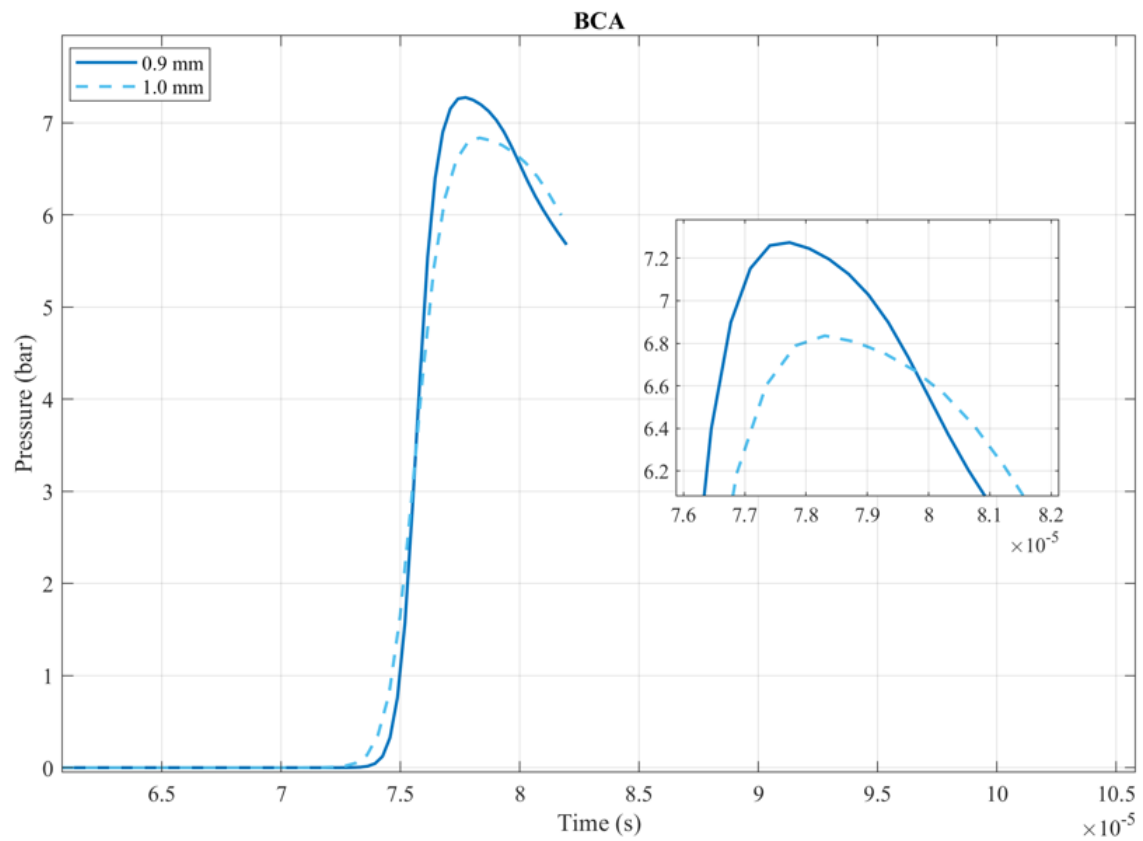


Figure AP 7.12. BCA Explosion severity CFD test results

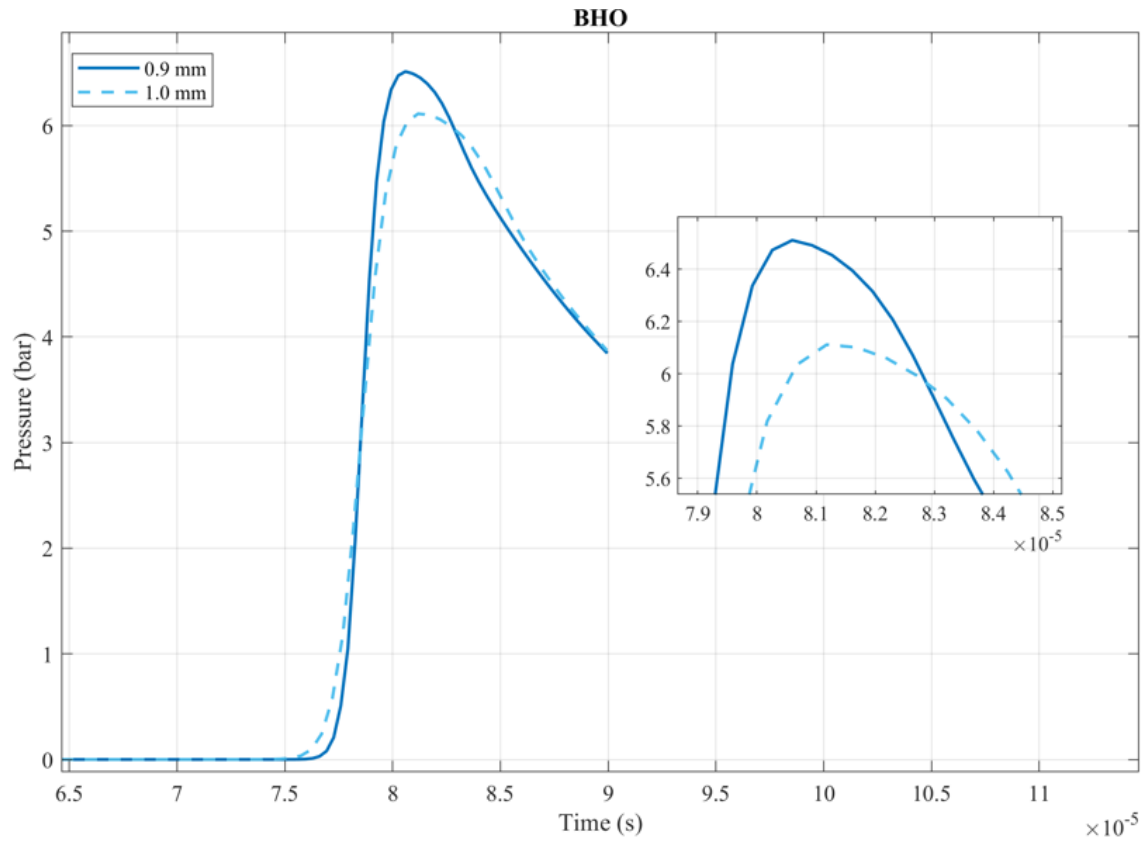


Figure AP 7.13. BHO Explosion severity CFD test results

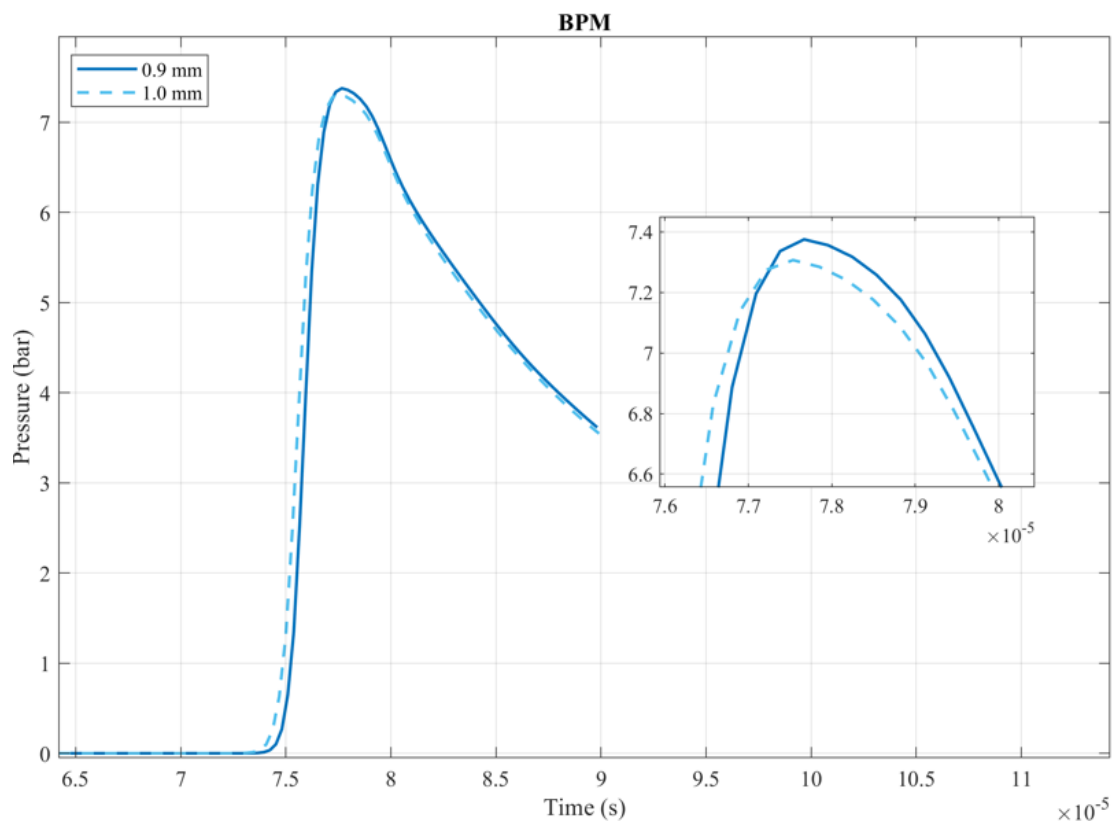


Figure AP 7.14. BPM Explosion severity CFD test results

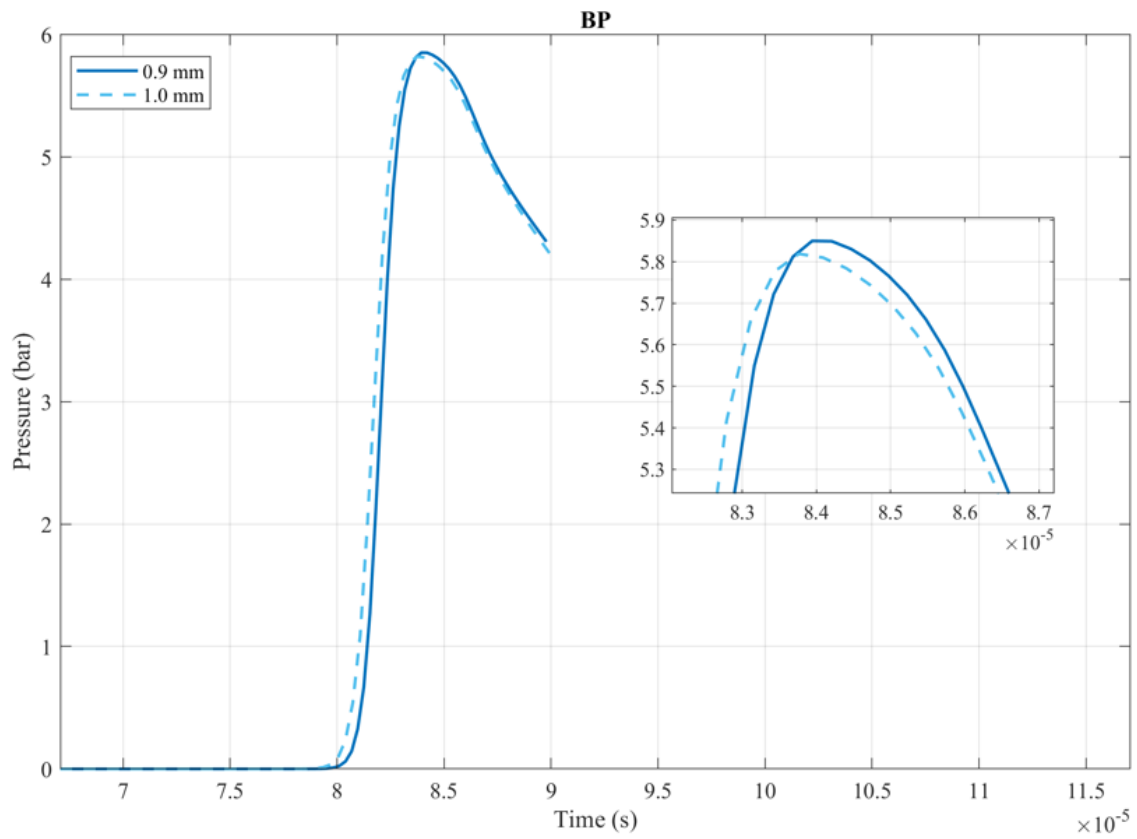


Figure AP 7.15. BP Explosion severity CFD test results

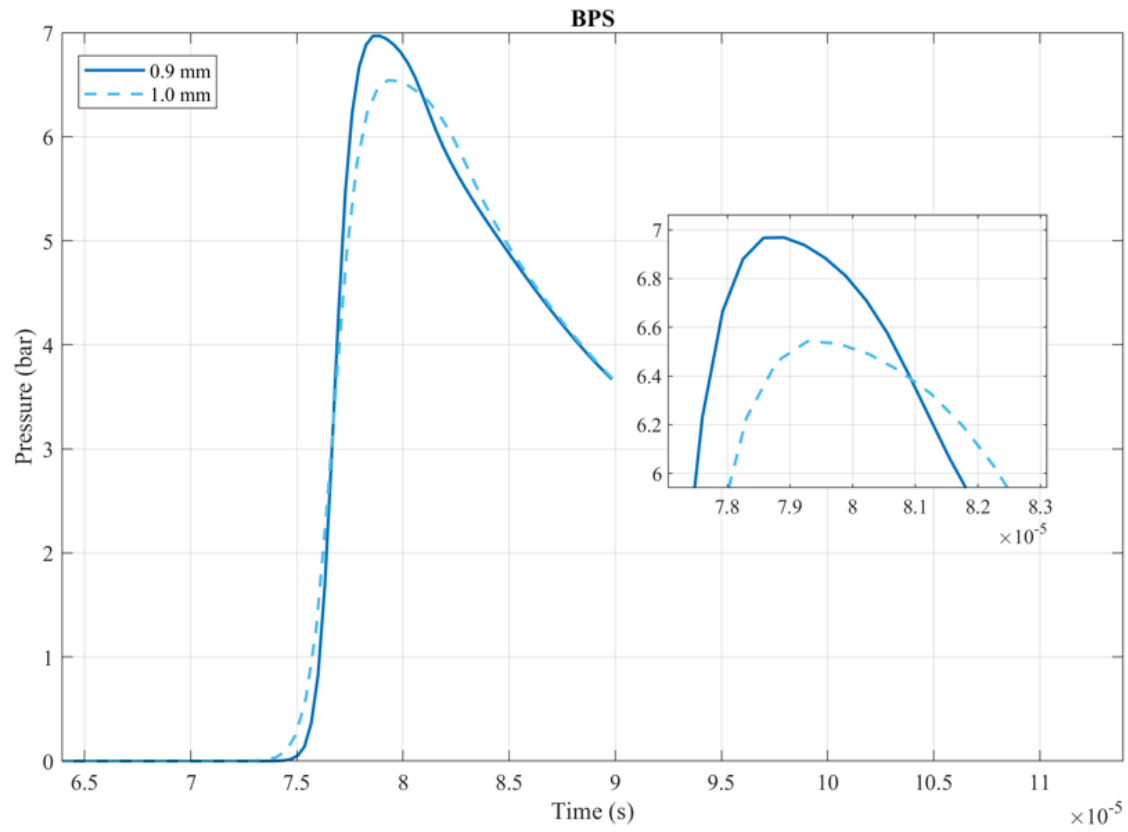


Figure AP 7.16. BPS Explosion severity CFD test results

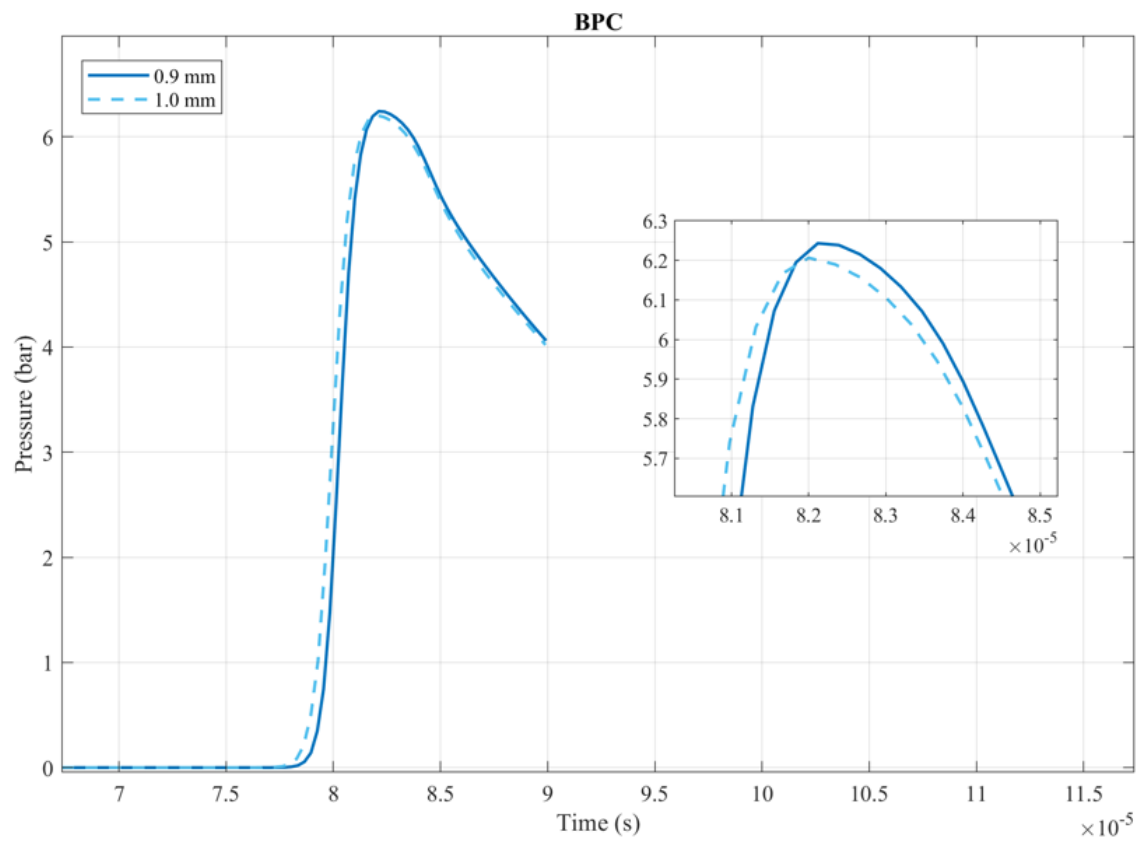


Figure AP 7.17. BPC Explosion severity CFD test results

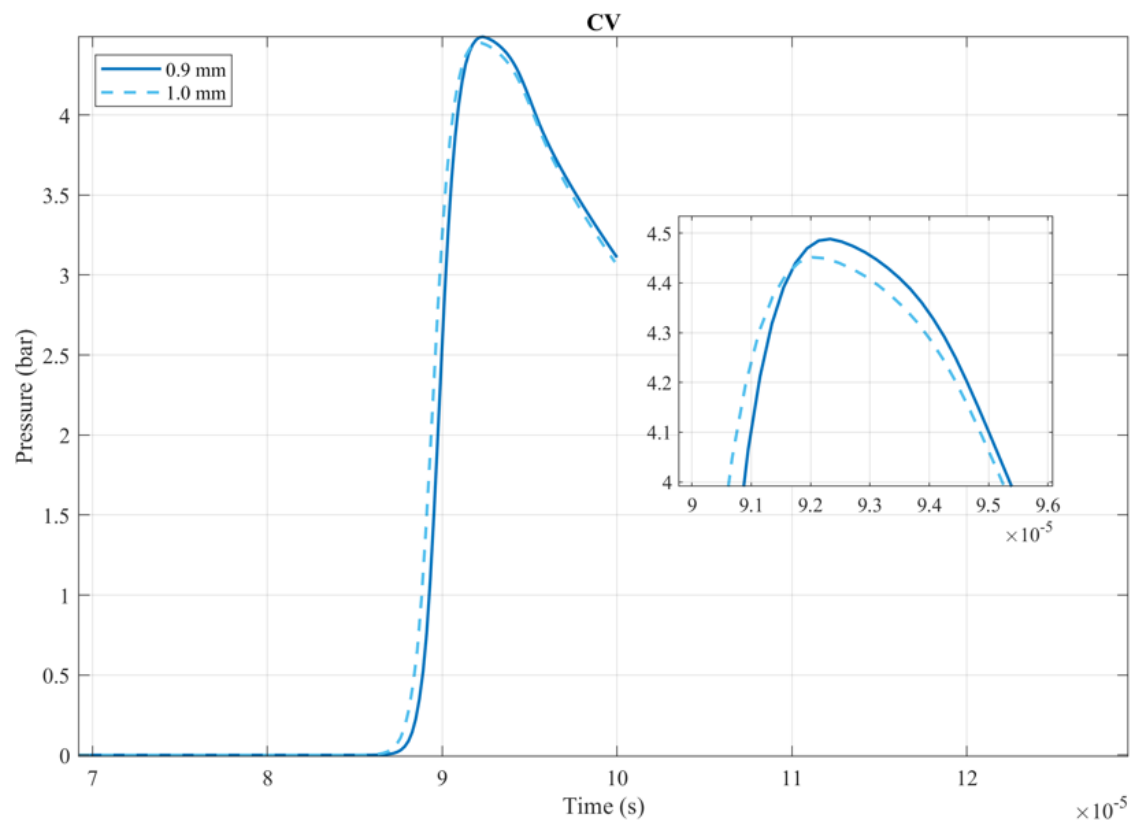


Figure AP 7.18. CV Explosion severity CFD test results

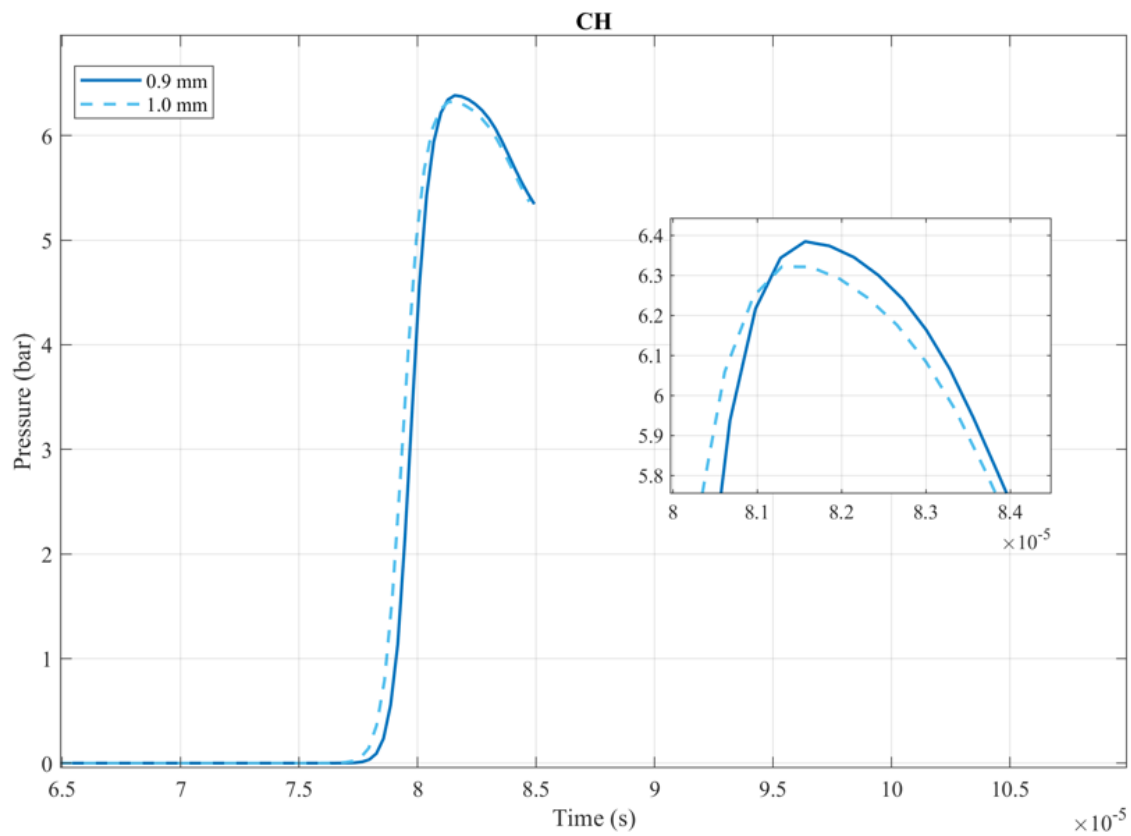


Figure AP 7.19. CH Explosion severity CFD test results

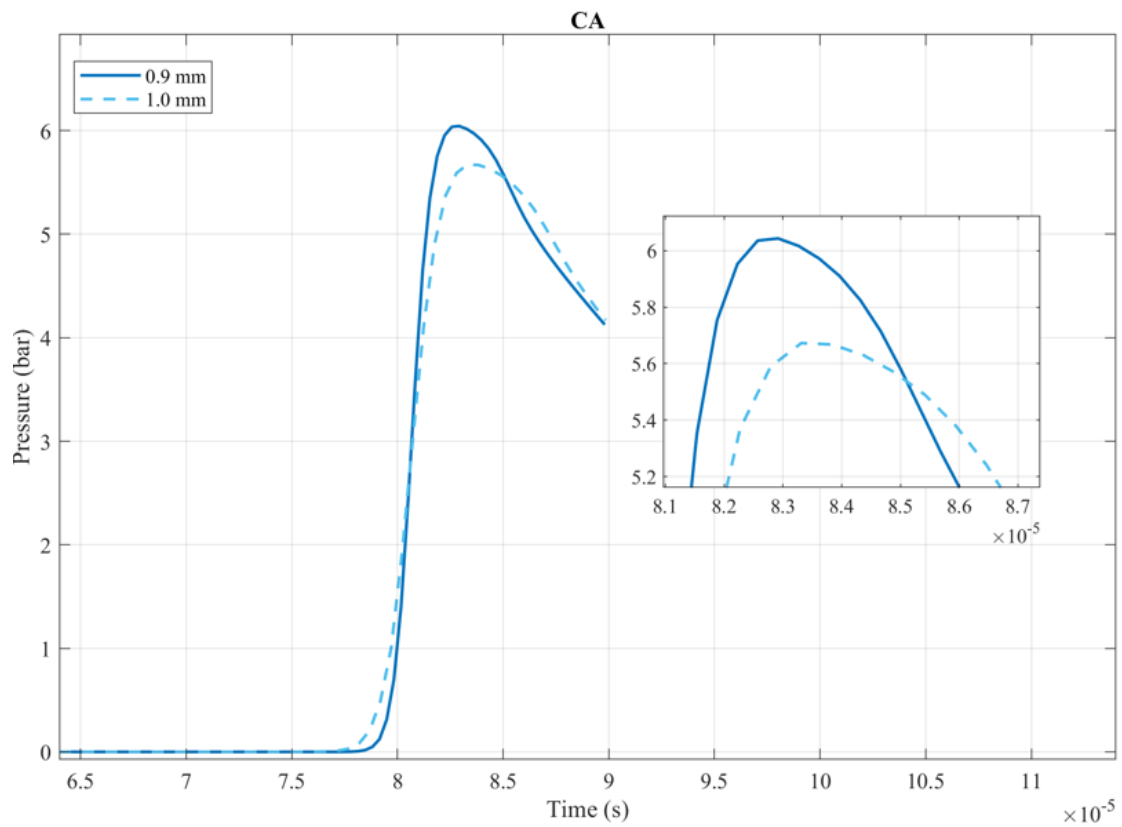


Figure AP 7.20. CA Explosion severity CFD test results

