

Investigation of grape marc combustion using thermogravimetric analysis. Kinetics modeling using an extended Independent Parallel Reaction (IPR) model.

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Abstract:

The increasing demand for renewable energies leads to a necessary diversification of biomass resources used as combustible. The present study focuses on the analysis of grape marc as a new potential resource. The combustion of wine residue is here evaluated experimentally through a thermogravimetry analysis. An IPR model is proposed to simulate the thermal decomposition of grape marc considering both devolatilization and char combustion.

Key words: *Biomass, Kinetics, Grape marc, Combustion, Thermogravimetric analysis*

1. Introduction

Because of the possible rarefaction of fossil resources, European countries have to diversify their energy sources. They also have to meet their environmental engagement in terms of overall carbon balance [1]. Biomass combustion is one of the ways to reach these goals. Research activities concerning the optimization of combustion processes on biomass products may contribute to innovate the use of sustainable biomass. Moreover, the waste to energy conversion is a promising process in terms of sustainable development. The Alsace Region (North-East of France) is known for wine production leading to large quantities of grape marc which should produce a relevant biomass resource.

Thermal degradation of biomass has already been studied by thermogravimetry

analysis (TGA) [2]. TGA indeed allows to measure quickly the thermo-chemical properties of different materials and to estimate the kinetic parameters which describe the combustion or pyrolysis processes. When dealing with grape marc, the literature is essentially focused on the pyrolysis process ([3],[4],[5],[6]). Only few studies are related to the combustion of wine residues and to the corresponding emission regulation ([7], [8]).

Among the different kinetics approaches, the Independent Parallel Reaction (IPR) and the iso-conversional models have already been used for the simulation of the thermal degradation of biomass resources ([9],[10]). They both exhibit a good accordance with the experimental data [11].

The aim of the present study is to investigate the combustion of different grape marcs by TGA and to propose a relevant model leading to the associated kinetic parameters. For the last purpose, we propose the IPR model and we decompose the biomass structure according to the lignocellulosic material representation [12]. The kinetic model is here extended to account for both devolatilization and char combustion.

2. Materials and Methods

2.1 Materials and characterization

The samples of wine residues (Sylvaner, Chasselas and Pinot Gris varieties) tested in this study have been produced in Alsace. The grapes were separated manually in three different parts: stalks, skins and seeds. Ultimate analyses (C,H,O,N,S) were performed for the Sylvaner variety (Tab. 1).

Table 1. Grape parts ultimate analysis

Ultimate analysis on dry basis	Sylvaner		
	Skins	Seeds	Stalks
C (wt %)	48.12	54.62	47.12
H (wt %)	5.36	5.80	4.83
O (wt %)	40.61	38.32	41.13
N (wt %)	2.12	1.64	1.30
S (wt %)	0.33	<0.10	0.11

The characterization of each sample was done following the standard XP CEN/TS for the moisture and ash contents and the calorific value (Tab. 2). The results obtained for the different grape marc samples of marc are very similar.

Table 2. Grape marc characterization

Samples	Sylvaner			Pinot Gris		Chasselas	
	Grape parts	Skins	Seeds	Stalks	Skins + Seeds	Stalks	Skins + Seeds
%Humidity	76%	46%	71%	57%	65%	68%	71%
%Ash (550°C) ^a	9.8%	3.3%	8.9%	5.9%	8.4%	6.8%	7.2%
HHV (MJ/Kg) ^a	19.7	22.8	19.1	20.8	18.4	19.7	18.0

^a on dry basis

The composition of grape marc for Sylvaner (Tab. 2) shows that carbon content is higher for seeds than for skins and stalks. As expected, humidity content is high for skins and stalks, while seeds exhibit the higher HHV. For Pinot Gris and Chasselas, the differences are less significant.

2.2 Thermogravimetric Analysis (TGA)

Experiments were performed in a thermobalance TA Q500 at heating rates of 5, 10 and 20°C/min, in the temperature range 30 – 800°C, and under a synthetic air flow of 3.6 NL/h (20% O₂, 80% N₂). Few experiments were also performed under pure nitrogen. Small masses (10 – 30 mg) of sample have been used, in order to avoid mass and heat transfer limitations, [13]. All the samples were previously been dried in order to spare a deviation, due to the heterogeneity of the humidity level.

2.3 Kinetic modeling

The combustion process is more complex than the pyrolysis one, because of the oxidation reaction which occurs between the oxygen and the volatiles and especially with the char. This combustion process is often described by two separate stages and iso-conversional models have been proposed [9], [14], [15]. However, its modeling may be described in a single stage.

We here propose the extended IPR model for the thermal decomposition kinetics of lignocellulosic materials under an oxidative atmosphere. TGA curves are described by four independent parallel reactions: three reactions for devolatilization of each constituents of the grape marc (Hemicellulose H, Cellulose C and Lignin L) and one for heterogeneous combustion of the Char produced (CH). The overall mass conversion rate during thermal degradation is expressed according to a first-order reaction:

$$m(t) = \sum_{i=1}^4 m_i(t) + m_{ash}$$

$$m_i(0) = c_i \times (m_0 - m_{ash})$$

$$\frac{dm}{dt}(t) = - \sum_{i=1}^4 A_i e^{\frac{-E_i}{RT(t)}} m_i(t)$$

where: $m(t)$ is the mass sample at time t ,
 $m_i(t)$ is the mass of the i^{th} constituent of the grape marc at time t ,

c_i is the contribution of the i^{th} constituent to the overall combustion process,

m_0 and m_{ash} are respectively the initial mass of the sample reaction and the mass of ash,

$\frac{dm}{dt}$ is the mass conversion rate of the overall sample,

A_i is the pre-exponential factor of the i^{th} constituent,

E_i is the energy activation of the i^{th} constituent,

R is the gas constant (8.314 J/mol.K).

3. Results and Discussion

3.1 Thermogravimetric experiments

The TGA experiments were realized at least three times with a good reproducibility. The mass losses versus time and corresponding DTG traces of two different samples (Sylvaner stalks and Pinot Gris seeds) are shown in Figure 1. The results obtained for three different experiments are compared.

In the case of Sylvaner stalks (Fig. 1 a)), the reproducibility of the experiments is high despite of the differences of the sample masses. In the case of Pinot Gris seeds (Fig. 1 b)), a slight difference occurs concerning the reactivity of the char oxidation. The temperature of the oxidation peaks occurs at 480, 500 and 510°C respectively for 29.7, 30.1 and 35.9 mg initially engaged. This could be a consequence of the size of the sample possibly modifying the accessibility of the oxygen to the carbon residue.

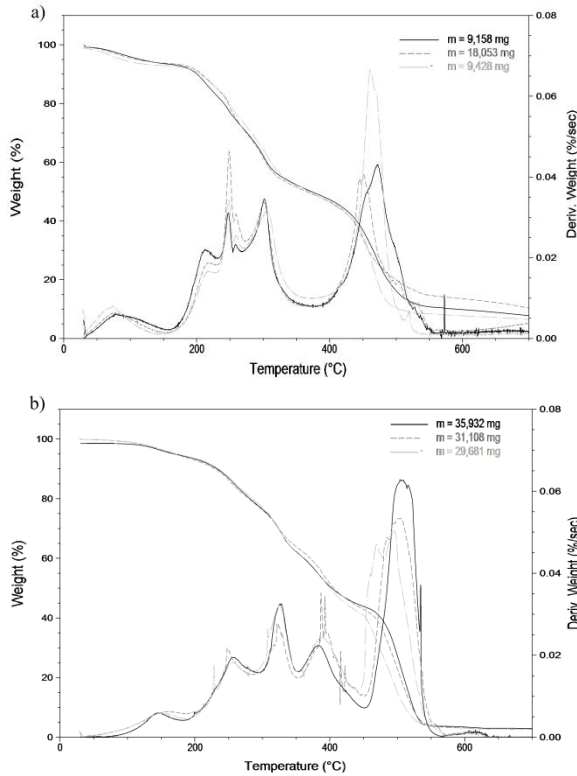


Figure 1: Grape marc TGA (%) and DTG (%/s); Heating rate: 5°C/min; Reproducibility: a) Sylvaner stalks and b) Pinot Gris seeds.

The combustion of the different constituents of the grape marc has been experimented on the Sylvaner variety (Fig. 2). The DTG analysis shows that each part of the grape marc reacts at different temperatures.

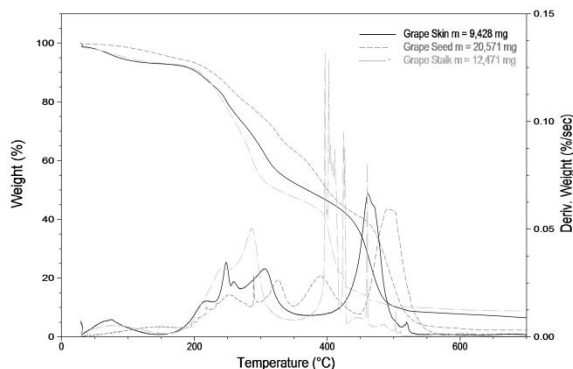


Figure 2: Grape marc TGA (%) and DTG (%/s); Heating rate: 5°C/min; Variability on different parts (skin, seed and stalk).

The devolatilization steps occur from 150°C to 400°C. The decomposition of skins and stalks take place in the same range of temperature. An isolated peak is observed around 390°C for seeds which is discussed hereafter. The char combustion step (from

400°C to 600°C) starts earlier and is faster for stalks (0.1 %/s at 401°C) than for the other parts. Inflammations are observed during the combustion process, because of this high reactivity. For grape skins and seeds, the oxidation peaks are respectively 0.06 %/s at 460 and 500°C).

Figure 3 presents the thermal degradation of seeds for three varieties. The discrepancies are of the same order of magnitude than for a single variety of grape marc.

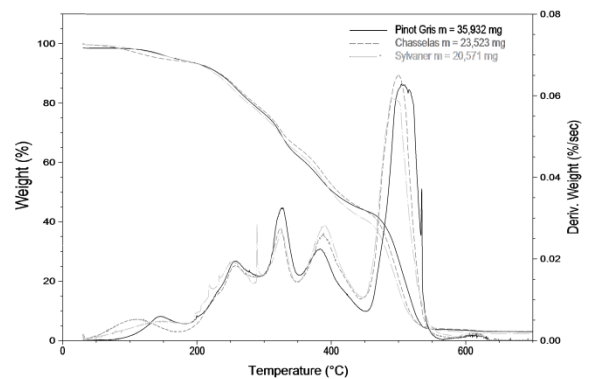


Figure 3: Grape seed TGA (%) and DTG (%/s); Heating rate: 5°C/min; Variability between Chasselas, Pinot Gris and Sylvaner variety.

The isolated decomposition peak which occurs at 390°C is found for different types of grape seed. However, for few samples (less than 1/5), this peak is not observed. Two assumptions may be discussed. They are both related to the lignocellulosic representation of the biomass:

- this peak occurs due to a bigger proportion of lignin in the grape seed than in the skin or stalk parts;
- another constituent like the grape seed oil may contribute to the combustion process.

Figure 4 presents the devolatilization step for three different Sylvaner seeds, under inert and oxidative atmosphere. Pure lignin decomposition in air was also studied and the results are presented in Fig. 4. This decomposition induces a single peak at 365°C.

The thermal degradation of pure lignin has been previously studied in oxidative atmosphere [12]. It was here reported that decomposition leads to two simultaneous processes occurring above 300°C: the

formation of volatiles and of carbon residue and the oxidation of this residue.

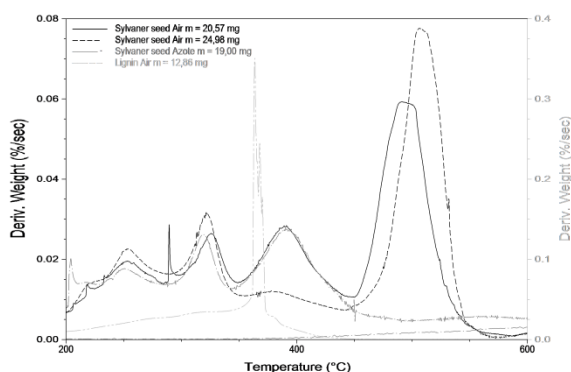


Figure 4: Grape seed and lignin DTG (%/s); Heating rate: 5°C/min; Variability within the same grape variety.

Under pyrolysis conditions, volatiles are also formed also around 390°C. The lignin pyrolysis takes place in a wide range of temperatures. Lignin composition is known to be greatly heterogeneous. Depending of the lignin composition and its proportion into the grape seed, its devolatilization may take place at temperatures around 390°C leading to the presence of the isolated peak put into evidence in this work. Concerning the second assumption for the presence of this peak, i.e. the consequence of the presence of another constituent like oil on the grape seed, a previous study [6] on grape residues performed in TGA pointed out different behaviours for thermal degradation of seeds, grape seed oil and oil-free grape seeds. It was shown that grape seed oil is devolatilized around 400°C and is totally pyrolyzed at 500°C. Whatever the assumption considered for the presence of this isolated peak, we observe (see Figure 4) that the combustion of the char occurs at lower temperatures in this condition. Char oxidation peak is respectively 0.08 and 0.06%/s at 508 and 491°C with and without the presence of the isolated peak of decomposition at 390°C. This difference in

reactivity may be due to an increase of char porosity improving the accessibility of the oxygen for combustion reactions.

Figure 5 gathers the results obtained for three different heating rates: 5, 10 and 20°C/min. As described in the literature ([13]), the increase of the heating rate shifts the thermal degradation process to the higher temperatures.

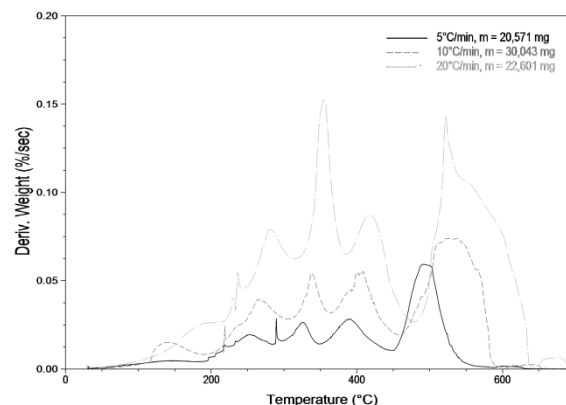


Figure 5: Grape seed DTG (%/s) at different heating rate (5, 10 and 20 °C/min).

3.2 Kinetic parameters

The resolution of the above first-order system through the SCILAB software leads to the following set of kinetic parameters for the four constituents of the grape marc. Figure 6 presents the simulated and experimental curves obtained for the grape seed.

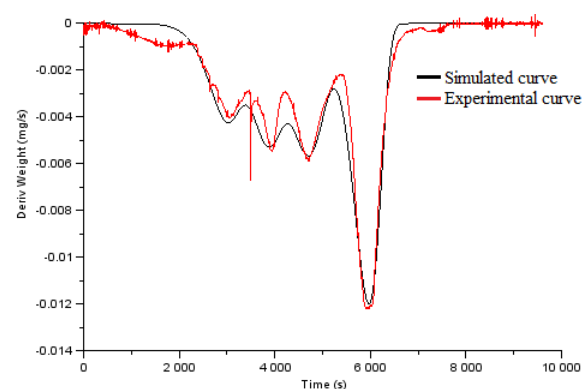


Figure 6: Grape seed DTG (mg/s) 5°C/min. Experimental and simulated curves.

Table 3. Grape seed; kinetic parameters extracted by the extend IPR model

Grape parts	Skins			Seeds			Stalks		
	Ea / KJ.mol ⁻¹	A / s ⁻¹	c _i	Ea / KJ.mol ⁻¹	A / s ⁻¹	c _i	Ea / KJ.mol ⁻¹	A / s ⁻¹	c _i
H	55	8.0e+2	0.210	80	3.5e+5	0.140	65	1.25e+4	0.198
C	95	1.05e+8	0.239	100	2.2e+6	0.176	110	5.0e+7	0.288
L	55	4.5e+1	0.123	115	3.15e+6	0.253	65	8.0e+1	0.091
Char	185	3.5e+10	0.429	205	3.0e+11	0.577	215	9.0e+13	0.569

Table 3 presents the results obtained for the different parts of the grape marc at the heating rate of 5°C/min. The error between the two curves is respectively evaluated as 0.03%, 0.04% and 0.05% for the skin, seed and stalk parts.

In order to evaluate the effect of the heating rate, the set of parameters obtained at 5°/min on seeds have been used for 10 and 20°C/min experiments. We observe that the error between the experimental and the computed signals increases in a significant way with the heating rate: 0.04%, 0.25% and 0.46% for 5, 10 and 20°C/min heating rates.

This probably proves a possible limitation for the IPR model. The lignin decomposition and char oxidation should indeed be in interaction for high heating rates [13].

4. Conclusions

In this contribution, we have studied the combustion process of grape marc with a thermogravimetric analyzer. The results have been modeled with the SCILAB software, using an extended IPR model. A set of kinetic parameters has thus been obtained for this combustion process.

A singular peak has been observed on grape seeds. The nature of the volatile decomposed is not currently fully determined. From the different observations made on the combustion process, an interactive effect could occur between the grape seed oil and the lignin decompositions.

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