UNIVERSITY „**POLITEHNICA”** of BUCHAREST

Faculty of Applied Chemistry and Materials Science

Department of Chemical and Biochemical Engineering

DOCTORAL SCHOOL OF APPLIED CHEMISTRY AND MATERIALS SCIENCE

Senat Decision Nr. **497** From **06.02.2020**

PhD THESIS

ADDING VALUE TO THE WASTE VEGETABLE OILS THROUGH THERMAL PROCESSES

(Thesis Summary)

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Bucharest

-2020-

CONTENT:

THANKS

An undeniable truth is that "the man, as he lives, learns" and I am conscious that after completing this stage of further education, I will face a long road paved with a lot of work and efforts to complete my professional career.

Mrs. **Emeritus Prof. Phd. Eng. Gheorghița JINESCU**, the scientific leader of the paper, sincere thanks for accepting to share from your rich experience and I am grateful for the support given in the elaboration of this scientific paper, as well as for the whole contribution to my professional training.

I also thank the support and suggestions given to all members of the guidance committee: **Prof. Phd. Eng. Claudia Irina Muntean (Koncsag)**, **Prof. Phd. Eng. Oana Pârvulescu** and **Prof. Phd. Eng. Alexandru Woinaroski** for the precious time granted, for the valuable scientific advices as well as for the competent and permanent guidance during the elaboration and realization of this doctoral thesis.

Many thanks to **PhD Eng. Monica Alina Mares** and **PhD Eng. Gabriela Isopenscu** for their support and attention during my doctoral's studies.

I thank the management of TURBOMECANICA and my colleagues for their suggestions, but especially for their confidence and support in every difficult moment.

With special love and gratitude, I dedicate this thesis to my dear parents, who were with me, surrounded with their affection and supported me from all points of view during this period.

Thank you!
Eng. Sivriu Ana-Maria

Keywords: waste vegetable oils, palm oil, pyrolysis, mathematical model, quench oil.

INTRODUCTION

The use of olefins in state-of-the-art industrial applications (such as plastics, solvents, constructions, synthetic materials) has grown significantly, being closely linked to the growing needs of the expanding global population [2].

The limitation of oil resources has led in time to the development of new technologies that can use renewable raw materials: biomass or products derived from it, such as vegetable oils. In recent years, have been developed advanced conversion technologies [3].

Vegetable oil is one of the most important natural sources of renewable energy. It is the raw material for biodiesel but can also be a source of gas fuel and newer, of olefins, by processing in pyrolysis processes [4]. An efficient process for the recovery of waste vegetable oil is the thermal conversion with the production of olefins, which has undergone rapid development in the last decade [11].

The main objective is to make original contributions for developing alternatives routes to improve thermal treatments of waste vegetable oils.

The main objective is achieved by pursuing **secondary objectives**:

- ❖ knowledge and development of the mechanisms of thermal decomposition of vegetable oils after their use and their influence on the physico-chemical properties of the oils;
- ❖ the study and analysis of waste vegetable oils through thermal processes from specialized literature;
- ❖ experimental research of the thermal processes carried out in different installations (with continuous operation or in vacuum oven) under different processing conditions;
- ❖ clarification of the reaction mechanisms of the conventional pyrolysis process and determination of the reaction products during the thermal processes;
- ❖ mathematical modeling of these thermal processes, in order to pass on an industrial scale.

The doctoral thesis is divided into two parts, as follows:

- **BIBLIOGRAPHY STUDY (**CHAPTER I - ADDING VALUE TO THE WASTE VEGETABLE OILS THROUGH THERMAL PROCESSES**)**

Chapter I details the study from the specialized literature where is presented the importance of adding value of waste vegetable oils through thermal processes.

There is neceessary a detailed research to optimize reaction conditions to obtain specific products, to understand reaction mechanisms and to fully evaluate the properties of the finished product.

Thus, the following theoretical aspects are highlighted:

➢ following the pyrolysis process, the following products are obtained: gaseous, liquid and coke;

➢ the reaction mechanisms that occur after the pyrolysis process are proposed and exemplified by the researchers in domain;

➢ the yield of the obtained products is influenced by the following factors: pyrolysis reaction temperature, residence time, the nature of the diluent (water and nitrogen), the nature of the raw material, the reaction inhibitor and the product collection procedure and the analytical techniques used to determine reaction compounds.

Also there are presented the advances from this domain as well as the technological processes realized in micropilot systems with the possibility of industrial application. Thermal pyrolysis processes are classified into several categories as follows:

- depending on the nature of the reactor:
  - simple pyrolysis of vegetable oils in the autoclave reactor;
  - electric arc pyrolysis;
  - microwave pyrolysis;
  - pyrolysis in a continuous reactor.
- in presence of inert materials:
  - analytical pyrolysis;
  - pyrolysis in presence of dilution steam;
  - pyrolysis in presence of the mixture of water and nitrogen;
- in presence of catalysts (catalytic cracking);
  - catalysts based on transitional metals and noble metals;
  - zeolitic catalysts and molecular sieves;
  - catalysts based on aluminum oxides, magnesium, silicon;
  - sodium carbonate.

- **SCIENTIFIC RESEARCH**

In chapter II is presented the experimental research regarding waste palm oil pyrolysis in a tubular reactor, with continuous operation and there are presented the experimental results (by the chromatographic analysis of the gaseous products and by the analytical determinations of the liquid products), as well as the statistical interpretation and processing of the experimental data.

Chapter III includes the experimental study of the waste palm oil through pyrolysis process, in presence of steam, carried out in the same tubular reactor and the influence of the process factors as well as the mathematical modeling in order to industrial scale-up.

In Chapter IV is elaborated the waste palm oil thermal process with reducing viscosity of the resulting liquid products and their recommendation for use as components for combustion fuel in outbreaks.

The experimental research in Chapter V performs the thermal treatment (thermal decomposition) of the waste rapeseed oil in the vacuum oven followed by the argon cooling and using of these oils as cooling media (quenching) in the process of hardening from the metallurgical industry.

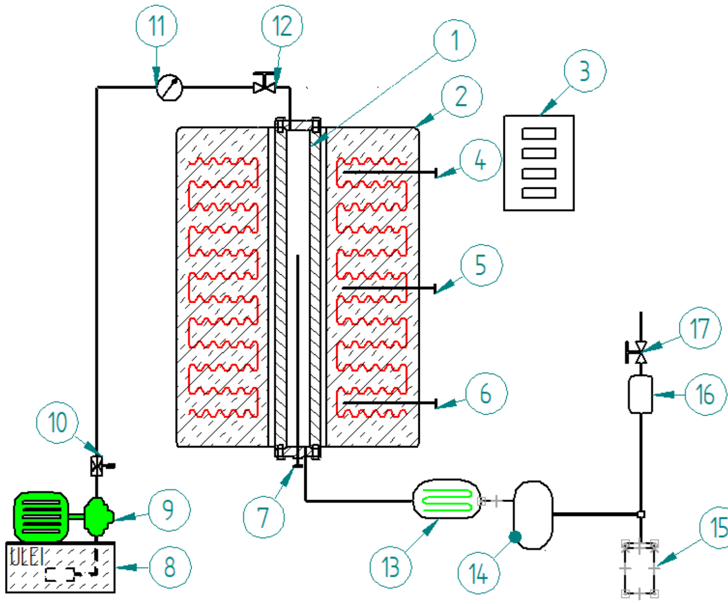
CHAPTER II
EXPERIMENTAL RESEARCH OF WASTE PALM OIL PYROLYSIS WITH GAS PRODUCTS

2.1 THE OBJECTIVES OF EXPERIMENTAL RESEARCH

The aim of the experimental research is to evaluate the possibility of obtaining valuable products from the waste vegetable oil, through a simple pyrolysis process especially to produce high yields of ethylene and propylene.

2.1.1 Experimental installation. The procedure and experimental conditions

The drawing of the micropilot system for the pyrolysis of waste palm oil is shown in the figure (2.2).



Legend:
1-pyrolysis reactor;
2-electric oven;
3-temperature regulator;
4÷7 -thermocouple of type K;
8-oil tank;
9-piston pump;
10,12,16-valve;
11- manometer;
13-condenser;
14- separator;
15- liquid collector vessel;

Figure 2.2. The micropilot system of the waste palm oil pyrolysis

The gas samples are collected in aluminum foil bags, with the capacity of 4 liters, usually used when collecting samples from nitrogen-oxygen installations. Liquid samples are collected in the liquid collector (Erlenmayer glass).

2.1.3 Experimental study of waste palm oil pyrolysis. Discussion of the results

The physico-chemical characteristics of the waste palm oil used as raw material in the pyrolysis plant were illustrated in table (2.1) [95].

Table 2.1. The physico-chemical characteristics of the raw material (waste palm oil)

No. crt.	**Characteristics**	**Methods of analysis**	**Value**	**Unit**
1.	Density d_{20}^{20}	Method with pycnometer, ASTM D1298-99	924,9	kg/m^3
2.	Kinematic viscosity at 40°C	Method with Ubbelohde viscometer, ISO 3104	$47,3 \cdot 10^{-6}$	m^2/s
4.	Flash Point	Marcusson device method, DIN12785	241	°C
5.	Iodine Value	The method to determinate the iodine value, ASTM D5768-02	4,62	g I2/100g product

The experimental study was carried out at temperatures between 450-630°C, with the residence time of 120 s, 180 s and 240 s.

The volume percentages (% vol.) in the chromatogram were converted to mass percentages (%), and the values presented in table (2.3) resulted, which are grouped by each class of compounds.

Table 2.3. The results of the chromatographic analyzes of the compounds in the gaseous products (in %) obtained at different reaction temperatures and residence time

Temperature, °C	**475**	**480**	**530**	**550**	**555**	**580**	**600**	**620**	**630**
Residence time, s	**240**	**120**	**120**	**120**	**180**	**180**	**240**	**240**	**180**
Hydrogen (H_2)	0.1764	0.1655	0.1703	0.2551	0.195	0.283	0.416	0.5859	0.299
Carbon monoxide (CO)	23.0788	25.4061	17.9543	14.2196	16.8247	14.8784	14.8437	14.3335	14.1366
Crabon dioxide (CO_2)	27.6921	28.9914	18.6089	16.9961	18.9367	18.3621	13.5814	12.9492	14.0094
Oxygen (O_2)	0.1685	1.3847	0.2632	1.3712	0.2018	0.2576	0.1711	0.1639	0.2894
Nitrogen	0.6898	4.2943	0.9824	4.5744	0.6949	0.898	0.6694	0.7235	1.0288
Methane (CH_4)	4.0439	2.7322	4.8286	5.6184	5.1594	6.2049	7.6564	8.2416	7.1167
Ethane (C_2H_6)	5.8007	4.8205	7.4234	7.3648	7.6734	8.0622	8.8876	8.995	8.5377
Propane (C_3H_8)	4.6241	4.0191	4.2241	3.2702	4.4625	3.8612	3.6214	3.7279	3.4111
Butane (C_4H_{10})	2.8902	3.1313	2.269	1.5901	2.1438	1.7895	1.587	1.6708	1.3825
Pentane (C_5H_{12})	1.3191	1.29	1.0309	0.7694	1.0226	0.9266	0.8708	0.9422	0.7072
Alkanes (C_6-C_{10})	0.7522	0.7499	0.2388	0.2081	0.8221	0.3369	0.2507	0.7029	0.3678
Ethylene (C_2H_4)	10.2222	9.1977	17.7444	18.7919	16.8519	17.2207	16.8316	15.6087	19.4244
Propylene(C_3H_6)	9.7753	7.6591	12.9233	13.3124	13.3147	14.1086	16.0264	16.5085	15.3561
1-butane	4.1124	4.2459	6.4223	6.0352	6.0074	5.3804	3.343	3.2607	5.6569
i-butane	0.3088	0.1421	0.2324	0.2602	0.2827	0.3726	1.2524	2.2568	0.4169
Butadiene	1.4449	1.188	2.8238	3.0152	2.53	2.4182	1.1198	0.5765	3.0715
Benzene (C_6H_6)	0.2807	0.5462	0.467	0.47	0.724	0.6503	0.7529	0.6563	1.1204
Toluene (C_7H_8)	0	0	0	0	0	0	0	0	0
Ethylbenzene (C_8H_{10})	0	0	0	0	0	0	0	0	0
o-Xilen (C_8H_{10})	0	0	0	0	0	0	0	0	0
2-Butene	2.3855	0.7387	1.2484	1.6654	2.038	3.7516	7.9459	7.9172	3.4649
Total	**99.9**	**100**	**100**	**99.95**	**100**	**100**	**100**	**100**	**100**

As can be seen from the table (2.3) after waste palm oil pyrolysis at different working temperatures and residence time were obtained high concentrations of valuable compounds, such as: methane, hydrogen, monoxide and carbon dioxide, olefins, benzene etc.

The graphical representation of the yields of the gaseous products that are the subject of the experimental research is shown in the figure (2.4) [95].

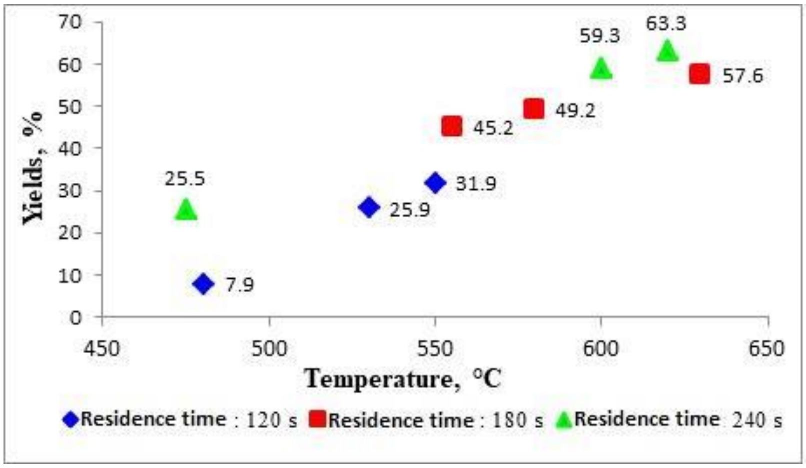


Figure 2.4. Graphical representation of the yields of the gaseous products depending on temperature

The yields of pyrolysis gaseous products depend on the reaction temperature and residence time of the raw material in the reactor. As can be seen from figure (2.3), the increase in temperature leads to high yields, so that at temperatures above 600°C, the gas yield increases over 50%.

Graphs from figures (2.5)-(2.9) represents the variation of yields with temperature and residence time for those products that are obtained in significant quantities: ethylene, propylene, methane, hydrogen, carbon oxides.

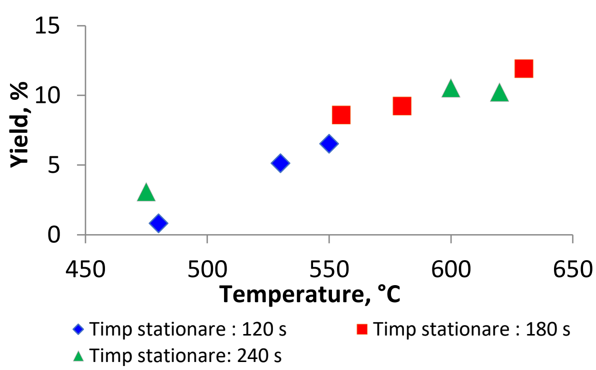


Figure 2.5. Ethylene yields

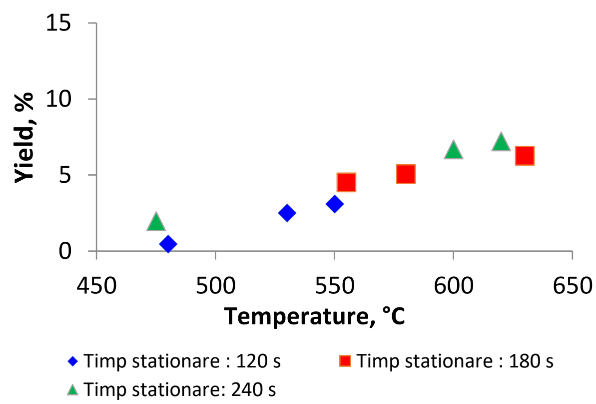


Figure 2.6. Propilene yields

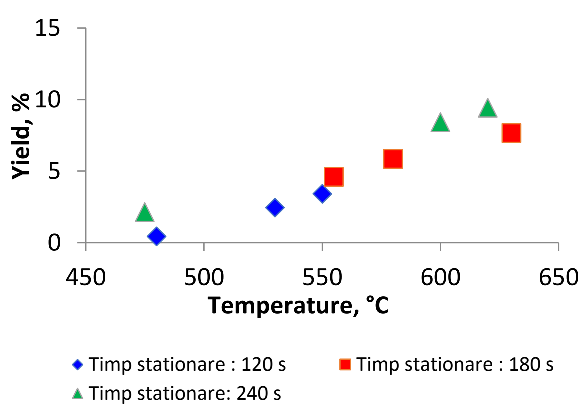


Figure 2.7. Methane yields

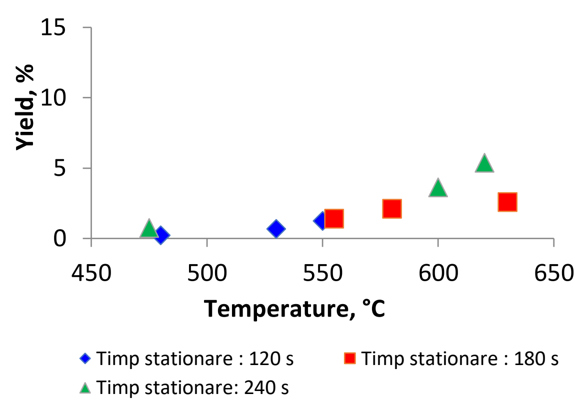


Figure 2.8. Hydrogen yields

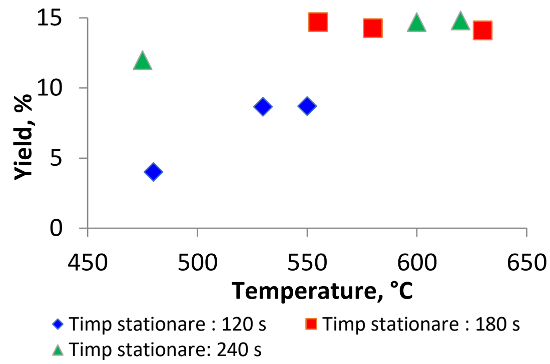


Figure 2.9. Carbon oxides yields

From the graphs above it can be observed that significant yields of ethylene and propylene are obtained at temperatures above 550°C: over 10% ethylene, respectively over 5% propylene, which justifies their separation from the gas product resulting from the pyrolysis reaction for recovery in the petrochemical sector. The oxygen and nitrogen in the pyrolysis gas comes from the small leaks of the plant or from the handling of the gas collection container.

The high yields of ethylene, propylene, methane and hydrogen are due to the increase of the temperature and the residence time, for example figures (2.4) - (2.8). *The effect of the same parameters on the yield of carbon oxides is weaker, especially at high temperatures (550-630°C), where the yield is kept almost constant around 15%*, the amount of carbon oxides that are formed is limited by the content of carboxylic groups of triglycerides.

As a result, the product can be used as a liquid fuel component.

2.2 MATHEMATICAL MODEL FOR PREDICTING YIELDS OF PYROLYSIS PRODUCTS

2.2.1. Semi-empirical model in experimental research

In the present experimental research, it is applied the mathematical model proposed by the researchers of the University of Florida, determining the parameters of the semi-empirical model (ASEM) corresponding to the yield of the products obtained from the own experiment [96].

- ***Description of the analytic semi-empirical model (ASEM)***

The ASEM model is valid for those applications where the time factor has no influence, in those very slow or very fast processes. Neglecting the time factor, the yields of different products are expressed as temperature functions which also include logistic parameters, such as equation (2.3). [101]:

$$y(T) = w[L(T:T_0,D)]^p[F(T:T_0,D)]^q \qquad (2.3)$$

where,

- $L(T:T_0,D)$ is a logistic curve called "learning curve" or main function;
- $F(T:T_0,D)$ is its complementary function *F(T) = 1-L(T)*, also called the "forgetting curve" or the residual function;
- T_0 și *D* are logistical parameters of the reaction system;

- w, p,și q are specific constants to the chemical compound.

The two curves are described by equations 2.4 and 2.5 where the yield is expressed as % mass and the temperature in K or °C:

$$L(T{:}T_0,D) = \frac{1}{[1+\exp\left(\frac{T_0-T}{D}\right)]} \quad (2.4)$$

$$F(T{:}T_0,D) = \frac{1}{[1+\exp\left(\frac{T-T_0}{D}\right)]} \quad (2.5)$$

- ***Application of the semi-empirical model in experimental research***

The logistic parameters resulted with the following values: T_0= 470°C and D=20°C. These values of T_0 and D remained the same for all other components and are constants for the model. According to the ASEM methodology, for each compound, w was determined from equation (2.3), for the condition: $q = 0$ and $p = 1$. Then p and q were determined by regression for the other compounds in the family; w, p and q are specific to the compound. The calculated parameters are presented in tables (2.8) - (2.10). Also, the predicted yields were calculated and then it was calculated the errors between predicted and experimental yield (at temperatures of 555, 580, 630°C).

Tabel 2.8. The ASEM model parameters for olefins (T_o= 470°C, D=20°C)

Compound	w	p	q	Y (predicted), %	Y (experimental), %	Error
Ethilen	15.0	1	0	9.508	8.588	0.92
	15.0	1	0	9.660	9.2496	0.41
	15.0	1	0	11.403	11.923	-0.52
Propilene	12	1	0.03	5.19	4.52	0.67
	12	1	0.03	5.04	5.067	-0.03
	12	1	0.03	6.13	6.71	-0.58
Butenes	10	1.5	0.04	4.17	3.77	0.40
	10	1.5	0.04	4.39	4.68	-0.29
	10	1.5	0.04	4.82	4.90	-0.08
Butadienes	3	1.5	0.04	1.25	1.14	0.11
	3	1.5	0.04	1.32	1.19	0.13
	3	1.5	0.04	1.45	1.58	-0.13

Tabel 2.9. The ASEM model parameters for parafins (T_o= 470 °C, D= 20 °C)

Compound	w	p	q	Y (predicted), %	Y (experimental), %	Error
Mehtane	5.5	1	0.04	4.38	3.67	0.71
	5.5	1	0.04	3.15	3.05	0.10
	5.5	1	0.04	1.57	2.33	-0.76
Ethane	6.5	0.8	0.02	5.01	4.40	0.61
	6.5	0.8	0.02	4.19	3.97	0.22
	6.5	0.8	0.02	2.96	3.47	-0.51

Propane	2.8	0.6	0.03	1.69	1.76	-0.07
	2.8	0.6	0.03	1.99	1.90	0.09
	2.8	0.6	0.03	2.12	2.02	0.10
Butane	1.5	0.9	0.04	0.88	0.97	-0.09
	1.5	0.9	0.04	0.90	0.88	0.02
	1.5	0.9	0.04	0.95	0.79	0.16

Tabel 2.10. The ASEM model parameters for permanents gases (T_o= 470°C, D= 20°C)

Compus	w	p	q	Y (prezis),%	Y (experimental),%	Error
Hydrogen	0.24	1.4	-0.1	0.12	0.09	0.03
	0.24	1.4	-0.1	0.13	0.14	-0.01
	0.24	1.4	-0.1	0.14	0.17	-0.03
Carbon oxide (CO)	20	2	-0.1	7.09	7.59	-0.50
	20	2	-0.1	7.65	7.33	0.32
	20	2	-0.1	8.80	8.12	0.68
Carbon dioxide (CO_2)	11	0.2	0.2	8.30	8.54	-0.24
	11	0.2	0.2	8.28	9.05	-0.77
	11	0.2	0.2	8.22	8.06	0.15

The mathematical model confirms the predictions yield values comparable to the results of the experimental research. The difference between the calculated (predicted) and the experimental values represents the absolute error and is below 1%, which leads to the conclusion that this type of mathematical model can be attributed to the experiment. The relative errors are significant in the case of hydrogen (± 24.1%), a gas component that has a low yield and for the rest of the gaseous components the actual error is below 10%. In conclusion, the applicability of the mathematical model is not affected.

2.2.2. The mathematical model obtained by linear regression

The independent variables (inputs) that influence the process of obtaining olefins by pyrolysis of waste palm oil are:

- reaction temperature;
- residence time;
- prezence/absence of an inert gas in the system.

These variables influence the following dependent variables (outputs):

- the yields of the gaseous products resulting from the pyrolysis;
- individual yields of gaseous compounds;
- liquid yield;
- coke yield.

From the experimental results [95], it is observed that the yields of the gaseous products increase with the temperature and it is influenced by the process time. For example, the total gas product yield at 480 ° C and the residence time of 120 s is 7.97%, while at 475°C and 240 s it is 25.47%.

The influence of process factors (temperature and residence time) on the total gas efficiency can be described by a polynomial equation of the second order (equation 2.9):

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_1 \cdot x_2 + a_4 \cdot x_1^2 + a_5 \cdot x_2^2 \qquad (2.9)$$

where:

- y este total yield of gaseous products,%
- x_1 – residence time of raw material in the reactor, s;
- x_2 – temperature, ^oC;
- a_0 ... a_5 - coefficients.

Regression analysis is a method that estimates the dependent variable *y* (total gas yield) at different values of the independent variables *x* (x_1 and x_2). Following this analysis, the degree of association of the variables represented by the correlation coefficient (R) is identified.

To determine the model coefficients was used the features of the Microsoft Excel program, "Data analysis" menu.

Table (2.11) presents the statistical regression parameters calculated by the Excel program. The analysis of variance (ANOVA) showed that most of the coefficients are significant ($p < 0.05$), except for the coefficient for the term x_1x_2, where p = 0.20495 (table 2.12). Also, the standard error for this coefficient, 0.00012, was too large compared to its absolute value: 0.00019, so the term x_1x_2 was eliminated.

Tabel 2.11. Statistical regression parameters for the equation model (2.9)

Correlation coefficients	
R	0.9997
R^2	0.9995
R^2 adjusted	0.9987
Standard error	0.6883
No. of experiments	9

Tabel 2.12. Analysis of variance (ANOVA)

Coefficients	**Value**	**Standard error**	**t Stat**	**P Value**
x1	0.501362	0.061947	8.093407	0.003942
x2	1.379573	0.110445	12.49109	0.001106
x1x1	-0.00069	0.000177	-3.90159	0.029889
x1x2	-0.00019	0.000118	-1.6139	0.204953
x2x2	-0.00099	0.000102	-9.6741	0.002345

The regression analysis resulted in the mathematical model described by the equation (2.10):

$$y = -458.459 + 0.501 \cdot x_1 + 1.374 \cdot x_2 - 0.00084 \cdot x_1^2 - 0.00102 \cdot x_2^2 \qquad (2.10)$$

The value of the coefficient of determination R^2 shows that 99.95% of the variation of y is explained by the regression equation, while 0.05% of the variation of *y* remains unexplained. Therefore, the mathematical model described by the polynomial equation of the second degree has a good accuracy.

2.3 PARTIAL CONCLUSIONS

The purpose of experimental research is to obtain olefins and other valuable products from palm oil, by pyrolysis, under thermal regime. The effect of the process temperature (475ºC÷630ºC) and the duration of the spent time of the waste palm oil in the reactor (120 s to 240 s) on the gaseous products was observed and quantified. The models have good accuracy and analysis of the variance has shown that the models are valid at a significance level of 95%.

The process was also modeled by another semi-empirical approach, through experimental investigation combined with the application of logistical functions, for the pyrolysis of canola oil (from rapeseed with an oil content of 80% in seeds) [57].

The parameters (w, T_o, D, p and q) of the ASEM mathematical model were calculated for each product with satisfactory accuracy and the results were compared with other experimental data in the literature.

CHAPTER III
EXPERIMENTAL STUDY OF THE
WASTE PALM OIL PYROLYSIS PROCESS IN PRESENCE OF STEAM

The main objective of the experimental research was based on the addition of an inert fluid (steam) in the pyrolysis process of the waste palm oil to determine its influence on the yields of high value products in the petrochemical sector.

3.2. EXPERIMENTAL RESULTS AND DISCUSSIONS

Following the experimental research of the pyrolysis of the waste palm oil in presence of steam, high concentrations of ethylene and propylene are obtained: *18.89-25.5% vol. ethylene and 13.33-15.05% vol. propylene*. The concentration values for each gas component identified in the gas samples, under different operating conditions are presented in the form of a graph in figure (3.2).

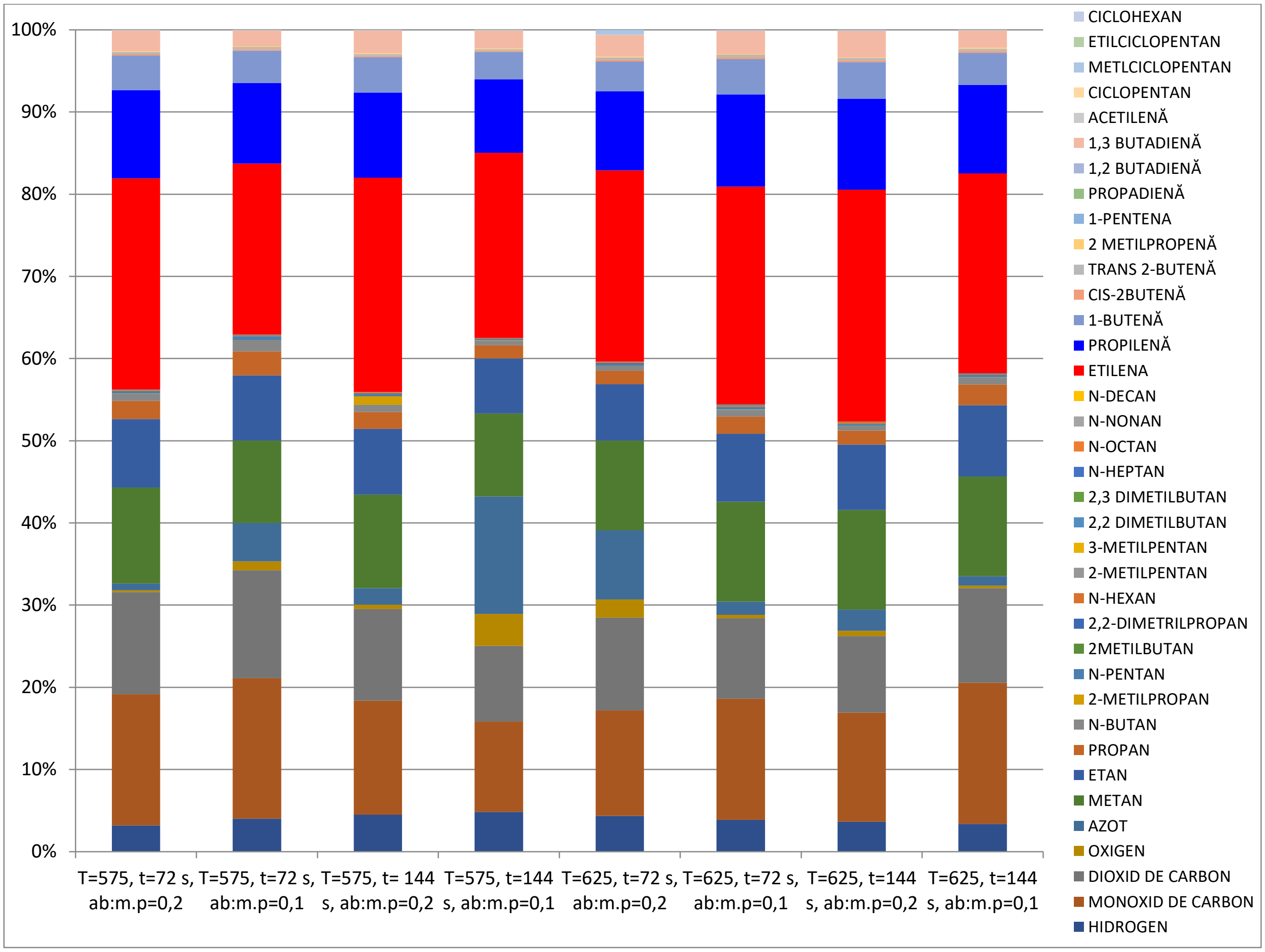


Figure 3.2. Graphical representation of concentrations of individual compounds in gaseous products, % vol.

The chromatogram concentrations of the chemical compounds in the gaseous products are expressed as % vol., which is converted to % mass, as described in Chapter II.

The concentrations of ethylene and propylene are higher than those obtained in experimental research in the absence of steam, where the concentration of ethylene was between 9.2% and 19.42%, and that of propylene between 7.7-16.5% [103]. It is also observed that the ethylene/propylene gravimetric ratio is higher in the case of pyrolysis in presence of steam being between 1.41 and 1.67, while in the absence of pyrolysis it was 0.95-1.41.

From this it can be concluded that the presence of steam favors the breaking of chains from triglyceride molecules into smaller molecules.

Table (3.3) shows the yields of gaseous products obtained in the eight experiments at different temperatures, residence times and steam mass: raw material ratio that were calculated with the same formula presented in Chapter II.

Table 3.3. Yields of gaseous products resulting from waste palm oil pyrolysis, in presence of steam, %

Experimental Sample	Residence time, (s)	Temperature, (°C)	Steam mass: raw material ratio (kg/kg)	Yields of gas resulting from pyrolysis, %
1	72	625	0.2	34.4
2	72	575	0.2	20.3
3	144	575	0.2	24.8
4	144	575	0.1	21.6
5	144	625	0.2	36.1
6	144	625	0.1	35.7
7	72	575	0.1	15.8
8	72	625	0.1	27.6

Compared with the experiment presented in Chapter II (pyrolysis of palm oil in the absence of steam), where the yields of ethylene were between 4.6-10%, in the case of this experimental research, the yields of ethylene are lower, approaching those earlier only the most severe conditions. It will be taken into consideration that the residence time of the raw material in the reactor is shorter (72s and 144s) in the case of pyrolysis in presence of steam.

The propylene yields are lower (between 2.11 and 5.43%) compared to the previous experiment (3.35-10%), which is also due to the higher ethylene / propylene mass ratio in the case of steam addition.

The yields of CO and CO_2 are lower in pyrolysis in presence of steam being between 5.46% and 10.86% than in its absence, where they were from 9.47 to 17.27%. This is due not only to the lower gas yield but also to the concentration of these compounds in gas, which in the absence of steam reached up to 50%, especially at lower temperatures (475 ^oC - 480 ^oC).

In presence of steam, no clear dependence on temperature, reaction time and steam / raw material ratio was observed. It can be assumed that in presence of steam, some reactions also occur between water and the compounds in the reaction mass, resulting in the nature of ethers, esters, aldehydes, ketones and other oxygen compounds.

3.3.1. Establishing the domain of variation of the process factors

In the process of pyrolysis of waste palm oil in presence of steam, the following three process variables (pyrolysis process factors) are considered design and operation:

- temperature of the pyrolysis reaction;
- the residence time of the raw material in the reactor;
- steam mass: raw material ratio.

The two values of the pyrolysis reaction temperature of waste palm oil in presence of steam were 575°C and 625°C. The lower level of the reaction temperature was set at 575 °C because at lower temperatures it is difficult to collect gas samples for analysis. The upper temperature level was determined according to the heating possibilities of the reactor reaching 625 °C.

The minimum residence time (72 s) depends on the maximum feed rate of the raw material pump and the reactor volume, and the maximum was limited to 144 seconds, being lower than in the previous experiment (240 s), due to the presence of steam in the system.

The steam gravimetric: raw material ratio was 0.1, respectively 0.2 kg / kg, the values being chosen for industrial applications.

In order to establish the optimal conditions of the pyrolysis process, a factorial experiment of type 2^3 was performed, where the three factors were varied at two levels (minimum and maximum), as shown in the table (3.5).

Table 3.5. The factors of the pyrolysis process and the levels of variation in experimental research

Factor	**UM**	**Factor code**	**The values of the factors at the two levels**	
			Lower **-**	**Higher** **+**
Residence time	s	x_1	72	Residence time
Temperature	°C	x_2	575	Temperature
The steam mass: raw material ratio	kg / kg	x_3	0.1	The steam mass: raw material ratio

$$y = A_0 + A_1 x_1 + A_2 x_2 + A_3 x_3 \qquad (3.3)$$

where:

y - represents the yield, % mass
x_1 – residence time, s
x_2 - temperature, °C;
x_3 - steam mass: raw material ratio, dimensionless;
$A_0 \div A_3$ - regression coefficients.

The coefficients of the equation (3.3) are calculated using the smallest squares method, using one of the features of the Microsoft Excel software, Data Analysis.

The program performs both the calculation of the regression coefficients and the correlation coefficients and the standard errors for each coefficient. It also performs the ANOVA analysis after which the significance of the coefficients is verified, thus determining the suitability of the model.

3.3.3. The model for predicting the yield of the gas product resulting from pyrolysis

Following the numerical regression for the prediction of the gas yield (y) obtained from the pyrolysis, the following model was obtained (equation 3.4):

$$y = -139.988 + 0.069792 x_1 + 0.2565 x_2 + 37.25 x_3 \qquad (3.4)$$

The value of the coefficients in equation (3.4) indicates the influence of the factors that control the pyrolysis process in presence of steam. The coefficients associated with the two factors in the pyrolysis process, represented by the residence time (x_1) and the reaction temperature (x_2) have small values (A_1 = 0.070 respectively A_2 = 0.257), which indicates that these factors have a lower influence on the yield of gaseous product.

The variable factor that significantly influences the yield of the pyrolysis process in this experimental research is the mass ratio of steam: waste palm oil, this being observed by the high value of the associated regression coefficient (A_3 = 37.25).

The quality of the model (equation 3.4) is demonstrated by the values of the regression coefficients presented in table (3.8).

Table 3.8. Regression coefficients for the equation (3.4)

Regression coefficients	
Correlation coefficient R	0.9870
Coefficient of determination R^2	0.9743
R^2 adjusted	0.9550
Standard error,%	1.6374
Number of experiments (observations)	8

From table (3.8) it is deduced that 97% of the values of the yields of the gaseous products obtained from the experimental research are adequate for the application of the statistical model. The value of the coefficient of determination R^2 is close to 1 which indicates a good accuracy of the model and there is a good correlation between the dependent variable y (the yield of the products resulting from the process) and the independent variables x_1, x_2 and x_3. The adjusted R^2 coefficient shows that there are no insignificant process variables in this mathematical model.

From a statistical point of view, the model represented by equation (3.4) is satisfactory.

The mathematical model was statistically verified; it results in a good verification of the experimental data with those predicted by the model, and all the statistical coefficients are significant, so the model is viable, with a correlation coefficient R = 0.9870.

3.4 PARTIAL CONCLUSIONS

The experimental research aimed to study the influence of the addition of an inert fluid (steam) in the pyrolysis process of the waste palm oil on the product yields.

Conclusions from the qualitative interpretation of the experimental results:

- the yields of gas product resulting from the pyrolysis are between 15.8% and 36.1%, which give industrial applicability of the process, if the priority is to obtain gas. The gas yields are lower than in the experiment presented in Chapter 2, where no dilution steam was used, but it must be taken into consideration that the current experiment was carried out at shorter residence times;
- the ethylene and propylene concentrations are higher (18.89 - 25.5% ethylene and 13.33 - 15.05% propylene) than those obtained in the experiments in the absence of steam, where the ethylene concentration was between 9.2% and 19.42%, and that of propylene between 7.7-16.5%;
- the ethylene / propylene gravimetric ratio is higher in the case of pyrolysis in presence of steam between 1.41 and 1.67, while at the pyrolysis in absence of steam it was 0.95-1.41. *The*

explanation is that the presence of steam favors the breaking of chains from triglyceride molecules into smaller molecules;

- the yields of all gaseous products increase with the residence time of the raw material in the reactor, the temperature of the pyrolysis reaction and the mass ratio of steam: raw material;
- the yields of ethylene and propylene are significant at the temperature of 625 ^{o}C and for the longest time, as well as when adding more steam. Due to the cracked gas yield lower than in the previous experiment, where the yields of ethylene were between 4.6 and 10%, here they are smaller, approaching the previous ones only under the conditions of high severity. The propylene yields here are lower (between 2.11 and 5.43%) compared to the previous experiment (3.35 - 10%), which is due to the higher ethylene / propylene mass ratio in the case of steam addition - CO and CO_2 yields are lower in pyrolysis in presence of steam (5.46% and 10.86%) than in its absence, where they were from 9.47% to 17.27%. *The lower yield of carbon oxides is explained by the fact that, in presence of steam, occur reactions in which some of the oxygen atoms in triglycerides reach other reaction products such as ethers, ketones, aldehydes, etc., in a more much more than in the absence of steam.*

CHAPTER IV
EXPERIMENTAL RESEARCH OF THE VISCOSITY REDUCTION OF THE WASTE PALM OIL

4.1. PURPOSE OF EXPERIMENTAL RESEARCH

The objective of the experimental research is based on the study of the pyrolysis process of the waste palm oil at reduced temperatures (350, 400 and 450 °C), which resulted in liquid products with promising calorific power for their use as components for liquid fuels for outbreaks, experimental values falling between 9226 and 9266 kcal / kg, as shown in subchapter (2.1.3).

Thus, in this chapter, the pyrolysis process will be studied from the perspective of obtaining focal fuel components.

The evaluation of the feasibility of the process of pyrolysis of spent vegetable oil for the purpose of obtaining liquid fuels for outbreaks is made both according to the characteristics of these products and to the favorable economic conditions, such as lower energy costs for heating the process reactor at lower temperatures and even more so because of the absence of catalysts.

4.2. ESTABLISHING OPERATING PARAMETERS

The raw material used in the experimental research was the waste palm oil with the physico-chemical properties presented in the table (4.1).

Table 4.1. Physico-chemical properties of waste palm oil

Characteristics	Value	UM
Kinematic viscosity	43.3	mm^2 / s
Density	916	kg / m^3
Flash point, Marcusson	251	°C
Iodine value	4.5	g I_2/100 g product
Neutralization index	2.28	mg KOH / g product

For the study of the influence of the process factors on the characteristics of the liquid products, the operating parameters for the pyrolysis process of the waste palm oil were set at the following values:

- **working temperature**: 350 °C; 400 °C; 450 °C;
- **reaction time** of the raw material in the continuous reactor: 600 s; 144 s, 72 s, corresponding to 12%, 50%, respectively 100% of the maximum flow rate of the raw material pump (4 l / h) and the reaction volume of 160 ml.

4.4. RESULTS AND DISCUSSIONS

Following the pyrolysis of the waste palm oil in the continuously operating reactor, nine liquid samples resulted in different operating parameters (reaction temperature, process duration and raw material flow). The material balance was carried out during the operating periods in stationary regime, with the formula (4.7), neglecting the coke which, under these reaction conditions (lowered temperature, short residence time), is formed in a negligible proportion:

mass of raw material = mass of liquid product + mass of gases (4.7)

The liquid products obtained at 450 °C had a similar appearance to the raw material (color), but they tend to solidify at room temperature, having more consistent deposits than the other samples.

The properties of the resulting liquid (kinematic viscosity, density, flash point, iodine value and neutralization index) were investigated, demonstrating that the reaction temperature is the most important factor influencing the pyrolysis process of waste palm oil in a continuous system, as seen in table (4.2).

Table 4.2. Properties of liquid products resulting from pyrolysis at different working temperatures and process times

Sample No.	Tempera-ture, °C	Duration of the trial, s	Kinematic Viscosity at 40°C, mm^2/s	Density, g / cm^3	Point of inflammation, °C	The iodine value, I_2/100 g product	The index of neutralization, mg KOH/g sample
1	350	144	41.97	0.9150	91	4.60	3.82
2	400	144	33.43	0.9129	54	5.40	6.42
3	450	144	32.16	0.9059	37	5.50	12.57
4	350	600	43.25	0.9147	84	4.74	6.24
5	400	600	36.66	0.9120	59	5.27	13.1
6	450	600	33.54	0.9124	32	6.05	20.5
7	350	72	44.15	0.9144	72	4.50	2.5
8	400	72	40.95	0.9137	68	5.30	4.22
9	450	72	36.86	0.9085	31	5.50	17.9
Raw material	-	-	43.3	0.9160	251	4.52	2.28

Thus, out of the nine samples in pyrolytic oils, the solid matter deposited at the bottom of the collection vessels was analyzed for the samples number 3 and 9 showed that the neutralization index was much higher than the samples: ***42.8 mg KOH / g sample, respectively 48.6 mg KOH / g sample.***

Within the structural analysis, the experimentally determined average molecular weight (770.5 g / mol) allows the designation of a hypothetical average molecule of triglyceride, glycerin ester formed with one palmitic acid molecule, one oleic acid molecule and one lauric acid molecule:

H_2C — $O\text{-}CO\text{-}(CH_2)_{14}\text{-}CH_3$

|

H_2C — $O\text{-}CO\text{-}(CH_2)_{10}\text{-}CH_3$

|

H_2C — $O\text{-}CO\text{-}(CH_2)_7\text{–}CH\text{=}CH\text{-}(CH_2)_7\text{-}CH_3$

This structure corresponds to the molecular weight 776 g / mol, which is close to that determined experimentally (770.5 g / mol) and confirms the main fatty acids found in palm oil from mesocarp (palmitic and oleic), as well as from pips (palmitic and lauric) [105].

4.5. PARTIAL CONCLUSIONS

The pyrolysis of waste vegetable oils can be considered when obtaining liquid products with modified characteristics, without obtaining gaseous products. This option is based on the fact that, at a slight pyrolysis, the temperatures are lower, so there will be lower energy consumption. Due to the high calorific value of pyrolytic liquids, previously determined in Chapter II, the problem of their use as components of outbreak fuels was raised, but for this, the physico-chemical characteristics of pyrolysis liquid products had to be studied to see if they are proper to this use. The following were noted:

- pyrolysis of waste palm oil up to 400 ^oC and reaction times of (72s - 600 s) produce only liquid products; even pyrolysis at 450 ^oC and the reaction time (72 s) produces only liquid, while that at longer times (144 s; 600 s), it also produces small quantities of gas (3% and 5% gas respectively);
- in the pyrolysis of waste palm oil, the density decreases slightly with increasing process temperature (in the range 350-450 ^oC) and also with increasing reaction time, indicating a composition made up of compounds lighter than those of which the material is made premium, as a result of its pyrolysis reactions;
- reducing the viscosity (the purpose of this study) is not significant to the process parameters in this study, but can use liquid product by the kinematic viscosity of 32-33 mm^2 / s as the fuel component of outbreaks, by mixing with residual oil fractions less viscous, to meet the quality specifications for these fuels (maximum 21 mm^2/ s);
- the flash point of the liquid products falls within the quality specifications for the outbreak fuels (over 55 ^oC) only if the process temperature is below 400 ^oC;
- the iodine value as well as the neutralization index increase with the increase of the temperature and the reaction time, indicating the increase of the unsaturated and acidic character of the liquid products, both properties being unfavorable to the storage and pumping of the product; upon storage, the unsaturated character of the product will induce oxidation instability and the acid character may cause corrosion of the metal equipment with which the product comes into contact.

In conclusion, by pyrolysis of waste vegetable oils, at temperatures of 350-450 ^oC and reaction time of 2-3 minutes, components of outbreak fuels can be produced.

CHAPTER V
EXPERIMENTAL RESEARCH OF WASTE RAPESEED OIL THERMAL DECOMPOSITION PROCESS IN VACCUM OVEN

5.1 PURPOSE OF EXPERIMENTAL RESEARCH

The oils used for the hardening of non-alloy or alloy steels is characterized by a low viscosity, provide excellent detergency properties, higher cooling rate, high flash point, resistance to oxidation and thermal degradation, extremely low water content and accelerated hardening properties [107].

At present, research is being carried out to find alternatives to mineral oils used for thermal processes and opportunities have been identified for using vegetable oils for this purpose.

Various investigations have been carried out regarding the use of vegetable oils as cooling environment. The first studies that involved the cooling rate curve and the analysis of the heat transfer led to interesting results and showed that rapeseed oil showed a considerable performance [109].

The raw material used in the thermal decomposition process under vacuum was the waste rapeseed oil. The characteristics of the raw material are presented in table (5.1) in comparison with the mineral oil that is used for cooling after the thermal process of steel hardening.

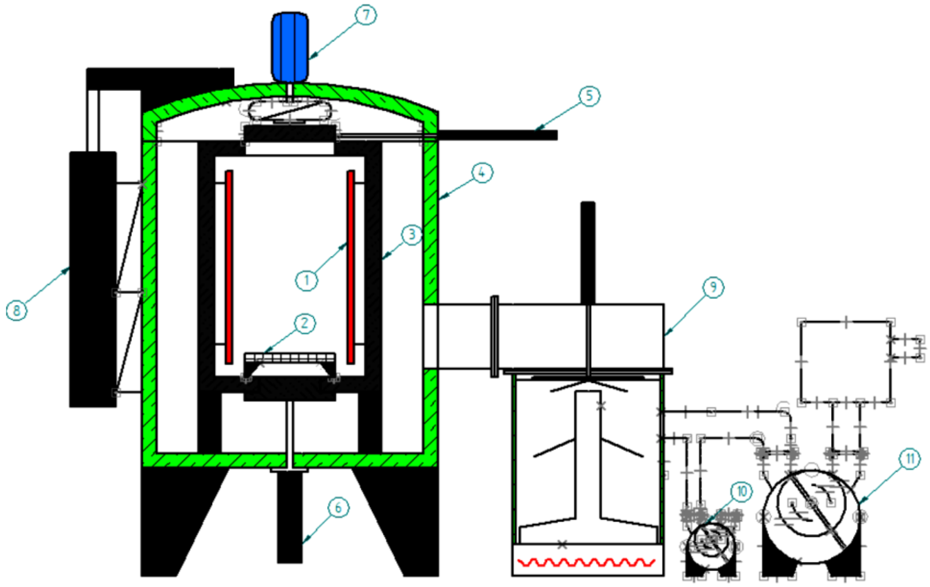
Table 5.1. Characteristics of oil waste rapeseed oil (raw material) compared to those of mineral quench oil used in steel hardening (Castrol Iloquench™1)

Characteristic	UM	Value for waste rapeseed oil	Value for mineral oil
Density at 15 °C	g/cm³	0.910	0.870
Marcusson flash point	°C	239	> 190
Kinematic viscosity, at 40 °C	mm²/s	43	20
Kinematic viscosity, at 100 °C	mm²/s	12.8	5
Cooling rate at 300 °C	°C/s	6.13	6.18

From table (5.1) it is observed that the two oils have the same cooling rate at 300 °C, which draws attention to the possibility of using the vegetable oil in the steel hardening process. However, the viscosity of the vegetable oil is much higher, and this can be corrected by the thermal treatment of (partial) thermal decomposition of the oil. For the preliminary determination of the operating parameters and the optimum conditions, the process was tested at two temperature values: minimum 300 °C and maximum 375 °C, with a processing time of 20 minutes, then the experiment was resumed within an interval of optimum temperature, established in the preliminary study.

5.2 DESCRIPTION OF THE TECHNOLOGICAL INSTALLATION. WORKING MODE AND ESTABLISHING THE PROCESS PARAMETERS

Figure (5.1) shows the installation used in the process of thermal decomposition (pyrolysis at low temperatures) under vacuum of the waste rapeseed oil.



Legend:
1-electrical resistors;
2-load bracket;
3-room heating;
4-outer sheath;
5-pneumatic cylinder for upper gear drive;
6- pneumatic cylinder for actions for the lower gear;
7-fan;
8- Hydro-pneumatic cylinder actuator cover lid;
9-molecular diffusion pump;
10,11 - preliminary vacuum pumps with eccentric drum and sliding pallet

Figure 5.1. The installation used for waste rapeseed oil pyrolysis

The method of working of the process of pyrolysis of the waste rapeseed oil in the vacuum oven is as follows: after the sample (charge) is inserted in the workspace, the oven door is closed, the vacuum system is started and after reaching a working pressure of the order of 10^{-3} mbar, the heating process automatically starts according to the settings made to achieve the speed of working temperature and the duration of maintenance on the desired thermal level. Finally, after exhausting the maintenance time, the furnace enters the gas inlet stage (99.99% pure argon) and starts the turbine which by convection ensures the cooling of the working space and implicitly the oil sample.

The monitoring of the thermal process of the waste rapeseed oil, under vacuum is provided by the digital recorder with a resolution of one second and provided with six channels that monitor the temperature of the workspace, the charge in three zones and the level of the working pressure (vacuum).

The diagrams for the two temperatures (310°C și 320°C) are shown in Figures (5.4) and (5.5).

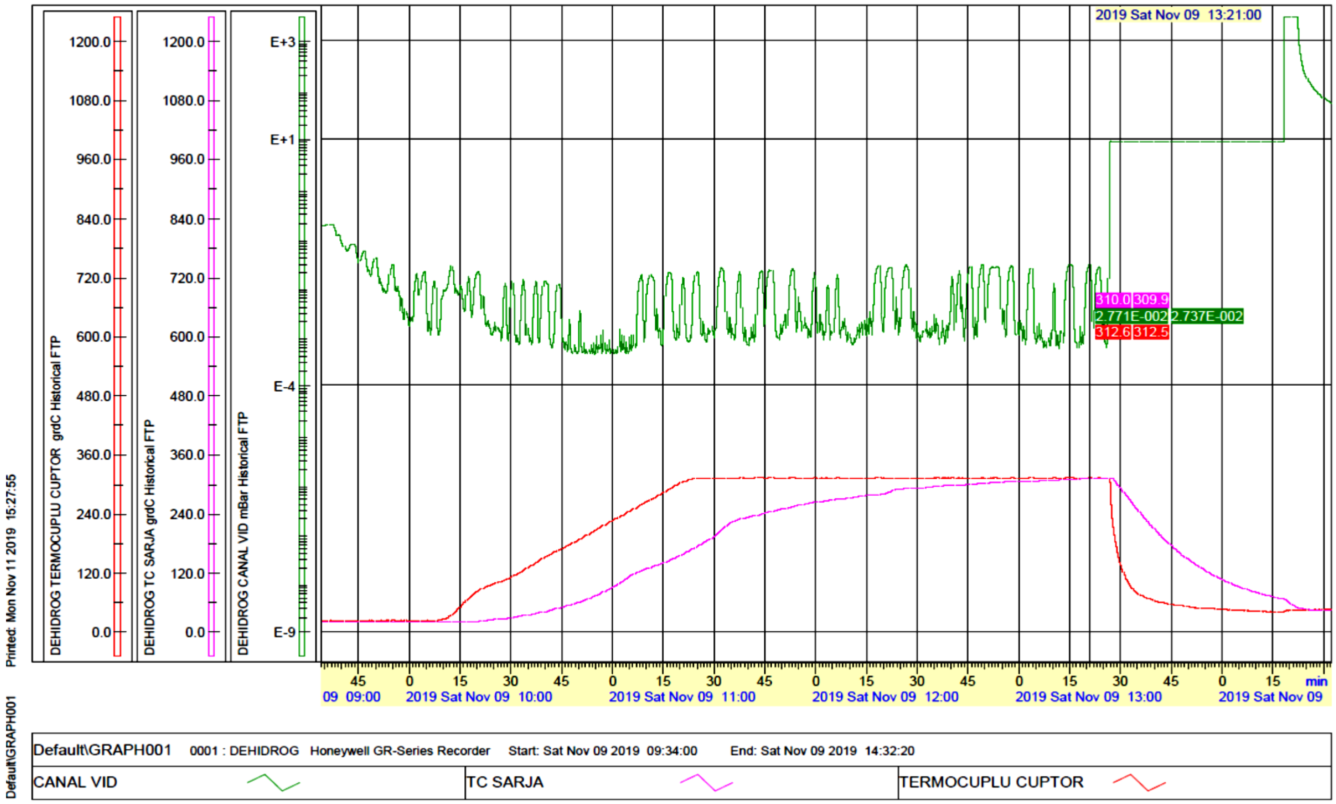


Figure 5.4. Process parameter recording diagram (working temperature 310°C, 5 minutes residence time)

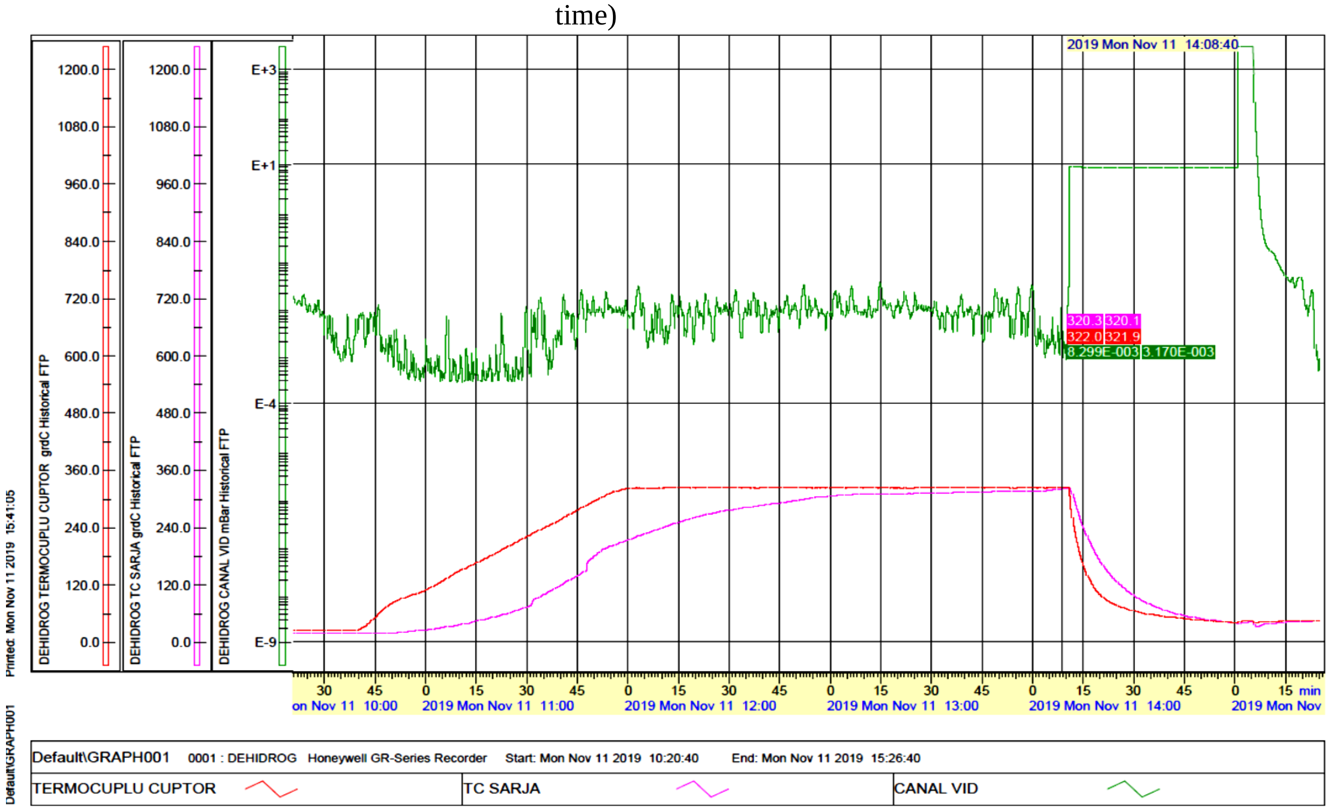


Figure 5.5. Process parameter recording diagram (working temperature 310°C, residence time 2 minutes)

From Figures (5.4) and (5.5) it is observed that the process was carried out under optimal conditions and the value of the depressurized environment (vacuum) remained constant for the entire duration of the desired thermal level.

5.3 RESULTS AND DISCUSSIONS

The yields of the liquid products resulting from the thermal process of the waste rapeseed oil in the vacuum oven as well as the mass balance are shown in table (5.2).

Table 5.2. Yields of liquid products obtained from thermal process, %

Operating temperature, °C	Residence time, minutes	Initial quantity, g	The resulting quantity, g	Liquid yield,%
300	20	910.43	789.99	87%
375	20	920.42	0	0%
310	5	872.72	534.75	61%
320	2	946.23	425.80	45%

From table (5.2), it is observed that the process factor that influences the process of thermal decomposition under vacuum and with argon cooling is the reaction temperature, and the time factor is not decisive in obtaininggood yields of liquid products. Thus, at a temperature of 300°C, liquid products with a maximum yield of 87% are obtained and, at a temperature of 320°C the yield of liquid products decreases to 45%. The explanation is that thermal decomposition reactions occur with the formation of gaseous products (which have not been collected in this technological system and are not subject to experimental research). The decrease in the yield of liquids from 87% to 45% over a rather restricted temperature range (20°C) is influenced by the depressurized environment (10^{-3} mbar vacuum) which favors the decomposition reactions, with gas formation.

Due to the thermal process of the oil used in this system, there was also a dehydration of the oil which eliminated the water content which can cause structural defects, even cracks in the material.

Table (5.3) shows the kinematic viscosities of the oils resulting from the process and used as cooling medium after hardening the steels.

Table 5.3. The viscosities of the liquid products obtained according to the working temperature

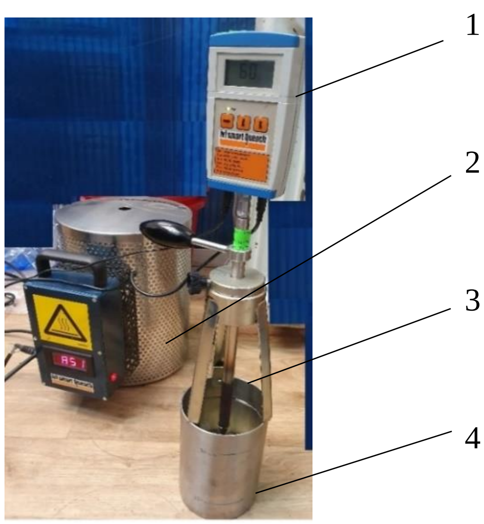
Type of oil	Kinematic viscosity at 40 °C, mm^2/s	Kinematic viscosity at 100 °C, mm^2/s
Raw material (rapeseed oil)	43	12.8
Liquid product resulting at 300 °C	42.9	10.9
Liquid product resulting at 310 °C	42.3	9.5
Liquid product resulting at 320 °C	38.7	9.3

Mineral oil	20	5

It can be observed that when processing under these technological conditions (in a heated oven in a depressurized environment and cooling the products in a controlled environment with 99.99% purity argon) the viscosity of the liquid products is inversely proportional to the working temperature. As the temperature rises, the share of long chain cracking reactions in triglyceride molecules will increase, resulting in smaller molecules that will give a lower viscosity to the liquid.

5.4 DETERMINING THE COOLING RATE OF OILS OBTAINED IN THE LOWER TEMPERATURE PYROLYSIS PROCESS

The mechanical resistance properties (structure and hardness) of the alloy steel materials that are subjected to the thermal process of heating are strongly influenced by the chosen coolingagent. In the first stage to determine ***the ability of cooling*** of the resulting liquid samples to be used as a cooling medium after the heat treatment (quenching). This method is performed with the help of the IVF SmartQuench device shown in figure (5.6).



Legend:

1- Transmission device for wireless data transmission to and from the computer;
2- furnace for heating the well;
3- test probe with handle and built-in thermocouple;
4- vessel with sample to be analyzed.

Figure 5.6. The SmartQuench IVF device for determining the cooling rate curve

Figure (5.7) shows the cooling rate curve of the different oil samples to be used as cooling medium after the hardening of the alloy steel samples. The curve is determined using the IVF SmartQuench device and describes the cooling rate of the oils as a function of temperature and time.

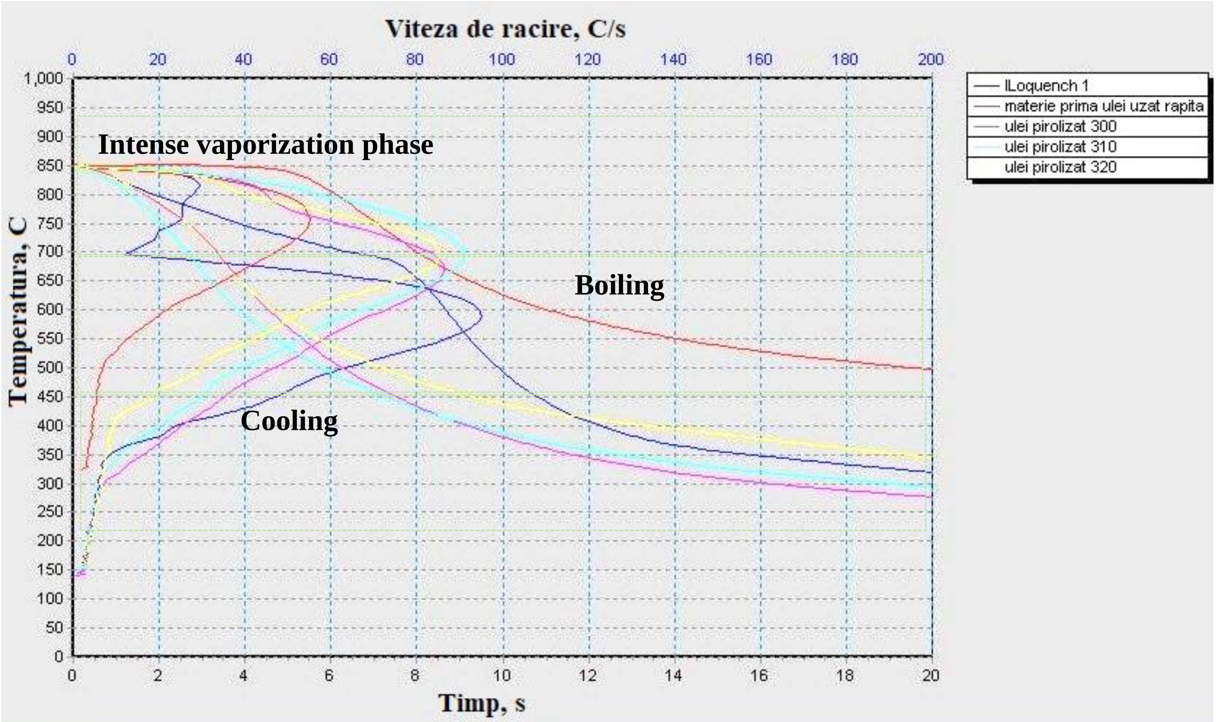


Figure 5.7. Cooling rate curve of the oils obtained from the pyrolysis process, at different working temperatures

From figure (5.7) it is observed that the cooling rate of the liquid products has a different appearance in the vapor phase compared to the cooling curve of the mineral oil.

The results regarding the cooling of the samples in the liquid products obtained by waste rapeseed oil through thermal decomposition, at different working temperatures, show that the resulting liquid at 320 °C had a low value of the maximum cooling rate compared to the samples obtained at lower temperatures (300 °C and 310 °C). The liquid obtained at 320 °C has a cooling rate comparable to that of mineral oil. Also, the cooling times at 600 °C, 400 °C and 200 °C are comparable to the time of mineral oil, for pyrolysed oils, but not for rapeseed oil - raw material. These results are promising for the development of an integrated system of methods of higher recovery of waste vegetable oils.

5.5 PERFORMING THE PROCESS OF THERMAL TREATMENT (HARDENING) OF THE TEST SPECIMEN (25CD4)

The heat treatment was carried out on a batch of five tubes of weak alloy steel of the type 25CD4 material with a carbon content of 0.25%, with the cylindrical shape and with the following dimensions: diameter of 8 mm and length of 300 mm.

The hardening of the samples was carried out in the heat treatment oven, with a controlled atmosphere shown in figure (5.8) and was followed by their cooling in the oil samples resulting from the pyrolysis process at low temperatures in the vacuum oven.

Figure 5.8. Heat treatment furnace used for hardening specimens

From a constructive point of view, the furnace in figure (5.8) is in the category of masonry furnaces, in which the electrical resistances are mounted and the workspace in which the specimens are inserted is made of refractory steel.

5.6 DETERMINATION OF SPECIMEN DURITY

The results obtained from the heat treatment applied to these specimens were evaluated by Rockwell hardness tests (HRC) performed using the Rockwell apparatus, the Wilson UH4250 model.

Following the hardness measurements of the hardened specimens in different cooling media, the following values have been shown, which are presented in the table (5.6) and are graphically represented in the figure (5.11).

Table 5.6. The results obtained from the heat treatment applied to the specimens

	Before hardening	**After hardening**				
		Cooling in mineral oil	Cooling in raw material	Cooling in oil resulting in 300 °C	Cooling in oil resulting in 310 °C	Cooling in oil resulting in 320 °C
Hardness (HRC)	29-30	45	46	44-45	43	43.5

5.7 PARTIAL CONCLUSIONS

In this chapter, the decomposition process at relatively low temperatures (300-320 °C) of waste rapeseed oil was obtained with liquid products, in the oven heated in a depressurized environment (in vacuum) and with cooling in an argon controlled atmosphere. (99.99% purity).

Two preliminary determinations were made at the temperature of 300 °C and 375 °C, with the process duration of 20 minutes in order to establish the optimal processing parameters under the presented technological conditions. At the working temperature of 300 ^{o}C, with the retention time on the thermal pad for 20 minutes, a high yield of liquid (87%) was obtained. At the same time, the thermal decomposition of waste oil in the same system, heated to the temperature of 375 ^{o}C, in the diagram that monitors the process parameters (working temperature, retention time and the value of the depressurized environment) was observed the increase of the depressurized environment (vacuum) from $1.79 \cdot 10^{-3}$ mbar to $1.9 \cdot 10^{-1}$ mbar during heating, which indicates the formation of gaseous compounds. As a result of these experimental conditions, the resulting liquid yield was zero, all gaseous compounds (100%) were formed. This increase in pressure occurred starting with the temperature of 330 ^{o}C, which is why working temperatures below this value were established and the duration of maintenance on the thermal pad was reduced from 20 minutes to 2 minutes. Establishing process parameters confirmed the obtaining of liquid products with 87% to 45% yields.

The liquids obtained from the thermal treatment of the waste rapeseed oil, had a much lower viscosity than the raw material, which is why they were used as a cooling medium in the hardening process, carried out on a batch of test tubes (four determinations).

The results obtained from the heat treatment applied to the specimens were evaluated by hardness tests (Rockwell) and showed that at 320 ^{o}C, the optimum hardness value (43.5 HRC) was obtained, which recommended the oil for use in industrial level as a cooling medium, after hardening.

GENERAL CONCLUSIONS

In the present scientific research, the topic of the waste vegetable oils collected as primaryresidue from the food industry was addressed, being subsequently subjected to parameterized thermal processes, so that products with value of use were obtained both in the petrochemical sector and in the metallurgical industry.

Three main directions were followed in approaching the theme of thermal processing of waste vegetable oils:

- **pyrolysis of waste palm oil** in presence and absence of steam, aimed at obtaining valuable products in the petrochemical industry (olefins);
- **reducing the viscosity** of the waste palm oil, without obtaining gas, in order to produce a component of the outbreak liquid fuel;
- **the thermal treatment (thermal decomposition) at low temperatures** of the waste rapeseed oil in depressurized environment (in vacuum) in order to obtain liquid products (oils) with environmental properties of cooling of the metal parts subjected to the process in the aeronautical industry.

A. CONCLUSIONS OF THE BIBLIOGRAPHICAL STUDY

The field of the use of renewable resources has become a challenge for the researchers in the last years, and the results are in a continuous development so that many processes tend to be applied at industrial level. In this context, the researches carried out by the thermal processing of the waste vegetable oils from the food industry are included, with the purpose of obtaining products of value for use in the chemical, petrochemical or even metallurgical industry.

The present scientific work is based on the study and analysis of the opportunities presented in the specialized literature on pyrolysis of waste vegetable oils under different conditions of temperature, pressure, residence time, in presence/absence of catalysts or of an inert fluid (steam, nitrogen). Following the study carried out in the specialized literature, the following conclusions were drawn:

➢ in order to optimize the conditions in the process of pyrolysis of the waste vegetable oil, *reaction schemes* have been proposed for deepening and knowing in detail the reaction mechanisms;

➢ results of pyrolysis depend on a number of factors, such as:

- *reactor type* (tubular or autoclaved);
- *operating mode* (continuous, discontinuous or thermal);
- *operating conditions in the reactor* (reaction temperature, residence time of the raw material in the reactor, pressure / vacuum);
- *absence / presence of diluents* (nitrogen or steam);
- *nature of raw material* (pure triglycerides, vegetable or non-food vegetable oils from different plants, waste vegetable oils from the food industry).

➢ improving the technological processes by developing reliable systems and with the possibility of application on an industrial scale (eg *electric arc or microwave*);

➢ laboratory simulation of the process at temperatures in the field of hydrocarbon pyrolysis (over 800 ^oC), by integrating *the pyrolysis process in the gas chromatographic oven* to obtain valuable product yields (eg ethylene, propylene) comparable to those from hydrocarbon pyrolysis;

- ➢ mathematical modeling of processes performed on a micropilot scale for industrial application purposes (eg: *ASEM semi-empirical model*, proposed by researchers at the University of Florida).

B. CONCLUSIONS OF EXPERIMENTAL RESEARCH

Experimental research on pyrolysis of waste oil in the palm of the tubular reactor, the temperature control continuously held at a temperature from 475 °C to 630 °C and residence time in the reactor between 120 ÷ 240 s resulting in gaseous products containing compounds of significant value for the petrochemical industry.

Following the pyrolysis of palm oil, high concentrations of ethylene (19-20% vol.) and propylene (9-10% vol.) were obtained.

The process factors that influence the yield of the gaseous products are the reaction temperature and the residence time of the oil in the tubular reactor.

- ➢ at high temperatures (620 °C) and the residence time of 240 s, high yields of gaseous products (63.3%) are obtained;
- ➢ at low temperature (480 °C) and the residence time of 120 s, the product yield of gas products was 7.9%.

Considerable yields of ethylene and propylene from the pyrolysis gas product are obtained at temperatures above 550 °C: > 10% ethylene and > 5% propylene respectively, which recommends their separation from the gas product obtained from the pyrolysis reaction, for use in the petrochemical sector, being used as raw materials in the polymer industry or in chemical synthesis.

The resulting liquid product has the appearance of a mineral oil and due to its high calorific value 9246 ± 20 kcal / kg and the ash content of 0.006% can be used as a component of liquid fuel for burning in outbreaks (FOCARE).

The results obtained in the experimental researches show that the parameters of the pyrolysis process have been optimized to obtain reaction products with added value to the raw material, which gives them a potential of higher recovery in the petrochemical industry.

Based on the data obtained from the experimental research of the pyrolysis of waste palm oil, two mathematical models were realized: ***the semi-empirical model***, with the application of logistic functions in the specialized literature of the type: $y(T) = w[L(T:T_0, D)]^p[F(T:T_0, D)]^q$ and ***the empirical model***, determined by a set of equations obtained by linear regression.

In the case of the *semi-empirical model*, the predicted yield values are close to the experimental values, and the model is validated and can be applied under different processing conditions. The good yields of olefins obtained from the experimental study (14-19%), as well as the possibility of accurately predicting them through mathematical equations, make the industrial application of the results attractive.

In the case *of the empirical model*, the *polynomial* type equation of *the second degree* is preferable when predicting the total gas efficiency. The coefficients of the polynomial model were determined by numerical regression and the correlation coefficient is R = 0.9997 and the standard average error is 0.6888%, indicating a very high accuracy of the second degree polynomial type mathematical model with the consequence that the process can be extended on an industrial scale.

In the experimental research of the waste palm oil pyrolysis, in presence of an inert fluid (steam), the influence of the process factors (reaction temperature, residence time and the molar ratio of steam: raw material) on the yield of gaseous products was tracked. The performance of the pyrolysis process was quantified by the yields of the gaseous products that had values between: 15.8% and 36.1%.

The concentrations of ethylene and propylene in gaseous products are determined by chromatographic analysis, obtaining higher values (18.89 - 25.5% ethylene and 13.33 - 15.05% propylene) than those obtained in the experiments in the absence of steam, where the concentration of ethylene is between 9.2% and 19.42%, and that of propylene between 7.7-16.5%.

The influence of the process factors on the yields of the different compounds were experimentally determined by the *variation of the three factors of the process, at two levels (factorial experiment of type* 2^3*) as* follows:

- *pyrolysis reaction temperature*: minimum = 575°C and maximum = 625 °C;
- *the residence time of the raw material in the reactor*: minimum = 72 s and maximum = 144 s;
- *steam: raw material mass ratio*: minimum = 0.1kg / kg and maximum = 0.2 kg / kg.

The coefficients of the model were statistically verified by regression analysis. The main variable that influences the yield of the products is the *presence of the steam in the system*, this being observed by the high value of the coefficient associated with the respective variable in the mathematical model equation ($A_3 = 37.25$).

The experimental research regarding the viscosity reduction of the waste palm oil by light heat treatment, at temperatures between 350-450 °C and atmospheric pressure, has led to the obtaining of negligible gas yields, obtaining mainly liquid products, with low viscosity, flammability increased with an unchanged or slightly increased unsaturated character and a pronounced acid character, favorable to use them as component for fires fuel.

Raising the process temperature above 400 °C is not advisable because the flash point decreases too much (liquid products obtained at 450 °C having 31-37 °C), which will increase the flammability of the final fuel, without reducing the viscosity to be significant by increasing the temperature from 400 °C to 450 °C (only 3-4 mm^2/ s). Also, with the increase of the process temperature, the acidity index (with 6-12 mg KOH / g sample) also increases, negatively influencing the quality of the final product, when using these liquid products as components of the outbreak fuel.

The liquid products obtained in this experiment have some physico-chemical characteristics similar to or even higher than the quality specifications of the focal fuels (calorific value, density, flammability, low ash and sulfur content), being able to improve, by mixing with residual oil fractions, the quality of the outbreak fuels, usually obtained only from these fractions. The effects of other characteristics, such as the acidic and unsaturated character of the products obtained from vegetable oil, can also be minimized by mixing with oil fractions but other treatments (neutralization, hydrogenation) may be considered.

The study of the reduction of viscosity of the vegetable oil allowed to clarify the first stages of the mechanism of thermal decomposition of triglycerides:

1. the decomposition of the triglycerides to fatty acids, ketene and acrolein [40];
2. breakdown of fatty acid molecules into lower molecular weight acids, alkanes and alkynes [43].

These have been demonstrated by increasing the acidity of pyrolytic liquids and their unsaturated character (iodine value), compared with the raw material, due to the fragmentation of fatty acids with high molecular weight into acids with lower mass and with higher acidity, as well as the generation of olefin molecules in the second stage of the mechanism.

Experimental research regarding the thermal decomposition of waste rapeseed oil in the electrically heated oven, in a depressurized environment (under vacuum) at the temperature of maintenance on the thermal range between 300-320 °C and the process duration between 2-20 minutes, followed by cooling in the controlled atmosphere (argon) was aimed at obtaining liquid products (oils) that will be used as cooling medium after the thermal treatment (hardening) of the metal parts.

Following these experimental determinations, the range of working temperatures was established in order to obtain returns between 45% and 87%.

Following the analyzes, it was observed that the liquid products obtained were strongly dehydrated and had a lower viscosity than the raw material, which recommends these products as cooling medium.

The cooling rate in the environment consisting of pyrolytic liquids increased considerably compared to the raw material (Table 5.4), thus approaching the mineral oil commonly used for this operation. This is the consequence of the influence of the decrease of the viscosity on the prevention of the phenomenon of heating and has as a result the improvement of the heat transference between the heated metal and the liquid.

For the experimental testing of the heating capacity and properties of the waste vegetable oil obtained after the heat treatment under vacuum conditions were used standard samples of low alloy carbon steel (25CD4).

The hardness values of the specimens that have been cooled in the liquid products obtained by thermal breakdown of the rapeseed oil are comparable (43-45 HRC) with the hardness obtained by cooling in the mineral oil (45 HRC), which recommends them as cooling mediums in the metallurgical industry.

CONTRIBUTIONS TO THE DEVELOPMENT OF KNOWLEDGE AND PERSPECTIVES

The theme of phd thesis: **"Adding value of waste vegetable oils by thermal processes"** has interesting contributions to knowledge in the field, through the following theoretical and practical considerations:

1. although the most popular way of recovering waste vegetable oils is the transformation into biodiesel through trans esterification, ***the bibliographic study was oriented towards the process of thermal processes***, which seemed to be an abandoned way, but it, in our opinion, offered worthy perspectives to be analyzed.

As a result of his literature study, was obtained information that served to carry out experiments in the present work.

2. were performed ***three experimental research*** on pyrolysis micropilot plant, provided with the cylindrical reactor in continuous operation: ***the study of simple pyrolysis, pyrolysis in presence of steam study and the study of low-temperature pyrolysis to reduce the viscosity of the waste palm oil.***

3. an experiment of thermal treatment of waste rapeseed oil, in a depressurized environment and at relatively low temperatures, *was carried out in* ***a fully automated batch reactor,*** *which allowed to obtain precise data on the oil behavior at different process parameters****, and the liquid products obtained have been tested, with the latest equipment, for a new purpose: the use in the treatment of hardening of metal parts.***

4. the results of the experiments carried out in the present work have demonstrated the following ways of ***recovering by thermal processes of the waste vegetable oils***:

- obtaining important yields of valuable chemical compounds for the petrochemical industry, by simple pyrolysis or in presence of steam, at high temperatures: ethylene, propylene, C_4 olefins, next to a gaseous fuel (methane, ethane, propane) and a liquid one, with high energy value;
- obtaining liquid fuels by pyrolysis at low temperatures / viscosity reduction, which could be used as such or in combination with residual oil fractions, as fire fuels;
- obtaining *quench* oils (coolingagent) to replace the mineral ones (which have high prices) at the thermal treatments for the hardening of the metal parts, by thermal treatment (partial decomposition) in the vacuum oven.

The research topic experiment of single presented in this doctoral dissertation develop single opportunity to provide ***opportunities*** for further experimental studies, such as:

- ***pyrolysis of waste vegetable oils mixed with oil residues***, at atmospheric pressure and at high temperatures, to obtain high concentrations of olefins and liquid products for different uses in the petrochemical industry ;
- ***realization of totally or partially*** bio ***liquid fuel recipes***, by using pyrolytic oils;
- ***making some quench oil recipes***, by using pyrolytic oils;
- ***development of stochastic mathematical models***, after enlarging the experimental database, on the existing installations.

DISSEMINATION OF SCIENTIFIC RESEARCH RESULTS

During the doctoral stage, the results of the scientific researches were published in specialized articles and communicating scientific papers as follows:

A. Articles in ISI journals:

1. Sivriu, A.M., Tîrpan, D.R., Koncsag, C.I., Mareș, A. M, Jinescu C., Analytical semi-empirical model (ASEM) for the prediction of products yields at the fast pyrolysis of waste palm oil, Rev. Chim. (Bucharest), 70 (6), 2019, p.1992-1995, FI (pe 2018)=1,605, SRI=0,28.
2. Sivriu, A.M., Jinescu G., Săpunaru (Țaga), O., Tîrpan, D.R., Koncsag, C.I., Pyrolysis of waste palm oil in presence of steam, Rev. Chim. (Bucharest), 70(2), 2019, p. 4175-4180, FI (pe 2018)=1,605, SRI=0,28;
3. Ţaga (Săpunaru), O. V., Koncsag, C. I., Sivriu, A. M., Jinescu, G., Isopropyl lactate obtaining by transesterification in reactive distillation system**,** Rev. Chim. (Bucharest), 70**,** 1, 2019, FI (pe 2018)=1,605, SRI=0,28.

FI (TOTAL)= 1,605+1,605+1,605= 4,815;
SRI (TOTAL) = 0,84.

B. Articles in BDI magazines:

1. Sivriu, A.M., Koncsag, C. I., Jinescu, G., Mareș, A. M. – Thermal cracking of waste vegetable oil-a preliminary research, UPB Scientific Bulletin, Series B: Chemistry and Material Sciences, 79 (3), 2017, p.67-74;
2. Sivriu, A.M., Jinescu, G., Săpunaru (Țaga), O., Tîrpan, D.R., Koncsag, C.I., Theoretical and practical aspects for thermal treatment of waste vegetable oils, Journal of Engineering Sciences and Innovation, 4, 2019, p. 349-360.

C. Summary published in volumes of national and international conferences:

1. Sivriu, A.M., Jinescu, G., Processes and techniques of waste vegetable oils via pyrolysis with olefins production. theoretical and experimental aspects, SICHEM 2016, 6-7 September Bucharest;

2. Sivriu, A.M., Koncsag, C.I, Jinescu, G., Modelling the thermal cracking process of vegetable oils, International Conference CHIMIA 2018, "New trends in applied chemistry", 24-26 May, Constanța Romania, Book of abstracts, vol.3., Ovidius University Press, ISSN 2360-3941, p.71;

3. Sivriu A-M, Koncsag C.I., Cioroiu Tîrpan D.R., Mareș A.M, Jinescu, G., Adding value to waste vegetable oils through thermal processing, SICHEM 2018 Bucharest, 6-7 September, Ed. Matrix, ISBN 2537-2254, *Book of abstracts*, p.29;

4. Sivriu, A. M., Koncsag, C. I., Mareș, A. M., Tîrpan, D.R., Ţaga (Săpunaru), O., Jinescu, G., Olefins and fuels from frying palm oil through pyrolysis, 4th International Conference on Chemical Engineering, 30 octombrie – 2 noiembrie 2018, Iași, Romania, *Book of abstracts*, S3-37;

5. Ţaga (Săpunaru), O. V., Koncsag, C. I., Mareș, A. M., Sivriu, A. M., Jinescu, G., Optimization of the lactic acid esterification in reactive distillation process, 4th International Conference on Chemical Engineering, 30 octombrie – 2 noiembrie 2018, Iași, Romania, *Book of abstracts*, S1-32.

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