Pyrolysis of Waste Palm Oil in the Presence of Steam

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This work ranges among studies dedicated to valorization of waste vegetable oils. In the present study, the pyrolysis of the waste palm oil was performed in presence of steam, in a tubular pyrolysis reactor operated in a continuous mode. The raw used in the pyrolysis reaction is the frying waste palm oil and the reactor was operated at high temperature (575 -625°C) and reaction time of 72s and 144s, at a steam: oil ratio of 0.1 -0.2. Valuable compounds such as olefins (ethylene, propylene) were obtained in the process, and they can be used further as raw materials in the chemical and petrochemical industry. The gaseous product resulted contained high ethylene and propylene concentrations: 18.89 - 25.5% and 13.33-15.05%, respectively. Based on the experimental results, some linear equations were developed to predict the products yields, and the coefficients of the model were statistically verified. These equations can serve at scaling up the pyrolysis process.

Keywords: Steam cracking, vegetable oil pyrolysis, yield prediction, mathematical model

Biomass is the only renewable energy source that yields solid, gaseous and liquid fuels [1]. It is well known that triglyceride based vegetable oils have the potential to be a suitable source of fuel or hydrocarbons under the right processing conditions. Vegetable oils are mainly processed for biodiesel production through transesterification [2] or hydroprocessing [3]. Another valorization path for vegetable oils is the pyrolysis. Pyrolysis is defined as a severe form of thermal cracking with subsequent rearrangement of fragments [4]. The resulting bio-oil can then be used as fuel or for the production of chemicals and other ‘‘bio-based’’ products. Pyrolysis or thermal cracking of triglyceride materials represents an alternative method for producing renewable bio-based olefins**.** Olefins are considered to be key components of the petrochemical industry. Ethylene and propylene are the most important olefins, with an annual production of roughly 1.5×10^8 t and 8×10^7 t, respectively [5]. This production is obtained from fossil resources. Efforts were made to replace some fossil resources with renewable ones even for the production of olefins [6,7].

Research in this study is focused on the production of olefins through a pyrolysis process of waste palm oil in presence of steam. High concentrations of ethylene and propylene were obtained in the gaseous product. This valuable compounds can be used further in petrochemical industry as raw material for polymers production.

Experimental part

The experiment was carried out in a micropilot reactor operated in continuous system. Pyrolysis of waste palm oil in presence of steam took place at atmospheric pressure and temperature range of 575-625°C. The reaction time was 72s and 144s and steam:waste palm oil mass ratio 01 -0.2. The physical-chemical properties of waste palm oil were shown in Table 1. A schematic diagram of the pyrolysis micropilot reactor is shown in figure 1.

Table 1
PHYSICO-CHEMICAL PROPERTIES OF WASTE PALM OIL

Parameter	Value	Unit
Density at 20°C	924.9	kg/m^3
Kinematic viscosity at 40°C	$47.3 \cdot 10^{-6}$	m^2/s
Flash Point	240	°C
Iodine value	4.62	g I2/100g

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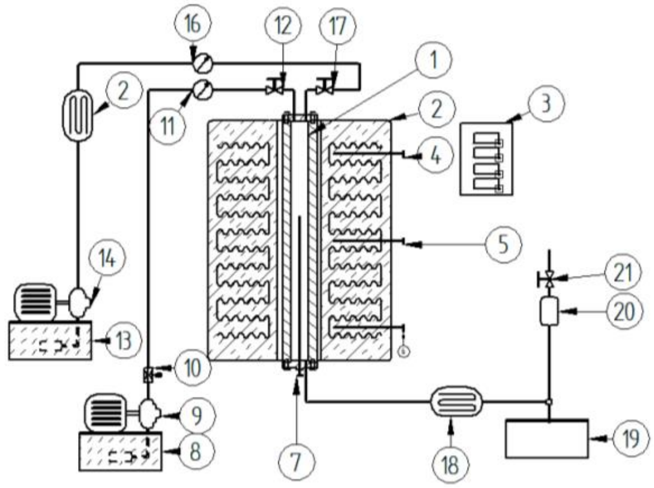

Fig. 1. Diagram of the pyrolysis micropilot reactor

A water circuit was added for the pyrolysis process of the waste palm oil (Tank no. 13, in figure 1) to produce steam. The steam is formed immediately after entering the reactor due the high temperature inside (above 550°C). The tubular reactor is filled with inert material (finely crushed rock) which acts as a heat conductor from the wall toward inside of the reactor. The porosity of the filling layer is $\varepsilon = 0.6$. As a result, the reaction volume decreased by 40%, affecting the reaction times in the reactor. The residence time of the raw material in the reactor was calculated as the ratio between the free volume of reactor and the volumetric flow rate of the raw material; at the maximum pump flow (100% piston stroke), it corresponds to a time of 72 s, and at the flow rate of 50%, a time of 144s.

Results and discussions

The effect of temperature, residence time and ratio steam:raw material on the products yield was determined. The composition of gaseous product resulted from pyrolysis of waste palm oil in presence of steam is listed in Table 2.

The composition of the cracked gas was determined by a gas chromatography method developed by Wasson ECE for extended analysis of gases, using an equipment with a complex configuration produced by Agilent-USA: one FID detector, two thermoconductivity detectors, capillary and packed columns depending on applications, injector split/splitless with EPC, and an auxiliary isothermal oven automatically controlled.

Table 2

COMPOSITION OF GASEOUS PRODUCT RESULTED FROM PYROLYSIS OF WASTE PALM OIL IN PRESENCE OF STEAM, % VOL

Samples/ Process parameters	Sample #1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	Sample #6	Sample # 7	Sample # 8
Residence time, s	72	72	144	144	144	144	72	72
Temperature, °C	625	575	575	575	625	625	575	625
Steam:raw material ratio	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1
Hydrogen	0.30	0.20	0.30	0.37	0.24	0.21	0.26	0.25
CO	12.48	13.94	12.53	11.84	12.03	14.79	15.50	13.10
CO2	17.24	17.06	17.31	15.55	13.23	15.64	18.74	13.70
Methane	6.06	5.83	6.09	6.21	6.27	5.97	5.19	6.18
Ethane	7.15	7.81	7.18	7.75	7.72	8.03	7.72	7.84
Propane	2.49	3.02	2.50	2.71	2.39	3.39	4.19	2.93
Butanes	1.25	1.59	1.25	1.33	1.14	1.55	2.59	1.58
Ethylene	22.61	22.44	22.71	24.26	25.50	21.00	18.89	23.51
Propylene	14.04	14.09	14.10	14.44	15.05	13.96	13.33	14.98

The gas yield resulting from waste palm oil pyrolysis in presence of steam is shown in Table 3.

Tabel 3
GAS YIELDS AT THE WASTE PALM OIL PYROLYSIS IN PRESENCE OF STEAM, % wt

Sample #	Residence time, s	Temperature, °C	Steam:oil ratio, kg/kg	Gas yield, % wt.
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

It was observed that products yield are between 15.8% and 36.1%, which shows industrial applicability. The gas yields are lower than in the previous experiment [8], where no steam was used, but one can take into account that the current experiment was carried out at shorter residence times.

Increasing the temperature by 50°C leads to the significant increase of gas yield (by 11.8-15.5%), which shows the important effect of temperature in the process.

The yields of main compounds in the gas are presented in Table 4. The yields (eq. 1) were calculated from total gas yield (Table 3) and the concentration of main compounds in the gas (Table 2), also taking into account the average molecular weight of the gas.

The yields of ethylene and propylene are significant (up to 9.21 % for ethylene and 5.42% for propylene) at 625°C, residence time 144 s and higher steam addition.

From table 3 it was observed that the yields of all compounds increase with reaction time, temperature and steam: raw material ratio increasing. The ethylene yield resulted from pyrolysis of waste palm oil in presence of steam are smaller (2.99 – 9.21%) than the previous experiment [8], where the ethylene yields were between 4.6-10%. The propylene yields are lower (between 2.11 and 5.43%) compared to the previous experiment (3.35-10%), due to the higher ethylene / propylene mass ratio in the case of steam addition as shown in table 3.

The yields of CO and CO2 are lower at pyrolysis in the presence of steam (between 5.46% and 10.86%) than in absence of steam where they were from 9.47 to 17.27%.

It can be assumed that, in the presence of steam, some reactions occur between water and the compounds in the reaction mass, resulting in the nature of ethers, esters, alehides, ketones and other oxygen compunds.

Model of pyrolysis process

In a previous work [9], an analytical semiempirical model was developed for the experimental data in the study [8], according to indications in literature [10]. According with qualitative analysis of the experimental results, now we propose a mathematical model of linear type (eq. 1) both for predicting the gas yield and for predicting the yields of each compound:

$$y = A_0 + A_1x_1 + A_2x_2 + A_3x_3 \quad (1)$$

Where:

y is the yield , % wt;
x_1 –residence time, s;
x_2 –temperature , ºC;
x_3 – steam:raw material ratio;
$A_0 \div A_3$ – regression coefficients.

Table 4
THE YIELDS OF MAIN COMPOUNDS IN THE GASEOUS PRODUCT RESULTED IN WASTE PALM OIL PYROLYSIS IN PRESENCE OF STEAM, % vol

Sample #/ Process parameters	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Sample #8
Residence time, s	72	72	144	144	144	144	72	72
Temperature, °C	625	575	575	575	625	625	575	625
Mass ratio steam: raw material	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1
CO	4.29	2.83	3.11	2.56	4.34	5.28	2.45	3.62
CO2	5.93	3.46	4.29	3.36	4.77	5.58	2.96	3.78
Methane	2.08	1.18	1.51	1.34	2.26	2.13	0.82	1.71
Ethane	2.46	1.58	1.78	1.68	2.79	2.87	1.22	2.16
Propane	0.86	0.61	0.62	0.58	0.86	1.21	0.66	0.81
Butane	0.43	0.32	0.31	0.29	0.41	0.55	0.41	0.44
Pentane	0.30	0.14	0.22	0.12	0.21	0.25	0.18	0.22
Ethylene	7.78	4.56	5.63	5.24	**9.21**	7.50	2.99	6.49
Propylene	4.83	2.86	3.50	3.12	**5.43**	4.98	2.11	4.14
Butenes	2.83	1.68	2.05	1.76	3.28	2.77	1.29	2.43
Butadiene	1.68	0.86	1.22	0.99	2.04	1.26	0.53	1.32

Coefficients of equation 1 are calculated using the smallest squares method included in the features of Microsoft Excel's Data Analysis software. The program performs the determination of the regression coefficients, the correlation coefficients and the standard errors for each coefficient. The ANOVA analysis showed if the coefficients were significant, thus determining the suitability of the model.

The model consists in four equations, one for the total gas yield and three for the most important compounds in the gas: ethylene, propylene and carbon oxides as follows:

-the model for predicting total gas yield (eq.2):

$$y = -139.988 + 0.069792x_1 + 0.2565x_2 + 37.25x_3 \quad (2)$$

The regression coefficients (r, r^2 and *adjusted* r^2) have high values: 0.9871, 0.9733, respectively 0.9551, which indicates a good accuracy of the model. All values of the statistical parameter p are below 0.05, which means that all coefficients are significant within the error range ± 5%. The relative errors (table 5) of the predicted values are small compared to the experimental values (-5.07 ... + 4.87) and are both positive and negative, so this is an indication that there are no systematic errors.

Table 5
RELATIVE ERRORS OF EXPERIMENTAL VALUES
VS. VALUES PREDICTED WITH Eq.2

Observation	Predicted yield, y	Experimental yield	Relative error,%
1	32.8	34.4	4.88
2	20.0	20.3	1.63
3	25	24.8	-0.8
4	21.3	21.6	1.53
5	37.8	36.1	-4.56
6	34.1	35.7	4.69
7	16.3	15.8	-2.77
8	29.1	27.6	-5.07

-the model for predicting the ethylene yield (Eq.3):

$$y = -35.6 + 0.01944x_1 + 0.063x_2 + 12.5x_3 \quad (3)$$

Ethylene is one of the main products. The accuracy of the model for predicting its efficiency is very important for any industrial applications.

All statistical parameters have good values but the relative errors are higher than he model for total gas: between -8.4% and 11.2%; also, they are acceptable.

- Propylene is the second main product which can be used in the chemical industry. The model for predicting propylene yield is (Eq.4):

$$y = -35.6 + 0.01944x_1 + 0.063x_2 + 12.5x_3 \quad (4)$$

The statistical analysis showed good fitting of the model, with r^2=0,9930 and small relative errors (-5.62% ... +3.57%).

- the model for predicting of carbon oxides yield

Carbon oxides are undesirable in the pyrolysis gas because they should be separated and treated, so rising the costs of an industrial process. The only use would be as synthesis gas ($CO+H_2$) but the very low concentration of hydrogen prevents it from being recovered. They appear in gases, because the oil molecules contain oxygen, along with carbon and hydrogen. It is very useful to be able to predict the yield from these gases, and therefore the linear model (eq.5) was proposed:

$$y = -32{,}75 + 0{,}013889x_1 + 0{,}063x_2 + 8.5x_3 \quad (5)$$

This model got insignificant statistical parameters, both in terms of the correlation coefficients (r=0.8962, r^2=0.8032 and *adjusted* r^2 = 0.6557), as well as in the regression coefficients; ANOVA analysis shows that 3 of the 4 coefficients are not significant within the confidence interval ± 5%, the value of parameter p being higher than 0.05. Relative errors are bigger (-12,68% …+15.04%). This indicates that the model for carbon oxides prediction is not reliable. The explanation would be that the factors controlling the carbon oxides formation are not entirely understood and probably this yield depends more on other factors, such as the molecular formula of the oil.

Conclusions

The aim of the study was to study the influence of an inert fluid (steam) on product yields, in the pyrolysis process of used palm oil. The experiment was performed in a continuous tubular reactor, at the residence time 72 s respectively 144 s, temperature of 575 °C and 625 °C, steam: raw material ratio 0.1, respectively 0.2.

The products yield of waste palm oil pyrolysis in presence of steam are between 15.8% and 36.1%, which gives industrial applicability to the process, if the priority is to obtain gaseous product.

The gaseous product resulted from the process contained high ethylene (18.89 - 25.5%) and propylene (13.33-15.05%) concentrations, comparable to that obtained from pyrolysis of liquid hydrocarbons. Also, the concentrations of ethylene and propylene are higher than those obtained in the experiences in the absence of steam from study [8], where the concentration of ethylene was between 9.2% and 19.42% and that of propylene between 7.7-16.5%.

Based on the experimental results, the equations of a linear type mathematical model were developed to predict the productes yields depending on temperature, residence time and steam: raw material ratio. The coefficients of the model were statistically verified.

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