An innovative kinetic model dedicated to mild degradation (torrefaction) of biomasses

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HIGHLIGHTS

- An innovative kinetic model for torrefaction of biomasses is presented.
- This study demonstrates the potentialities of the "*model free*" methods in setting up a completely consistent kinetic model.
- The new introduced computational scheme can be applied to any heating program.
- The model performances are very satisfactory also on a predictive working option.

ARTICLE INFO

ABSTRACT

This study proposes an innovative approach to investigate the thermal degradation kinetic of biomasses when submitted to torrefaction. This process is expected to have a relevant impact in exploiting the potentialities of biomasses in many major end energy uses. The main motivation of this work moves from the observation that the adoption of the "*model-free*" isoconversional approach is applied, conventionally, limited to the activation energy (*E*) determination. This work extends the potentialities of these methods and demonstrates their feasibility in setting up a complete kinetic model.

Moving from the fundamentals of the isoconversional analysis, this study identifies a specific constrain linking together the Arrhenius pre-exponential factor (*A*) and the reaction model function *f(α)*. This achievement is exploited to derive a new kinetic parameter (*φ_α*) which replaces the two terms *A* and *f(α)* that, jointly with *E*, constitute the conventional *kinetic triplet*.

The introduced parameters *E* and *φ_α* found the new two parameters kinetic equation whose solution is achieved by defining an innovative computational approach based on a finite difference scheme.

As main result this study introduces an original exploitation of the "*model-free*" methods that avoids, contrarily to conventional solutions, any assumption for the *f(α)* function. Besides, the introduced equation solver scheme can be generalized to any heating program, isothermal or not.

Three biomasses, belonging to the same *hardwood* family, have been specifically investigated. The performances of the model reach, in terms of Absolute Average Deviation, a predictive accuracy level within 1–5%.

Considering the encouraging achieved results, the proposed model can be directly applied to support the design procedures specifically pertaining to biomass torrefaction plants.

1. Introduction

This paper investigates the potentiality of the isoconversional methods to describe the thermal degradation of non-homogeneous materials as biomasses when submitted to torrefaction treatment. In this work "*torrefaction*" is referred to a thermolysis process carried out in inert atmosphere within the temperature range of 200–300 °C. This thermal pre-treatment is considered particularly promising to overcome the drawbacks of biomass feedstocks [1–3] and to upgrade low values lignocellulosic materials for their use as co-combustion fuels in coal-fired power plants [4–6]. Despite this, the limited information on both the performances of existing plants and the lack of fundamental knowledges of the process are even now limiting factors for the diffusion of this technology and the recognition of torrefied biomasses as a strategic resource within the renewable energy supply chain [7–9]. Considering the complexity of the reactions network involved on

Nomenclature		φ_α	parameter (min^{-1})
		N	number of isothermal step (–)
A	pre-exponential factor (min^{-1})	ER	Error Percentage (–)
E	activation energy (kJ mol^{-1})	AAD	Absolute Average Deviation (–)
K	rate constant (min^{-1})	Max	Maximum Error Percentage (–)
n	order of reaction (–)	Δ	α increment (–)
R	universal gas constant (8.314 J mol^{-1} K^{-1})		
T	temperature (K)	*Subscript*	
t	heating time (min)		
m	weight of sample (g)	0	reference state sample ($\sim$150 °C)
α	extent of reaction (–)	∞	Final state sample (400 °C)
β	heating rate (°C min^{-1})	i	i^{th} isothermal step (–)

thermal degradation of organic materials, this process cannot be described by detailed mechanistic models. It is generally accepted [10,11] that the kinetics parameters obtained from fitting procedures referred to limited data ranges are unreliable when used outside the experimental ranges utilized for their derivation. On the contrary, isoconversional methods are now generally accepted as particularly appropriate to estimate the activation energy (E) of reactions from TGA measurements. Considering also that these methods are mostly much easier to be implemented, they look promising for kinetics analysis in view of direct engineering applications [12–14]. In detail, this work integrates an improved "*model-free*" isoconversional approach with an innovative computational scheme to solve a new kinetic equation. As widely discussed on a previous work of the Authors [15], the advantages of the *model-free* approach are founded on their simplicity and on the avoidance of errors connected to the assumption of a reaction model [16]. Making reference to the conventional kinetic analysis, the thermal degradation rate is described by means of a single simplified reaction:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

in which the introduction of the Arrhenius equation to account of the $k(T)$ contribution provides the base Arrhenius-type kinetic equation:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{E}{RT}\right) \cdot f(\alpha) \tag{2}$$

The parameter α is the extent of reaction while the pre-exponential factor (A), jointly with E and the reaction model function $f(\alpha)$ form the so-called *kinetics triplet*. The *model free* option is particularly attractive since, if addressed only to E estimation, it does not require the preliminary selection of the $f(\alpha)$ term. This is the reason why the parameter A and the kinetic exponent included on $f(\alpha)$ are, in most cases, not computed when these methods are utilized. In case their determination is required, the selection of a suitable equation form for $f(\alpha)$ becomes a mandatory constrain. In kinetic analysis the correct choice of the reaction model is a critical issue widely debated by many researchers [17–20]. Sets of conversion functions ($f(\alpha)$) are conventionally derived from a variety of models: from those based on complex theories to determine independently the A term [21] to those utilizing advanced statistical models [22,23] until the recent distributed activation energy and deconvolution models [24].

Other methods as those of Coats-Redfern [25], Malek [26,27], Freeman and Carroll [28] in addition to those named "*Compensation Kinetics Effects*" (*CKE*) models [29–31], are lower complicated from a computational point of view. The adoption of traditional functions has been criticized [32] for forcing researchers to pick the best statistically model to describe the experimental results instead of exploring the application of more reliable schemes. In any case, the A term determination looks like an interlinked problem [29,30]: as matter of fact, the constrain due to $f(\alpha)$ selection induces a corresponding compensation on the resulting A parameter. From this point of view, the usual adoption of the term "*kinetics triplet*" is not rigorously correct since only two terms of the triplet are effective independent: the activation energy E and the selected $f(\alpha)$ model, while A inevitably counterbalances the choice of $f(\alpha)$. Besides, while for the cases of homogeneous reactions the kinetic parameters are highly indicative of the involved mechanisms, for heterogeneous reactions the concepts of "*order of reaction*" and "*concentration*" lose relevance [30]. Within this contest, the research of precise physical meanings to attribute to $f(\alpha)$ and A terms poses questionable remarks. This becomes a critical aspect in particular for non-isothermal conditions where the simultaneous change of both the extent of reaction (α parameter) and temperature makes the separation of the $k(T)$ and $f(\alpha)$ contributions practically impossible. It is to wonder whether, for heterogeneous reactions involving solids, the kinetic characterization expressed in terms of three contributions (*kinetic triplet*) is a redundant problem. The need of a simplified and more reliable approach to account for thermal degradation of solids is a perceived and debated question emphasized by several Authors [32–34]. Following this research line, an interesting approach is the non-parametric kinetics (NPK) method proposed by Serra et al. [35,36]. It is an interesting extension of the *model-free* approach derived from a set of non-isothermal experiments at different heating rates without any prior knowledge of the reaction mechanisms. Despite presenting some interesting aspects, the application of this method has revealed rather complicated and time-consuming so that it has not gained widespread uses. The study carried out in this paper places itself on this direction since it provides a direct end-use tool for engineering applications without loosing the fundamentals of kinetic analysis. The main novelties introduced can thereby be so summarized:

– an innovative kinetics approach is proposed by introducing a new parameter φ_α replacing the two conventional ones A and $f(\alpha)$;
– a modified version of the conventional (*model free*) Flynn method is derived by introducing the new φ_α parameter;
– an improved finite difference computational scheme, suitable to be applied to any heating program, is implemented to solve the two parameters kinetic equation;
– the model is tested both on an *implicit* and *predictive* mode. This last option, applied to model the thermal degradation kinetics of biomasses belonging to the same *hardwood* family, allows to reach high accuracies with a limited amount of experimental data only target to a single biomass.

2. Experimental

The kinetics of the biomass-torrefaction-derived materials has been studied via non-isothermal thermogravimetric analysis (*TGA*). The obtained experimental results have been presented and detailed on the cited paper [15] that includes also a description of the utilized experimental equipment and summarizes the main parameters characterizing the raw biomasses. In summary, three different types of biomasses, belonging to the *hardwood* family, have been investigated: