IOSUD - Universitatea Politehnica Timişoara
Şcoala Doctorală de Studii Inginereşti

Optimization possibilities for industrial technologies of biomass valorisation through pyrolysis

Doctoral Thesis-Summary
For obtaining the scientific title of Doctor at
The Politehnica University Timisoara
In the doctoral study field of Industrial Engineering
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April 2018

CONTENTS

Objectives and structure of the thesis

The main objective of the doctoral thesis is **the optimization of the slow pyrolysis process of biomass in order to obtain the ideal proportion of secondary products (with superior caloric properties), with a low energy consumption, by establishing the optimal parameters of the technological process for industrial application.**

The following secondary objectives can be contoured from the main objective:
1. The analysis of the state of the art situation regarding the main pyrolysis systems and technologies;
2. The analysis of the thermo-chemical discomposure phenomenon of biomass through the pyrolysis process and identification of the main conversion steps
3. Identification of several fast and precise determination methods of physical-chemical properties of the used raw material (biomass);
4. Establishing various partial optimization functions by modelling the main factors which influence the bio-fuel proportions that are to be obtained
5. Analysis of kinetics in the pyrolysis process by applying kinetic calculus models, comparing them and assuring their relevance in system designing
6. Determining the influence of biomass species and of the process parameters on the physical-chemical properties of the obtained pyrolysis char.

Chapter 1 analyzes the current state of biomass energetic valorisation through various technologies (general presentation), followed by a critical analysis of the pyrolysis technologies mainly used in industrial systems.

Chapter 2 represents the beginning of the experimental part. It is structured into 3 different parts, starting with the presentation of the raw materials used in the experimental research in the thesis and of the processing and pyrolysis equipment for biomass. A part of the experimental research conducted during the doctoral studies is presented in the second part of the chapter. The influence of temperature and heating rate on the slow pyrolysis process is studied through this research.

The results of several experimental researches on kinetics investigation of biomass pyrolysis are presented in chapter 3.

The presentation of the experimental research is continued in chapter 4. It is structured into two different parts.

The results of a physical-chemical analysis of the raw material are presented in the first part. The analysis used a fast determination method for humidity, volatiles, fixed carbon and ashes.

The results of the experimental research on the analysis of pyrolysis char are presented in the second part of chapter 4.

Chapter 5 is dedicated to the general conclusions and personal theoretical, experimental and applicative contributions, including the presentation of some research perspectives and the improvement for some pyrolysis technologies in industrial systems.

The studies conducted using the applications developed on the slow pyrolysis process open new possibilities regarding the development of efficient systems for the industrial pyrolysis of biomass, including the conversion possibilities of unexploited biomass waste into bio-fuels.

1. ANALYSIS OF THE STATE OF THE ART SITUATION FOR INDUSTRIAL BIOMASS VALORISATION SYSTEMS

In the current context, biomass is presented as one of the most interesting and perspective resources from the category of renewable energy resources, with intensely studied and often subsidized energetic valorisation technologies [2].

At national level, Romania holds important biomass sources, due to the rich forests fund and widely spread agricultural fields, which are exploitations of various cultures, rich in energetic content and finally yet importantly, it is also due to urban establishments which attract the development of industry and food consumption that lead to important quantities of urban waste biomass.

Biomass offers an energetic potential, which can be valorised, through various biological or thermo-chemical transformation methods, into biofuels that end in generating energy through the process of burning in the presence of oxygen. The main energetic valorisation methods for biomass are combustion, biological conversion (biochemical), thermo-chemical conversion.

Pyrolysis is one of the most important biomass conversion methods. Through this industrial process. Biomass is subjected to a thermic treatment at 300-1000 ºC, in the absence of oxygen, producing three energetically valuable fuels: bio-oil, syngas and bio-char.

The development of the biomass pyrolysis industry is currently prevented by the following factors:

(1) Many of the existent technologies have been designed by engineers or researchers with limited knowledge regarding the specific processes of this technology;
(2) The applied technologies were not chosen in relation to the specific raw material and to the area;
(3) The currently available information on the pyrolysis technologies, in specialty literature is insufficient and/or superficial;
(4) Lack of refineries in rural areas with an increased potential for obtainment of pyrolysis oil, which can be stabilised and subsequently used in existing oil refineries; there are few clean technologies, developed for the use of pyrolysis oil in the production of heat or electricity [3];

The Hanover principles design for sustainability [5] has outlined a series of ideas and guidelines for the design of various pyrolysis reactors that have no negative impact on the environment:

(1) Pyrolysis installations must export energy and must function on renewable energy sources, without depending on conventional sources;
(2) The heat necessary for the process has to be efficiently integrated into the designed system and needs to be generated by renewable energy sources;
(3) The entire process needs to use water rationally
(4) The benefits of rain water have to be integrated in the system design
(5) The short and long-term impact on the environment has to be analysed during the design process
(6) The project needs to have flexibility and adaptability to various necessities of the production
(7) In the evaluation of the project, the availability of air, water and soil will be taken into consideration, in order to eliminate the polluting residues.

The industrial process of pyrolysis offers a competitive alternative to valorisation of numerous renewable energy sources but also for the treatment and energetic valorisation of city waste, industrial or medical waste or from different polluting industrial fields. It is considered the most environment-friendly thermo-chemical, compared to combustion or incineration.

2. BEHAVIOUR STUDY OF SOME TYPES OF BIOMASS IN THE PYROLYSIS PROCESS

The analysed **materials** used in the slow pyrolysis process in the present study are: sorghum, energetic willow, Paulownia, sawdust from industrial processing and straw (agricultural waste, main crops).

Equipment

The experimental research has included several stages. Different equipment for biomass grinding and sorting from these materials, was used in the first stage.

The second experimental stage, the actual pyrolysis experiment, was conducted using an experimental stand (presented in the figure 2.14. a) from the Research Institute for Renewable Energies "Wroclaw University of Environmental and Life Sciences" for the study of pyrolysis and thermogravimetric analysis

Fig.2.14.a A Experimental stand for the slow pyrolysis process

The influence of temperature and heating rate on the pyrolysis process

Experimental methodology

Thirty-three thermal analysis experiments were conducted under pyrolysis conditions for the 5 studied materials. Seven experiments were conducted for the sorghum materials, energetic willow (Salix), straw and sawdust and 5 experiments were conducted for Paulownia.

The methodology was mainly based on the thermal analysis under specific conditions of slow pyrolysis.

The physical and chemical changes of the sample, according to the programmed temperature and total duration of the process were studied, using thermal analysis.

Thermogravimetric analysis (TGA) is an operational method used for thermal analysis, which represents the variation of the sample mass in relation to temperature or time, under the conditions of a well-established temperature programme, under inert atmosphere.

The synthesis of the process is revealed by the TGA graphic, a mass-loss curve (considered a dependent variable, on the ordinate), in relation to temperature or time, considered independent variables, on the abscissa. The DTG graphic is also used in the study.

It represents the first TGA derivative, a function of mass-loss over time-period. Practically, the DTG graphic represents the discomposure rate of pyrolysed material, expressed in % over time unit, compared to the initial state.

In order to determine the influence of temperature, a 1.2 g biomass sample was used in each experiment. It was introduced into the reactor and it was subjected to a heating process, with final temperatures of 400°C, 500°C, 600°C, and 800°C.

In order to determine the influence of heating rate, a 1.2 g biomass sample was used in each experiment. It was introduced into the reactor and it was subjected to a thermic treatment, at a final temperature of 800°C and 10°C·min^{-1}, 20°C·min^{-1}, 40°C·min^{-1} and 65°C·min^{-1} heating rates.

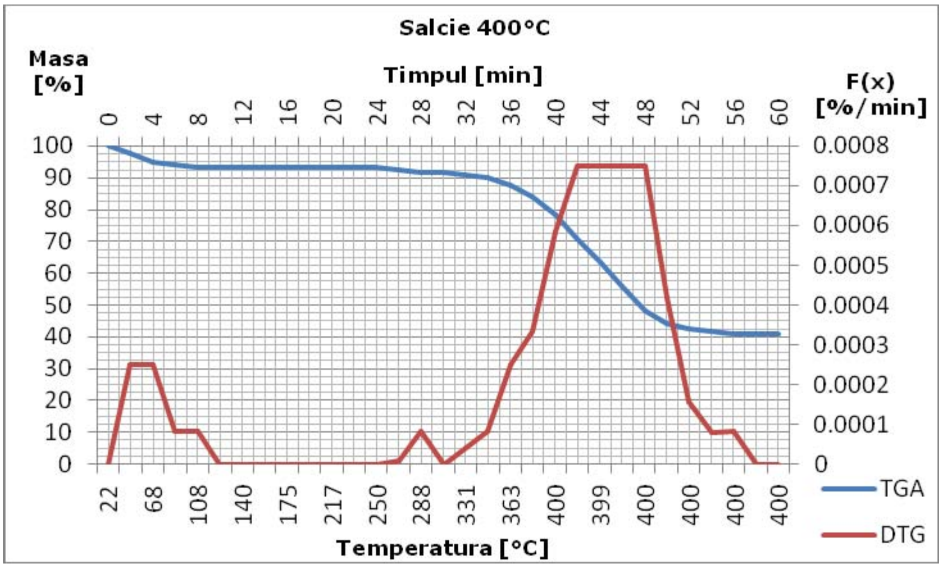

Fig.2.16 TGA and DTG diagrams of the slow pyrolysis process for energetic willow, at 400˚C and 10ºC·min^{-1} heating rate

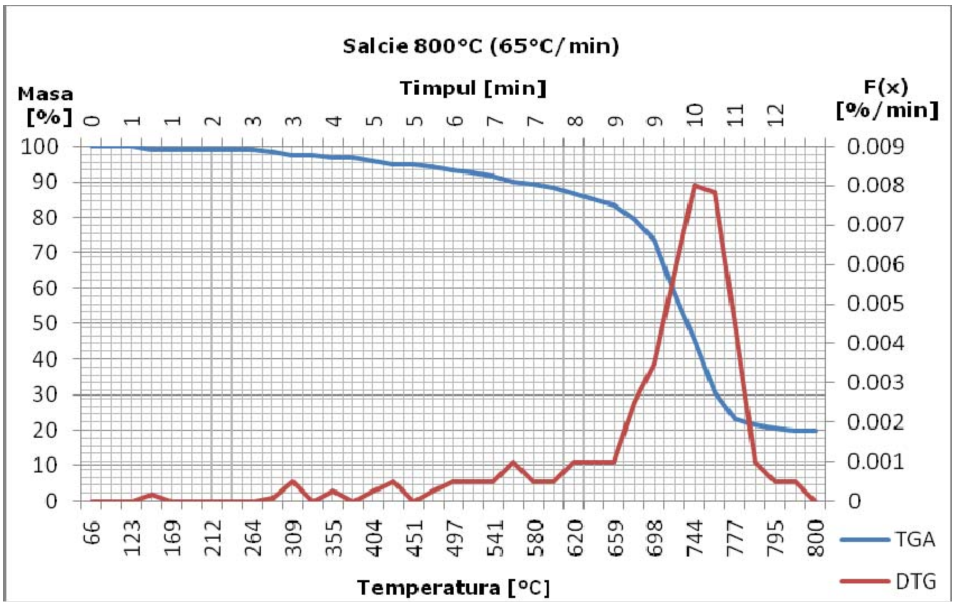

Fig.2.22 TGA and DTG diagrams of the slow pyrolysis process for energetic willow at 800˚C and a 65ºC·min^{-1} heating rate

Table 2.1 is a synthesis of the results from the slow pyrolysis process of energetic willow. Similarly, it has also been done for the other 4 types of biomass.

Tabelul 2.1 Thermal analysis of the slow pyrolysis process for energetic willow

Exp.	Final temp.	Process dur.	H.Rate	Drying	Torrefraction	Devolatilization	Carbonization, Gazeification	Char
	[°C]	[min]	[°C/min]	[°C]	[°C]	[°C]	[°C]	[%]
1	400	60	10	0-121	121-306	306-400	Nu apare	40.88
2	500	70	10	0-121	121-306	306-500	Carbonizare	30.00
3	600	80	10	0-121	121-306	306-523	523-600	23.73
4	800	85	10	0-121	121-306	306-523	523-800	22.5
5	800	45	20	0-121	121-375	375-584	584-800	21.66
6	800	24	40	0-201	201-401	401-718	718-800	20.66
7	800	12	65	0-164	264-539	539-800	800	19.84

Estimation of char production at various process parameters, using mathematical model based on the results obtained from the slow pyrolysis process

Following the 33 experiments, the results of the bio-char production analysis (presented in figures 2.49 and 2.50), were mathematically modelled using the multiple regression, to obtain a relation that can predict the bio-char production from industrial pyrolysis of biomass.

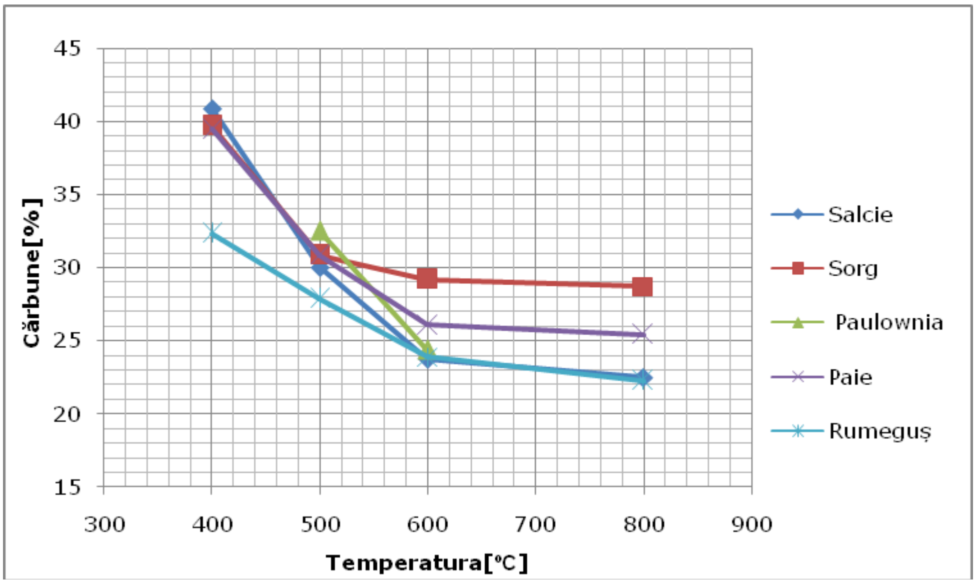

Fig.2.49 Dependency of the bio-char percent on the heating rate

Multiple regression has been used to determine the dependency relationships between the bio-char percent (dependable variable) and the final temperature of the process, respectively the heating rate (considered an independent variable). It has been done by determining coefficients of the mathematical model, specific for each type of raw material (type of biomass) [1].

It started from the general mathematical model for linear multiple regression with two variables:

$$X = p_1 + p_2 \cdot X_t + p_3 \cdot X_r \qquad (2)$$

where:
X – bio-char percent, [% mass].
Xt – final temperature of the process, [ºC].
Xr – heating rate [ºC · min^{-1}].
p1, p2, p3 – estimated parameters for regression.

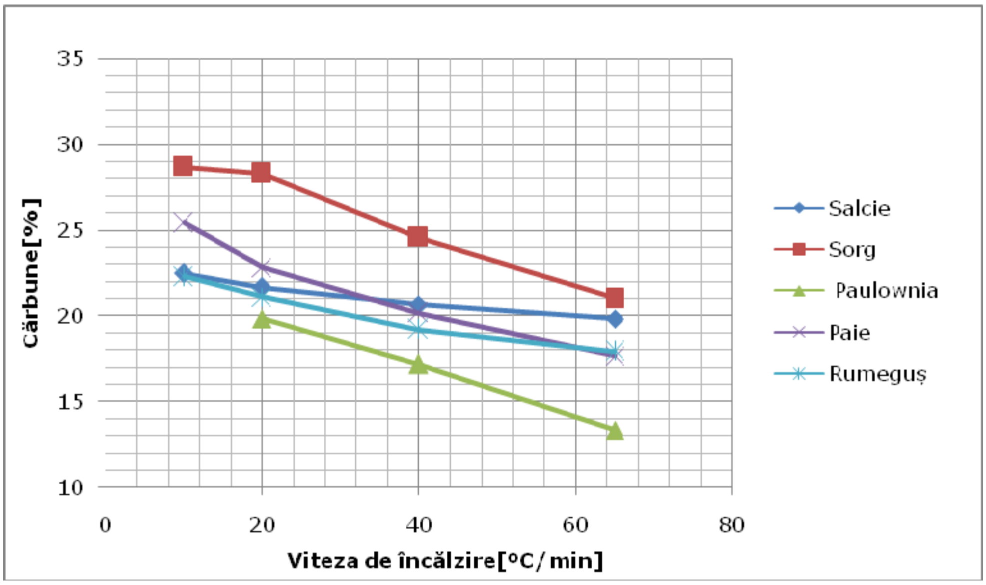

Fig.2.50 Dependency of the bio-char percent on the heating rate

The modelling was conducted for every material. As a result where established the general estimation equations for the bio-char percentage.

The following relation expressed the mathematical model:

$$X = 45.1553 + (-0.02001) \cdot X_t + (-0.1183) \cdot X_v$$

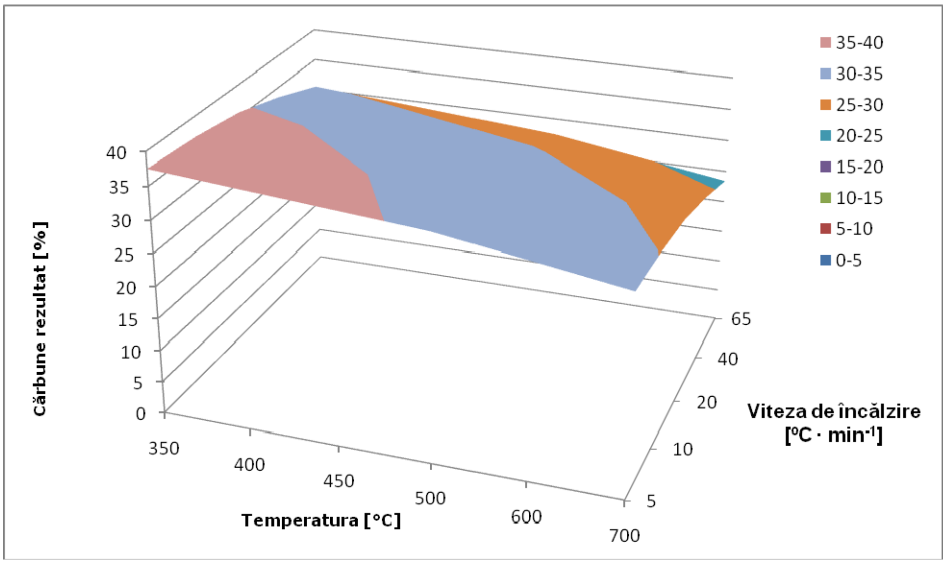

Fig.2.52.a 3D representation of the mathematical model for bio-char estimation resulted from sorghum pyrolysis [1]

3. EXPERIMENTAL RESEARCH REGARDING KINETICS OF BIOMASS PYROLYSIS

Two types of biomass samples were used in the experiments: sorghum and Paulownia, described in chapter 2.

The experiments were conducted using a high-precision thermoanalyzer, type Libra TG 209, shown in figure 2.2.1.

Each experiment used 5-10 mg of material that was introduced in the aluminium crucible of the thermoanalyzer and were subjected to a thermal treatment from 25ºC to 800ºC, with continuous recording of temperature and of sample mass during the process.

The four experiments were conducted at 2,5°C·min^{-1}, 5°C·min^{-1}, 7,5°C·min^{-1} and 10°C·min^{-1} heating rates.

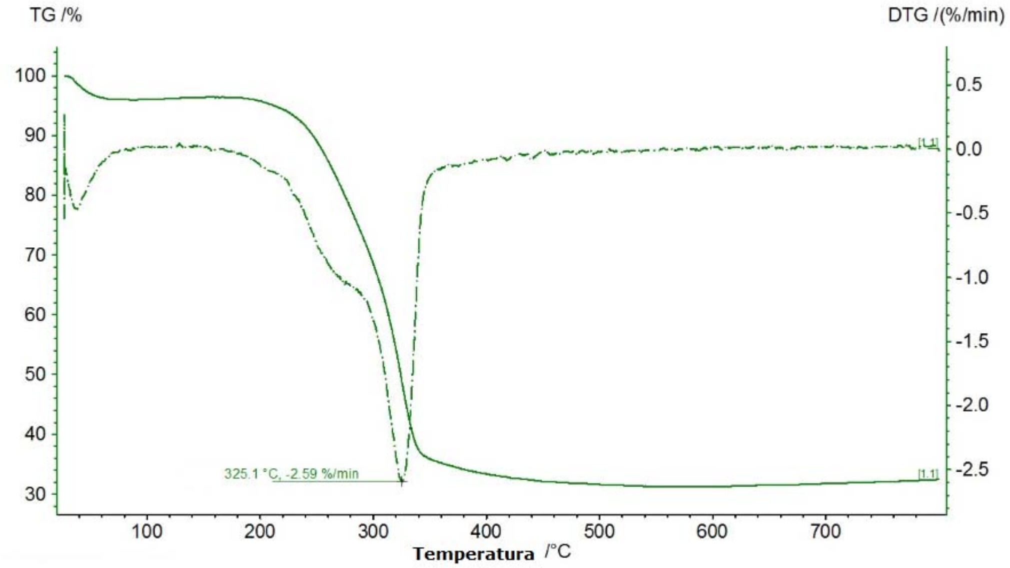

Fig.3.6 TGA-DTG diagram of the thermal analysis experiment for Paulownia at 2,5ºC·min^{-1} rate

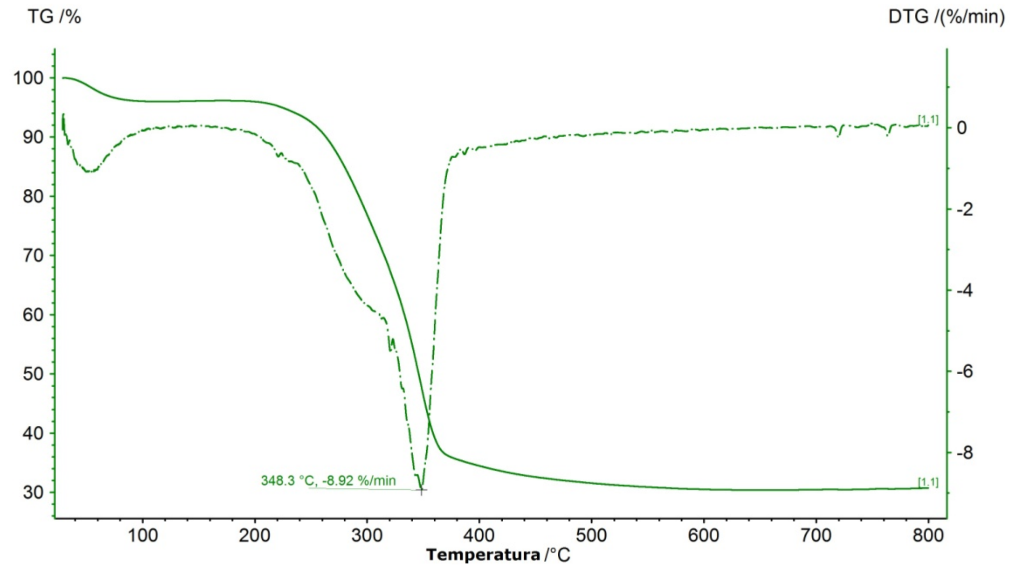

Fig.3.9 TGA-DTG diagram of the thermal analysis experiment for Paulownia at 10ºC·min^{-1} rate

To apply the isoconversional methods for kinetic calculus in the case of solid biomass, it is necessary to have curves and results of pyrolysis processes at various heating rates. The same conversion values should be identified in them.

Using the Kissinger method, we have determined the global values for the activation energy and the pre-exponential factor (A) for the entire process.

The Kissinger model has been graphically represented in figure 3.14, as function of $\ln\left(\frac{\beta_i}{T_{mi}^2}\right)$ in relation to $\frac{1000}{T_m \cdot K^{-1}}$.

A linear regression was calculated and the R^2 coefficient, respectively the regression equation was obtained.

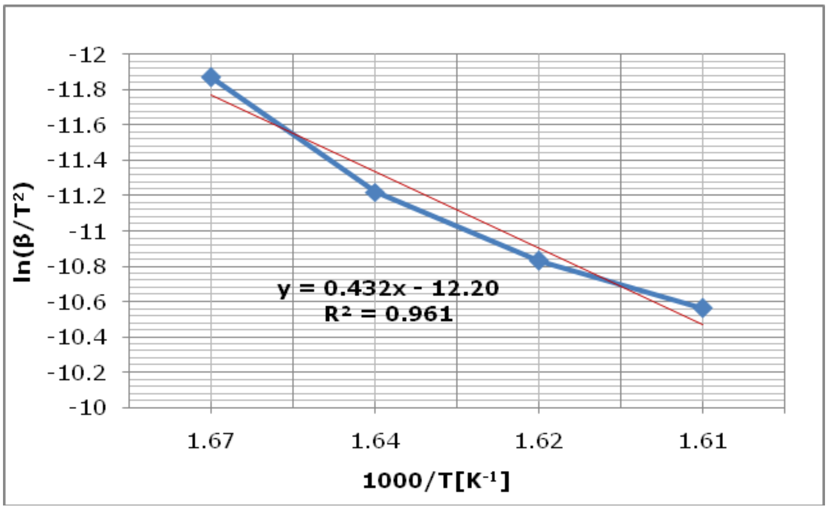

Fig.3.14 Graphic representation of the Kissinger mathematical model for Paulownia

The value obtained for Paulownia using the Kissinger calculus model was 177,43 kJ·mol^{-1} for activation energy and 9,3·108 min^{-1} for the pre-exponential factor.

For Sorghum, the obtained value was 198,87 kJ·mol^{-1} for activation energy and 3,35 x 10^{11} kJ·min^{-1} for the pre-exponential factor.

Several other values of the kinetics parameters were determined with the second KAS (Kissinger-Akahira-Sunose) calculus method, which appeared as a result of multiple reactions that take place during the pyrolysis process.

Several α conversion points were chosen using the results from the thermo-analysis graphics, comprised in the 0.1-0.9 interval, for which the corresponding temperatures T_m were extracted.

In every α conversion point we determined the activation energy and the pre-exponential factor through equations obtained from the identification of temperatures corresponding to the same α, in experiments conducted at various rates.

The values of the activation energy in the conversion points are ranged in the 156,93 - 188,12 kJ·mol^{-1} interval for Paulownia and 65,14 - 308,83 kJ·mol^{-1} interval for sorghum.

The values of the activation energy determined for the conversion points differ, fact which indicates the existence of a discomposure mechanism extended over several stages, in which the activation energy is expressed as a conversion function-seen in figures 3.18 and 3.19.

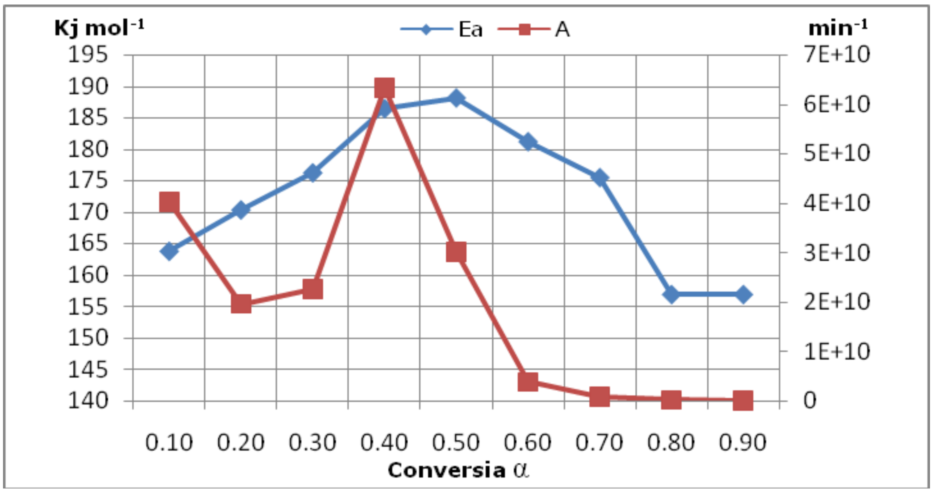

Fig.3.18 Representation of kinetic parameters as conversion function for Paulownia

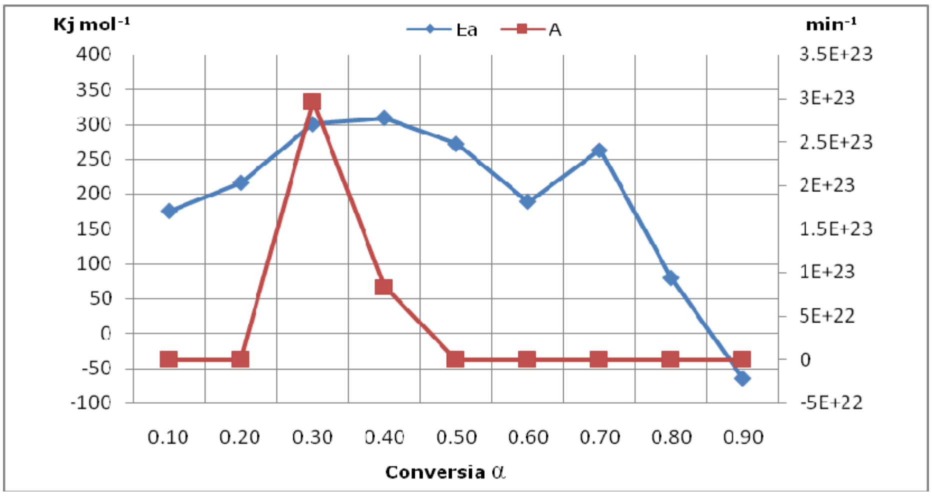

Fig.3.19 Representation of kinetic parameters as conversion function for sorghum

From the obtained results, it can be noticed that the kinetic parameters calculated for both types of biomass had significant differences. This demonstrates that the compositional structure (cellulose, hemicellulose, and lignin) of the two materials (sorghum and Paulownia) is different and their introduction in the process of pyrolysis, at identical temperature and heating rate parameters, causes different reactions.

By comparing the two kinetic calculus models, it is noticeable that by using the KAS model, the determination of kinetic parameters in various stages of the process is possible, revealing the complex mechanism of discomposure in pyrolysis. On the other hand, the Kissinger method estimates a global value of the activation energy and of the rate constant for the entire process.

By comparing the activation energy values obtained through the Kissinger method (177,43 kJ·mol^{-1} for Paulownia and 198,87 kJ·mol^{-1} for sorghum) to average values obtained using the KAS method (172,83 kJ mol^{-1} for Paulownia and 193,10 kJ ·mol^{-1} for Sorghum) it is noticeable that the values are similar. Thus, the Kissinger method can be considered an appropriate method for global estimation of activation energy in pyrolysis.

4. THE INFLUENCE OF THE PHYSICAL-CHEMICAL COMPOSITION OF BIOMASS ON THE QUALITY OF THE BIO-CHAR OBTAINED THROUGH INDUSTRIAL PYROLYSIS PROCESS

The analysis of the physical-chemical properties of the biomass samples using thermogravimetry ("technical or immediate analysis")

The proximate analysis was aimed towards determination of physical-chemical properties for four types of raw material: energetic willow, sorghum, straw and sawdust.

The experiments were conducted for each material separately, programming the system based on parameters synthetized in table 4.1.

Tabelul 4.1 Process parameters for determination of technical analysis settings

Proprietăți	Initial temperature, [ºC]	Heating rate, [ºC·min^{-1}]	Final temperature, [ºC]	Isothermal duration, [min]	Inert gas	Time [min]
Umiditate	30	50	110	15	CO_2	17
Volatile	110	50	600	30	CO_2	41
Carbon Fix	600		600	60	Oxigen	60
Cenușă						118

The measurements were recorded using specialised equipment for thermal analysis. This equipment offers the possibility to control the temperature, the isothermal duration and heating rate (independent variables) while simultaneously measuring the weight of the biomass samples with an analytical scale. The equipment is presented in chapter 2.

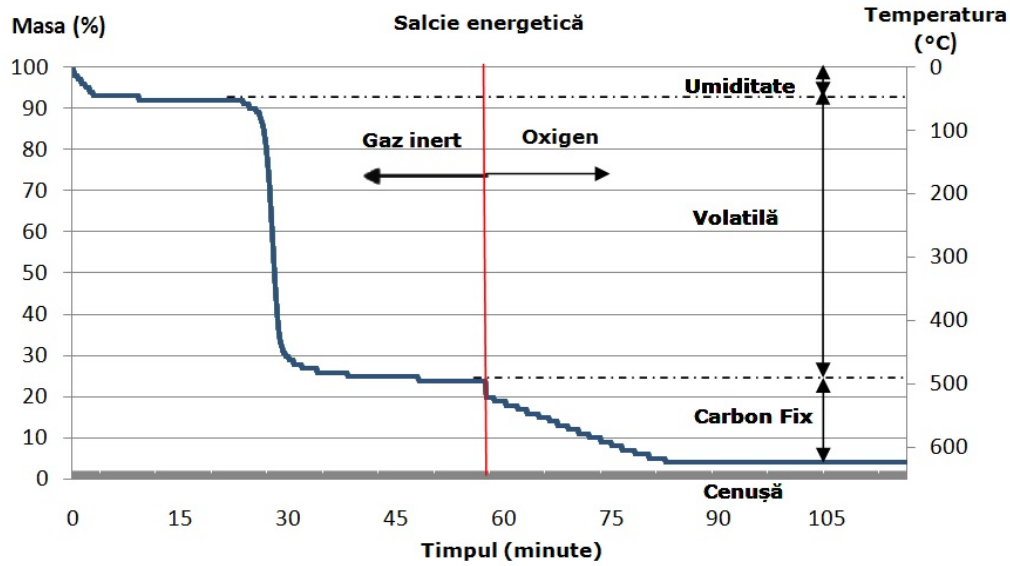

Fig.4.2.a Proximate analysis experiment for energetic willow

Although most of the researches conducted in the field of proximate analysis of biomass were done using inert gas such as nitrogen, argon or helium [52, 21, 76], the experimental model proposed by the author brings an original contribution because it uses CO_2 as gas to maintain the environment inert.

An argument that sustains the utility of this contribution is the fact that in the study conducted by Lilian D.M. [4], the author claims and argues that volatiles cannot be clearly determined when using nitrogen as inert gas because most of the organic components will generate bio-fuels as a result of pyrolysis at temperatures higher than 500˚C.

In the proposed experimental method, the maximum recommended temperature for determination of volatiles is 600˚C, in order to prevent the kindling of the Boudouard reaction, following contact with CO_2. This temperature has been chosen also to avoid initiation and amplification of the gasification process that appears changing from the inert environment to the oxygenated environment.

Analysing the results of the four material samples, it is noticeable that the percentages for the humidity content, the volatiles, the fixated carbon and the ash are similar.

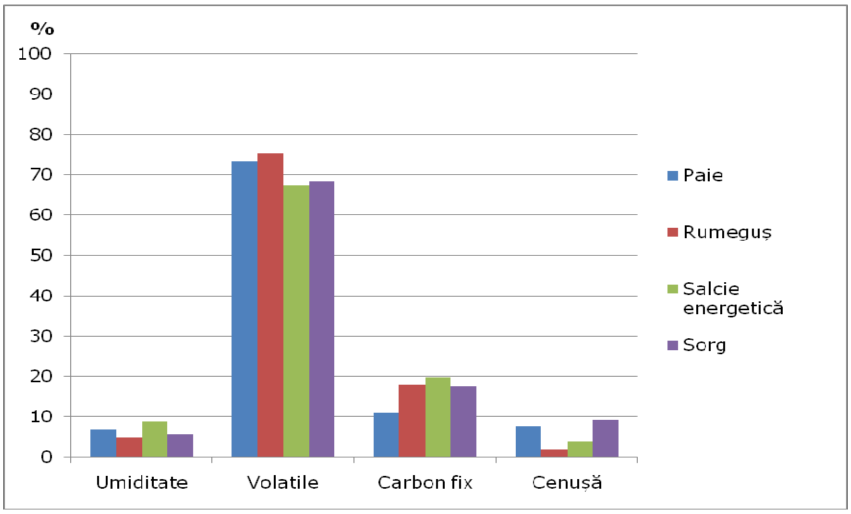

Fig.4.3 The centralised results of the application of proximate analysis for humidity, volatiles, fixed carbon and ash contents determinations

Determination of caloric capacity and physical-chemical properties of bio-char obtained through pyrolysis

According to the conclusions of the research conducted in chapter 2, the pyrolysis char was obtained by applying a thermal treatment at 400˚C with a $10^{\circ}C \cdot min^{-1}$ heating rate. After reaching the pre-set temperature in the reactor, the sample was maintained in the same conditions for 10 minutes until no visible mass reduction could be observed.

During the entire process, inside the reactor, the inert atmosphere was ensured using CO_2 gas, introduced under atmospheric pressure conditions.

The caloric power and the physical-chemical properties from the obtained bio-char were analysed.

Following the adequate standard procedures, we have determined:

- Humidity content
- Volatiles content
- Fixed carbon and ash content
- Caloric capacity for all four types of bio-char

The graphic interpretation of the physical-chemical analysis results is shown in the histograms in figure 4.11.

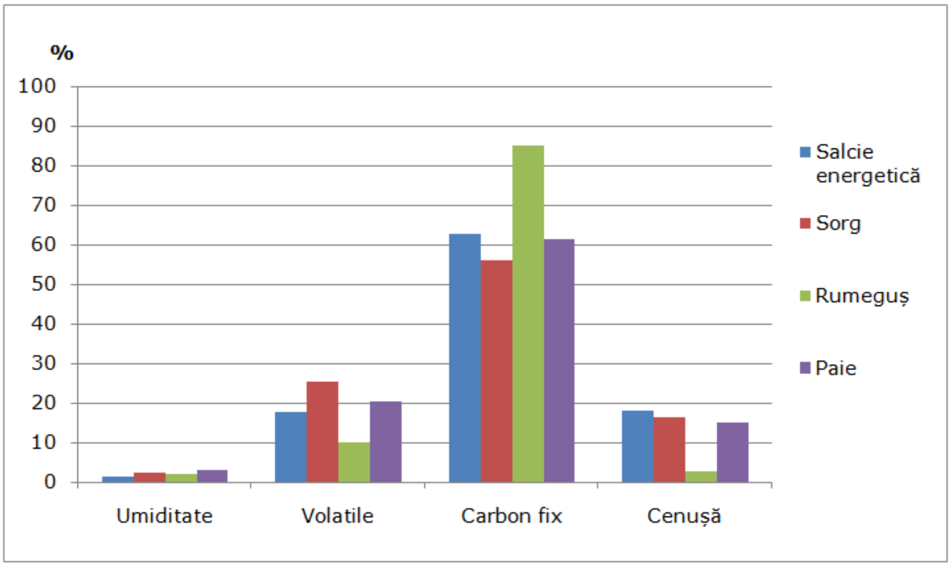

Fig.4.11 Experimental results for the four types of biomass resources

According to the obtained results (histograms from fig. 4.12) we can notice that the caloric power values of the four bio-char samples are high and comparable to the caloric power of conventional fuel char.

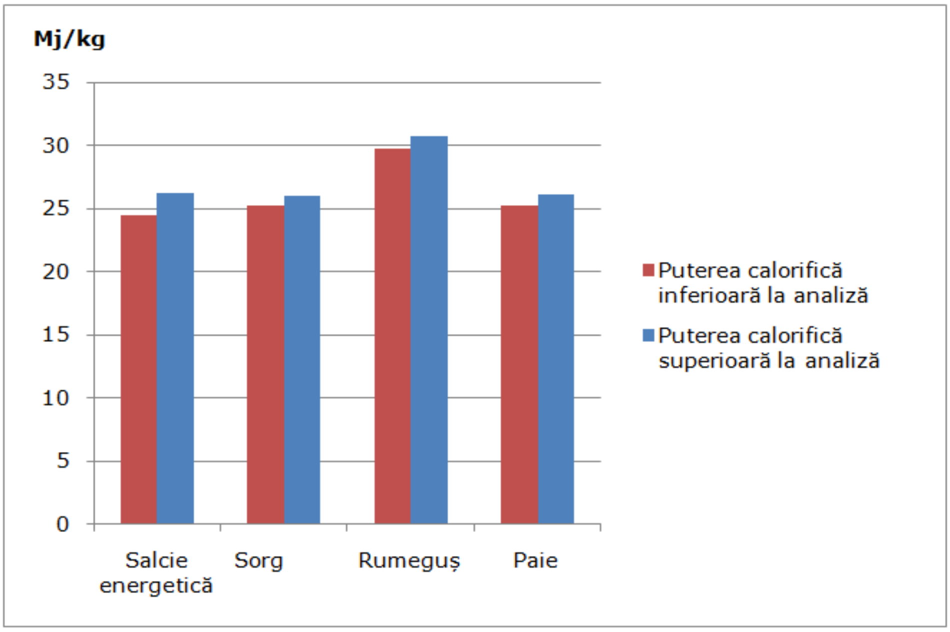

Fig.4.12 Comparative values of caloric power in all four types of biomass resources

5. PERSONAL CONTRIBUTIONS AND CONCLUSIOS. RESEARCH PERSPECTIVES

General conclusions

The conducted research involved thermic analysis experiments, physical-chemical analysis, interpretation and mathematical modeling which allow extract the conclusions.

Thus:

-Through the study of transformations from pyrolysis of the vegetal materials, we have identified the main stages (correspondent do various process conditions) through which biomass is converted into secondary products such as bio-fuels: drying, torrefaction, devolatilization, carbonization and gasification;

-It has been demonstrated through research that CO_2, as inert gas in pyrolysis, can become a genuine alternative to the most commonly used inert gas in pyrolysis-nitrogen. Thus, the results would be almost identical but the operation costs would be considerably lowered due to the small price of CO_2 compared to all the other inert gases

-In order to obtain high performances in bio-char production through pyrolysis, the maximum recommended temperature is 500˚C and a top heating rate of 10°C·min^{-1};

-For a high content in bio-oil, it is recommended that the industrial process of pyrolysis function at temperatures above 500 ˚C, with higher heating rates;

-The rise in the percent of syngas obtained through pyrolysis is possible, under the following functioning conditions- temperatures above 800˚C and low heating rate;

-After comparing the values obtained from the experiments, it was noticed that the pyrolysis parameters (factors) had similar influence on the bio-char production in all types of tested biomass;

-The influence of temperature had a bigger influence than the heating rate over the obtained bio-char yield;

-The maximum yield for the pyrolysis bio-char, in the conducted experiments, were: 40,88% for willow, 39,67% for sorghum, 32,5% for Paulownia, 39,45% for straw and 32,43% for sawdust similar to those stated in specialty literature but for other types of biomass)

-The kinetic calculus results for both types of biomass had noticeable differences, fact which leads to the conclusion that the compositional structure (cellulose, hemicellulose and lignin) of the two materials (Sorghum and Paulownia) is different. Pyrolysis performed under identical temperature and heating rate conditions will have different reactions for different materials.

- Following the interpretation of the experimental results for thermogravimetric analysis at 2,5, 5, 7,5 and 10ºC min^{-1} heating rates, the existence of the 3 regions presented in the specialty literature was highlighted: dehydration, active and passive pyrolysis;

-Under a comparative, methodologic aspect, it can be affirmed that the KAS kinetic calculus model is more relevant for the explanation of the pyrolysis phenomena by determining kinetic parameters in several stages of the process, compared to the Kissinger method;

-The values of the activation energy, obtained through the Kissinger method, are similar to the average values obtained through the KAS method. This demonstrates that the Kissinger method can be used to obtain a global estimation of the activation energy in the pyrolysis process;

-The values of the pre-exponential factor (rate constant) obtained through the Kissinger method are substantially different compared to the average values of this factor obtained through the KAS method. The explanation can be given by the theory of the activated complex. The Kissinger method is based on the theory of a single reaction with a certain number of particle collisions, while the KAS method states that there are several reactions and the number of efficient collisions differs that is not all particles with activation energy have a favourable orientation towards forming new bonds);

-The experimental results of the physical-chemical analysis for the biomass samples (humidity, volatiles, fixed carbon and ash) have comparable values to similar experimental attempts on other types of biomass from specialty literature;

-The tested materials display a similar composition, which means the same pyrolysis installation can be used in all cases;

-Following the results of the technical analysis of pyrolysis bio-char, it is noticeable that the samples rich in carbon have a low ash content;

-The results for the volatiles content had a maximal variability in the case of the four bio-char samples. The minimum percent of volatiles was recorded for the bio-char obtained from sawdust and the maximum percent was recorded for bio-char obtained from sorghum.

-The high percentage of volatiles from the sorghum, energetic willow and straw bio-char is due to the incomplete conversion of biomass, which can be generated by factors of physical-chemical nature (different structure of lignocelluloses in biomass samples, humidity of raw material or diameter of particles, etc.)

-The results of the calorific power determinations for the pyrolysis bio-char are different, according to the type of biomass, mainly due to the elementary chemical composition;

- If initially, the caloric power of the biomass species is 18.51 $Mj\cdot kg^{-1}$ for sawdust and 19.7 $Mj\cdot kg^{-1}$ for willow, the caloric power of the obtained bio-char from the experiments was 30,68 $Mj\cdot kg^{-1}$, for sawdust and 26,26 $Mj\cdot kg^{-1}$, for willow (this is a 30-50% higher caloric capacity than the caloric capacity for the corresponding raw material).

- To establish the ideal conditions for financial profitability, is necessary to make an analysis that implies: operation costs for pyrolysis, determination of caloric capacity for bio-char and the possible price of energetic valorisation.

Industrially applicable contributions

- the obtainment of bio-fuels with high caloric properties (pyrolysis bio-char) from new types of biomass (sorghum, Paulownia and energetic willow) is highlighted. They can be used as an alternative source of energy for conventional fuels;
- the use of CO_2 for maintaining an inert environment during the pyrolysis process instead of the most widely used inert gases in pyrolysis (nitrogen, argon), with substantial economic advantages;
- the establishing of optimal parameters for the slow pyrolysis process for all five types of biomass (sorghum, willow, Paulownia, sawdust and straw), through thermogravimetric analysis, in order to ensure a rational conversion into biofuels.
- optimisation of the industrial process of slow pyrolysis, by experimentally determining the prediction functions for the bio-char content, obtained through slow pyrolysis for all five types of bio-char (sorghum, willow, Paulownia, sawdust and straw). The independent variables are temperature and heating rate.

Ulterior development perspectives

The main study directions identified through the experience accumulated in the present research are:

- Extension of experimental research for other raw materials from the biomass category, but also for other biological products with untapped energetic potential;
- Extension of the experimental research regarding the characteristics analysis of other valuable products that are results of biomass pyrolysis (bio-oil and syngas);

- New research perspectives, related to the study of the physical properties of raw material (biomass), study of the influence of process duration and inert gas flow on slow pyrolysis.

- Development of an industrial prototype for slow pyrolysis of a wide range of biomass raw material, which can allow a better valorisation.

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