



“Gheorghe Asachi” Technical University of Iasi, Romania



OLEFINS AND FUELS FROM FRYING PALM OIL THROUGH PYROLYSIS

Ana Maria Sivriu^{1*}, Claudia-Irina Koncsag², Alina-Monica Mares¹,
Roxana Tirpan², Olga Sapunaru², Gheorghita Jinescu³

¹University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science

²University Ovidius of Constanta, Faculty of Applied Science and Engineering, 124, Bld. Mamaia, 900527, Constanta, Romania

³Romanian Academy of Technical Sciences, Bucuresti, Romania

Abstract

The pyrolysis of frying palm oil was studied in continuous stationary process, in a micropilot plant. The main factors affecting the products yields are temperature and residence time. For the studied parameters range (temperature: 475°C - 630°C and residence time: 120 s - 240 s), the gas yield varied between 7.9% (w/w) and 63.3% (w/w), related to feed. Unsaturated hydrocarbon yields (olefins) can reach 24-29% (w/w) related to feed, at the right processing parameters, the main products having good yields: up to 10% w/w for ethylene and 10.5% (w/w) for propylene. Also, the liquid fractions produced in the experiment were characterized having in view the use as fuel oils. The low viscosity (4.4-8.3 cSt at 20°C) and high heat of combustion value (9225-9260 kcal/kg) demonstrated that liquids are fit for use as fuel oil. These results are encouraging for industrial applications consideration. For this reason, mathematical modeling for the prediction of products yields was performed. The individual models for the main compounds (ethylene, propylene, methane, ethane, propane, carbon oxides) are in form of second degree polynomial equations; they are accurate as the statistical analysis proved.

Key words: biofuel, mathematical model; pyrolysis mechanism; renewable olefins; vegetable oil

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1. Introduction

Global polyethylene (PE) and polypropylene (PP) production grew in last decade (Esposito, 2019) but this growth is based on building new capacities based on petroleum and gas. Also, the fuels required in increasing quantity, for transportation and energy generation, are mainly produced from oil&gas. The deployment of fossil reserves leads to search for alternative resources such as recycling of plastics (Olugu et al., 2017) or producing monomers and fuels by pyrolysis of PE, PP waste (Kuncser et al., 2010) or tyres (Miandad et al., 2018; Neri et al., 2018; Osayi et al., 2018; Umeki et al., 2016).

Hydrocarbons can be also produced from renewable resources such as agricultural and forest

waste or waste resulted in biomass processing (tall oil, lignin, glycerol) (Marton, 2013). Waste vegetable oils can also count for feedstock in valuable chemicals production (Wiggers et al., 2017). Best known for their use as fuels, either directly or after conversion into biodiesel by transesterification, or into Diesel-like oil by thermocatalytical processes (Xu et al, 2016), waste vegetable oils are also prone for olefins production with good yields (Kubatova et al., 2011).

There are three ways in olefins production from vegetable oils: the thermal cracking in presence or in absence of steam or another inert gas, the thermal cracking over an inert solid material also with and without steam, and thermal catalytic cracking over a large variety of catalysts: zeolites (Biswas and Sharma, 2014), mesoporous metallic catalysts (Yu et

* Author to whom all correspondence should be addressed: e-mail: sivriu_ana@yahoo.com

al., 2013), sodium carbonate (Zaher et al., 2017), vanadium pentoxide (Yigezu and Muthukumar, 2015), biomass derived heterogeneous catalysts (Aslam et al., 2015) etc.

The thermal cracking over an inert solid material and catalytic cracking are intended for Diesel-like fuels production, so gaseous products are considered as by-products. Liquid products yield are in range 62.3-73.9% (w/w) when using ZSM-5 (Biswas and Sharma, 2014). In other catalysts case, such as sodium carbonate (Dandik and Aksoy, 1998) and mesoporous Ni-Al-MCM-41 (Zaher et al., 2017), the liquid yields range from 51.6 to 57.9 % (w/w) (Zandonai et al., 2015).

Pyrolysis is a thermal cracking occurring in inert environment (in absence of oxygen) and in absence of a catalyst, at high temperature (300-1000°C). Unlike the thermal cracking over an inert solid material or the catalytic cracking, the pyrolysis is a process intended for high gaseous products yields. The gaseous products yield and distribution depend on temperature, residence time and presence of other gas in the system (inert gas, steam, hydrogen). The literature data indicated the thermal cracking of the vegetable oils as an effective way to obtain olefins. With pyrolysis performed in a tubular reactor, at 400°C, Sadrameli and Green (2007) obtained 55.5% (w/w) gaseous product from canola oil, with 28.1% (w/w) unsaturated hydrocarbons. Idem et al. (1996) obtained similar results in similar conditions. In fast pyrolysis of soybean, palm and rapeseed oils (residence time 0.3 s) and at high temperature (820°C) (Zamostny et al., 2012), the product yields and distribution was very close to that in case of hydrocarbon steam cracking, and good ethylene and propylene yields were reached: 28% (w/w) and 12% (w/w), respectively.

The more saturated vegetable oil produced more ethylene and propylene. The propylene and propane yield is an indicator of triglycerides conversion (Zandonai et al., 2015).

Taking into account the waste frying palm oil as a raw material, the present study is focused on olefins and fuels production by thermal cracking, since large amounts of waste cooking oils are generated worldwide, some countries (e.g. Mexico, Malaysia, Japan, USA) producing between 450,000-1,000,000 tons/year (Owolabi et al., 2011), and making this resource economically attractive for industrial processing.

2. Experimental

2.1. Reagents and materials

The raw material for this study was a waste palm oil supplied by a restaurant in Bucharest; it resulted from frying of potatoes chips and was passed in our laboratory through a metallic sieve to retain grossly the mechanical impurities, then filtered through filtering paper for finer separation. Some characteristics were determined to observe the

degradation level of the oil. The only indication of degradation was the small Iodine Number of 3.84 g I₂/100 g oil comparing with 44-51 in fresh oil (Thomas, 2002), indicating that double bonds were oxidized during cooking, so they were not available for further iodine oxidation. High kinematic viscosity (47.3 cSt at 40°C) and high flash point (240°C) indicate that thermal cracking of the oil during cooking was moderate. The oil density at 20°C was 924 kg m⁻³.

The elementary analysis of the raw material oil lead to the following composition: C=75,7% wt; H=11,9% wt; O=12,4% wt which compares with data in literature (Xu et al., 2016) of fresh palm oil: C=76,7% wt., H=11,5% wt., O=11,8% wt. or of waste frying oil: C=76,9%, H=11,3%, O=11,8%. No big difference before frying and after can be noticed in the elementary composition of the oil, even though new compounds formed in thermolytic reactions (n-alkanes, alkenes, low molecular weight fat acids, symmetrical ketones, oxo-propyl esters, CO and CO₂) oxidation (hydroperoxydes, aldehydes and acids) and hydrolysis (free fat acids, glycerol, mono- and diglycerides). The loss of oxygen with CO and CO₂ produced in thermolytic reactions must have been compensated by molecular oxygen included in oxidation reactions.

2.2. Experimental set-up and procedure

The thermal cracking runs took place in a micropilot plant presented in Fig.1. The main equipment consists in a tubular reactor with electrical heating, temperature control and temperature digital monitoring.

The oil is fed by a reciprocating pump with adjustable flow rate 0-4 L/h, in order to perform the experiment at different residence times (120 s, 180s and 240 s respectively).

The internal diameter of the reactor is 0.019 m and its length is 0.47 m. The heating is made with three electrical coils placed in a ceramic shell around the metallic reactor, in three zones: up, middle and bottom, with thermostats, so the temperature profile can be established. We chose to have a uniform temperature profile along the reactor shell. The temperature inside the reactor can be monitored in one point at choice (T₁, T₂ or T₃), and we chose to have it registered in the middle (T₂). During this experiment, temperature was in range of 475 °C - 630 °C; running over 630°C was avoided due to the limitations of the heating system. Since the temperature in the heating shell can be established (with variance ±5°C), the temperature in the reactor was influenced by the feed rate, so small variations in temperature from one set of data to the other occurred, without influencing the conclusions of the work. Pressure in the effluent was 2 barg, needed to fill the gas sample bags. The pressure also corresponds to industrial systems working at "atmospheric pressure", in order to compensate the pressure drop downstream. Pressure is measured with a Bourdon manometer, calibrated in the range 1 - 40

barg. The thermal cracking takes place in a continuous stationary regime, and the effluent is cooled and condensed at 30°C, with running water at 15°C. During the experimental runs, the valve between the manometer and the cooler was shut up, so all effluent passed out at the bottom of the reactor. The vapor condensation system (a coil exchanger) is 0.4 m long. The transfer line from the reactor to the cooler is 0.31 m in length and has a 0.004 m internal diameter. In the separator, a liquid and a gaseous phase are separated; the separator provided with a cooling mantle itself is 0.4 m long and 0.1 m external diameter. The temperature in the liquid-gas separator is approx. 30°C. Samples of gas product are collected at the separator for gas-chromatographic analysis in special aluminum foil bags (5L) and liquid samples are collected in glass containers sealed to the gas-liquid separator.

2.3. Samples characterization procedure

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. The working parameters for hydrocarbons and permanent gases determination are presented in Table 1.

The yields of different gaseous compounds were calculated from the chromatographic composition % (v/v), transformed into % (w/w) through the average molecular weight of the effluent, also taking into account the total gas yield.

Liquid samples were summary characterized: density by pycnometer (method ASTM D1298-99), kinematic viscosity at 20°C by Ubbelohde viscometer (method ISO 3104-02) and Iodine Number (STAS 315-74, in use, for mineral oils, adapted to vegetable oils). Three composite samples were characterized for the heat of combustion with method ASTM D240-14, in order to find their suitability as fuel oils. A short description of the analysis methods is given further on:

Density by pycnometer serves to establish in first instance the relative density of the oil towards water as reference liquid. The method was chosen in detriment of a modern method (by digital density analyzer) because of the fouling caused by the oil in the capillary tube of the apparatus. The density of the oil at 20°C relative to water at 20°C, d_{20}^{20} , is calculated with Eq.(1):

$$d_{20}^{20} = \frac{m_{oil} - m_{empty}}{m_{water} - m_{empty}} \quad (1)$$

where: m_{oil} and m_{water} is the weight of pycnometer filled with oil and water respectively, and m_{empty} is the weight of empty pycnometer, all measured at 20°C; then, the density of the oil at 20°C is calculated with Eq. (2):

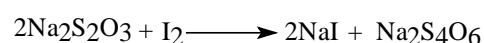
$$\rho_{oil}^{20} = \rho_{water}^{20} \cdot d_{20}^{20} = 998.2 \cdot d_{20}^{20}, \text{ kgm}^{-3} \quad (2)$$

Kinematic viscosity at 20°C was measured with an Ubbelohde viscometer, by clocking (t) the flowing of the oil in the capillary between two marks, and calculating with Eq.3:

$$\gamma = k \cdot t, \text{ cSt} \quad (3)$$

where, k is the constant of the apparatus, in this case $k=0.05113$.

Iodine number gives an indication of the amount of unsaturation either in the original oil formula or as the result of dehydrogenation reaction during thermal decomposition process; the double bonds react with alcoholic solution of iodine in an alcoholic anhydrous medium, and the excess iodine is consumed in titration with sodium thiosulfate, in presence of starch:



Then, the iodine number (IN) is calculated with Eq.4:

$$IN = \frac{(V - V_1) \cdot 0.01269 \cdot F}{m} \times 100, \text{ g I}_2/100 \text{ g oil} \quad (4)$$

where: V is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ 0.1N sol. consumed in titration of blank essay (all components included but oil), ml; V_1 – the volume of $\text{Na}_2\text{S}_2\text{O}_3$ 0.1N sol. consumed in titration of essay with oil, ml; F – the factor of $\text{Na}_2\text{S}_2\text{O}_3$ 0.1N sol.; 0.01269 – grams of iodine stoichiometric corresponding to 1 ml $\text{Na}_2\text{S}_2\text{O}_3$ 0.1N sol., g; m – the quantity of oil taken into analysis, (cca. 1g).

Heat of combustion was measured in bomb calorimeter Parr Instruments, model 1261. The principle of the method is to measure the heat released at the combustion of 0.5-1 g of fuel, transferred to a known quantity of water, increasing the temperature.

3. Results and discussions

The yields of products obtained in nine runs of thermal cracking experiment are presented in Table 2.

3.1. Total gas yields

Since a large part of gas produced was collected for analyses purposes, the direct measurement of the quantities was difficult to perform. The total gas yield is usually calculated from the material balance with Eq. (5):

$$y_{gas} = \frac{m_{raw} - (m_{liquid} + m_{coke})}{m_{raw}} \cdot 100, \% \quad (5)$$

The quantity of raw material (m_{raw}) and that of the liquid - pyrolysis oil (m_{liquid}) can be precisely determined but coke formation is difficult to measure in a continuous system like this; the quantity of raw was calculated from the pump flowrate and the measured time of the run; the liquid product accumulated in one run was weighed.

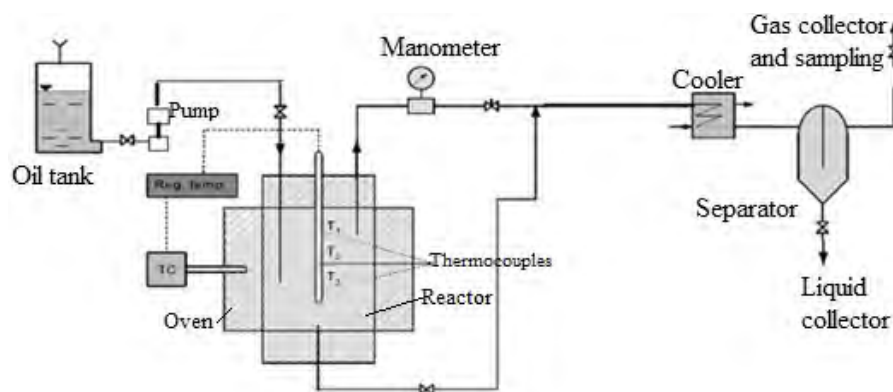


Fig. 1. Micropilot plant for thermal cracking of waste palm oil (Sivriu et al., 2017)

Table 1. Working parameters for hydrocarbons and permanent gases determination with the gas-chromatograph 6890N-Wasson ECE

	Initial temperature, °C	Temperature ramp, °C/min	Flow, mL/min	Split ratio	Pressure, psig
Inlet mode: split	150	-	He: 32.5	5:1	7.35
Oven	75	15, up to 165°C 30, up to 175°C			
Auxiliary oven	90	-	-		
Detector TCD B	50		He: 30		
Detector TCD C	50		N ₂ : 40		
Detector FID	250		H ₂ : 30; Air:300; Makeup He: 30		
Capillary columns			He - 5		7.35
Packed columns			He - 40		

The coke is deposited and accumulated on the reactor coil during the entire experiment, including the intermediary periods between two runs. Even weighing it at the end of the experiment is useless for balance purposes. In other articles describing vegetable oil pyrolysis experiments in continuous systems, the coke yields are not reported (Kozliak et al, 2013, Wiggers et al., 2009, Zamostny et al, 2012.). Unlike the mineral oil, plastic (Kuncser et al., 2010) or tires pyrolysis (Andreola et al., 2016), the formation of coke is much reduced in case of vegetable oils because of the high content of oxygen in molecules (12.3 % wt) reacting with carbon to result carbon oxides which are found in high yields in the pyrolysis gas (as seen in Table 2). In this case, the coke yield is charged to the total gas yield.

Comparing the total gas yields obtained in this study with other authors findings is not easy task since the reaction conditions are different.

For example, in a review from 2017, Wiggers et al., acquired and synthesized a large amount of data between 1996-2016, for all kind of vegetable oils, in very different reaction systems. The pyrolysis temperatures were between 300°C-600°C, the residence time between 1 min-1800 min. The average gas yield was 28.77±21.06%. At the pyrolysis of canola oil, Sadramelli and Green (2007) reported, in range of 300-500°C, in a very slow process (residence time 90 min - 360 min) gas yields of 15-75% w/w. Experimental data for temperature over 600°C, are found rarely. Zamostny et al. (2012) pyrolysed

different vegetable oils at 800°C, in the oven of a gas chromatograph, in presence of nitrogen, but they only reported yields of the main compounds; however, one can calculate that the gas yield is over 80%. In conditions closed to the present study (residence time 3 min and temperature 470°C), from Jojoba oil, Kozliak et al (2013) obtained a total gas yield of 23.5 ±3.5% wt/wt, comparing with ours 25.47% wt/wt, at the same temperature and 4 min time residence.

From our experimental results, it is obvious that the total gas yield increases with temperature and also it is strongly affected by the residence time. For example, the gas yield at 480°C and 120 s residence time is barely 7.97% (w/w), since at 475°C and 240 s, it was 25.47% (w/w).

The maximum gas yield was obtained at longer residence time: 63.31% (w/w) at 620°C and 240 s, since at comparable temperature (630°C) and 180 s, the gas yield was 51.51% (w/w).

3.2. Gaseous products

As the feedstock contains C, H and O, the pyrolysis gas contains hydrogen, hydrocarbons and carbon oxides. Based on gaseous compounds obtained in this experiment, and in accordance with mechanisms presented in Maher and Bressler's (2007) work, the pathway to the products starts with triglycerides decomposition into fat acids, acroleine and ketenes, followed by the fat acids decomposition producing carbon dioxide and alkanes.

Table 2. Experimental data at the thermal cracking of waste palm oil in a continuous stationary regime (pressure: 2 barg; temperature range: 475 °C - 630 °C; residence time: 120 s - 240 s)

Sample #	1	2	3	4	5	6	7	8	9
Residence time, s	240	240	240	180	180	180	120	120	120
Temperature, °C	620	600	475	555	580	630	550	530	480
Average Molecular Weight, g/mol	29.0	29.6	33.1	31.6	30.6	29.9	30.6	31.4	32.6
Total gas yield, % (w/w) from which:	63.31	59.32	25.47	45.24	49.20	51.51	31.92	25.91	7.97
Hydrogen	0.37	0.25	0.04	0.09	0.14	0.15	0.05	0.04	0.01
CO	9.07	8.80	5.89	7.60	7.32	7.28	5.73	4.65	2.01
CO ₂	8.20	8.05	7.06	8.56	9.03	7.21	5.94	4.82	2.29
Oxygen	0.10	0.10	0.04	0.09	0.13	0.15	0.08	0.07	0.11
Nitrogen	0.46	0.40	0.18	0.31	0.44	0.53	0.31	0.25	0.34
Methane	5.22	4.54	0.54	2.33	3.05	3.67	1.54	1.25	0.22
Ethane	5.69	5.27	1.48	3.47	3.97	4.40	2.37	1.92	0.38
Propane	2.36	2.15	1.18	2.02	1.90	1.76	1.35	1.09	0.32
Butanes	1.06	0.94	0.74	0.97	0.88	0.71	0.72	0.59	0.25
Pentanes	0.60	0.52	0.34	0.46	0.46	0.36	0.33	0.27	0.10
Alkanes C6+	0.44	0.15	0.19	0.37	0.17	0.19	0.08	0.06	0.06
Ethylene	9.88	9.98	2.61	7.62	8.47	10.00	5.66	4.60	0.73
Propylene	10.45	9.50	2.49	6.02	6.94	7.91	4.12	3.35	0.61
1-Butene	2.06	1.98	1.05	2.72	2.65	2.91	2.05	1.66	0.34
2-Butene	5.01	4.71	0.61	0.92	1.85	1.78	0.40	0.32	0.06
i-Butene	1.43	0.74	0.08	0.13	0.18	0.21	0.07	0.06	0.01
Butadiene	0.36	0.66	0.37	1.14	1.19	1.58	0.90	0.73	0.09
Cyclopentane+Cyclohexane	0.13	0.12	0.03	0.09	0.12	0.12	0.06	0.05	0.01
Benzene	0.42	0.45	0.07	0.33	0.32	0.58	0.15	0.12	0.04

Decomposition of acrolein and ketenes leads to carbon monoxide and alkenes. Hydrogen can proceed from dehydrogenation of alkanes to alkenes, or even from hydrocarbon decomposition in elements. Long chains of paraffins are decomposed into shorter alkane chains and alkenes. Cyclopentane and cyclohexane are formed by cyclization of nC₅-C₆ olefins. Benzene results from cyclohexane dehydrogenation. Of course, in the literature, the mechanism is more complex, explaining the presence of other compounds such as: aldehydes, ketones, alcohols, dimethyl ether, most of them in the liquid phase. We could add to this mechanism, the reaction between carbon (coke) with oxygen containing radicals (e.g. carboxylate) which could explain the high content of carbon oxides in gas (up to 17.27% wt.) very close to that of 18.5%, if all oxygen in the raw would transform in carbon oxides (1:1 CO/CO₂ mass ratio); this would be impossible because not all triglycerides decompose and if so, the oxygen is also found in other products: acrolein, ketenes, free carboxylic acids, ethers, aldehydes, ketones, etc.

Yields of the most interesting gaseous compounds are reported in literature but they are very different from an experiment to another, as the experimental conditions differ very much. For example, at relatively low temperature (400-500°C) and long residence time (90-360 min), Sadramelli and Green (2007) obtained from canola oil 17-23.7% w/w ethylene and 10.3-13.6% w/w propylene, since Zamostny and al.(2012), from the same oil obtained 28.5% w/w ethylene and 11.5% w/w propylene, at 800°C and short (unspecified) residence time; at temperature of 475-630°C, and residence time between 2 and 4 min, we obtained 0.73-9.88 % w/w

ethylene and 0.61-10.45% propylene, from waste palm oil. In the present study, were obtained 4.39-17.27% w/w carbon oxides, which is much comparing with Sadramelli and Green (2007): 2.9-3.9% w/w, but close to 15.2% w/w obtained by Zamostny et al (2012): 15.2%.

Concerning the yield of gaseous products obtained in this study, the following are observed:

- The hydrogen is in concentration of little importance for recovery and purification, but hydrocarbons are predominantly olefins in good yields. As seen in Table 2, the olefins yields are highest at high temperature and residence time: 28.8% (w/w) at 620°C and 240 s. At 480°C and 120 s, the olefins yield is merely 1.75% (w/w). The carbon oxides yield also increases with temperature and residence time, having a maximum of 17.27% (w/w) at 620°C and 240 s. It is obvious that longer residence time and higher temperature favor the breaking of oil molecules into numerous smaller molecules.

-The olefins: alkanes ratio also increases with temperature and residence time from 1.58 at 480°C and 120 s to 2.76 at 620°C and 240 s. Correlated with hydrogen yield increasing at higher temperature and longer residence time, this is a proof of dehydrogenation being favored in such conditions.

3.3. Liquid products

In every run, a liquid product was obtained, with a yield varying between 26.69% w/w and 92.03% w/w, as seen in Table 3. The liquid yield was calculated as product weight percent from feed weight. In general, the pyrolytic oil yield is lower at higher temperature and shorter residence time.

Comparable results were obtained by Wiggers et al (2009) from soybean oil pyrolysis, in absence of water or inert gas at 450°C (92% w/w) and at 600°C (58% w/w), but at shorter residence times (12 s and 36 s, respectively). Kozliak et al (2013) studied the pyrolysis of Jojoba oil and, at 180 s (like us) and temperatures between 430°C-470°C. They obtained a liquid yield of 95% w/w at 430°C and 73% w/w at 470°C. It is notable that reactors were different: Wiggers et al. (2009) worked on a similar tubular continuous reactor but with a bigger diameter (0.067 mm) and Kozliak et al. (2013) worked on a continuous stirred reactor. The type and geometry of the reactor affect the results. In general, to obtain large yields of liquid, the pyrolysis is recommended at temperature between 300°C and 450°C. Some characteristics of the liquid obtained in this study are shown in Table 3.

As seen in Table 3, the density of the liquid products, in range of 852- 879 kg m⁻³, is sensibly under the density of feed oil (924 kg m⁻³), this proving the breaking of large molecules during the process. Differences among the nine samples are small, noting lower values for higher process temperature. The flash points are in range of 45-50°C, due to volatile compounds in the samples (light hydrocarbon, aldehydes, alcohols). The kinematic viscosity is much lower (4.4 - 8.3 cSt at 20°C) than that of the feed, as a result of cracking reactions. The Iodine numbers, as an indicative of the unsaturated character, is sensibly higher than the oil's, noting highest values at process temperature over 600°C, showing that the influence of temperature is greater than of residence time.

All these characteristics indicate the opportunity for the use of the pyrolysis oil as it is or as a component of fuel oil, but the main characteristic counting for such use is the calorific power. Three composite samples were made-up, one for each residence time runs, and the heat of combustion (the lower calorific power) was determined. All samples had very close calorific power: 9225, 9253, and 9260 kcal/kg, respectively (1 kcal = 4.184 kJ). These are considered good values for fuel oils and are in range

of other experimental data. For example, in their review from 2017, Wiggers et al. reported a calorific power of 8015 ±3670 kcal/kg.

3.4. Mathematical modelling

Since the internal diameter of the reactor (0.019 m) in this study is of the same size grade as the industrial tubes (0.07-0.08 m), the experimental data could be processed for drawing-up mathematical models serving to scale-up the process for industrial applications.

Firstly, the total gas yield was modelled. The experimental results for the dependency of total gas yield on the process factors (temperature and residence time) suggest that a polynomial equation of second order (Eq.6) should describe the process:

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_1 \cdot x_2 + a_4 \cdot x_1^2 + a_5 \cdot x_2^2 \quad (6)$$

where: y is the total gas yield, (%) (w/w); x₁ - the residence time, (s); x₂ - the temperature, (°C); a₀...a₅ - the model coefficients.

The model's coefficients were calculated by linear regression and statistically explored with "Data analysis" facility of Microsoft Excel. The regression statistics shows apparently a good fitting of the model's coefficients to the experimental data, since the correlation coefficient *r*² and adjusted *r*² are very high: 0.9995 and 0.9987, respectively. The analysis of variance (ANOVA), presented in Table 4 shows that most of coefficients in (Eq.1) are significant (p < 0.05), except the coefficient for the term x₁x₂, where p=0.204953; also, the standard error for this coefficient, 0.00012, is too high comparing with its value: 0.00019. As a consequence, this coefficient is not significant for the model, so it was discarded from (Eq.6), and the other coefficients were re-estimated.

The resulted model is presented in Eq.7:

$$y = -458.459 + 0.501 \cdot x_1 + 1.374 \cdot x_2 - 0.00084 \cdot x_1^2 - 0.00102 \cdot x_2^2 \quad (7)$$

Table 3. Physico-chemical characteristics of liquid products at the thermal cracking of waste palm oil

Sample #	1	2	3	4	5	6	7	8	9
Residence time, s	240	240	240	180	180	180	120	120	120
Temperature, °C	620	600	475	555	580	630	550	530	480
Liquid yield, %w/w from which:	26.69	40.68	74.53	54.76	50.8	48.49	68.08	74.09	92.03
Density, kg m ⁻³	852	860	873	870	860	856	875	866	879
Flash point, °C	45	47	50	48	47	46	48	47	49
Kinematic viscosity at 20°C, cSt	5.4	5.6	6.3	5.2	4.9	4.4	5.9	4.4	8.3
Iodine number, g I ₂ /100 g oil	7.54	7.37	5.07	6.50	6.77	7.90	5.54	5.47	4.62

Table 4. Coefficients and ANOVA analysis for the model (Eq.6)

	Coefficients	Standard Error	t Stat	P-value
Intercept	-465.89	30.39789	-15.3264	0.000603
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

This time, the statistical analysis proved that the model has a good fitting (adjusted $r^2=0.9981$) and all coefficients are significant ($p<0.05$), so it can be considered as reliable.

For the main products in gas, a polynomial model of second degree was also preferred because it seems more appropriate for the results obtained in the experiment. The complete model is in Eq.6 form, but after many trials, only the significant coefficients were taken into account and only the models with good fitting remained. In Table 5, the model's parameters are presented succinctly, for the main products in the pyrolysis gas.

Even though butenes and butadiene are also important, the modeling lead to nothing and there is an explanation: due to the final condensation conditions (cca. 30°C; 2 barg), an important part of these compounds can be found in the liquid product and so, not all the produced C_4 was quantified in gas.

As seen in Table 5, the gaseous products yields are predicted with good fitness by a second degree polynomial but propane's yield by a first degree polynomial equation, describing correctly the tendency of linear increasing with temperature and residence time; the model's accuracy is not so high in case of propane. The models are valid in the studied temperature range (475°C-630°C) and residence time (120-240 s).

4. Conclusions

This work investigated the obtaining of olefins and other valuable products from waste cooking palm

oil through pyrolysis, in continuous stationary regime. The effect of process temperature (475°C - 630°C) and residence time (120 s- 240 s) on gaseous products was observed and quantified. Higher temperature (620-630°C) and longer residence time (240 s) lead to highest gas yield and olefins. Yields could be even higher at temperature over 630°C, but the experimental set is limited to this. However, olefins yield between 24% and 29% w/w, and particularly good yield of ethylene (up to 10% w/w) and propylene (up to 10.5% w/w) are significant even in these experimental conditions. Also, liquid product obtained in the process, with yields varying between 26.69% w/w and 92.03% w/w, had good heat of combustion value and physical characteristics fit for use as fuel oil itself or as a component.

For total gas and separately for ethylene, propylene, methane, ethane, propane, and carbon oxides, polynomial models were developed predicting yields as a function of temperature and residence time. The models have good accuracy and analysis of variance proved that models are good at 5% significance level. The olefins yield, good quality of pyrolysis oil as liquid fuel and the possibility to predict their yields with accuracy, recommend the results of this study as a step in scaling up for industrial applications.

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Table 5. Summary of models for predicting the main products yields at the pyrolysis of waste palm oil

Product	Model	Analysis of variance for the Eq.6 coefficients, p values	Adjusted correlation coefficient, r^2	Standard error
Ethylene	$y = -105.16 + 0.0174 \cdot x_1 + 0.3425 \cdot x_2 - 0.00026 \cdot x_2^2$	a ₀ :0.0024 a ₁ :0.0033 a ₂ :0.0038 a ₅ :0.0079	0.9858	0.408
Propylene	$y = -70.58 - 0.0551 \cdot x_1 + 0.2429 \cdot x_2 + 0.00015 \cdot x_1x_2 - 0.00021 \cdot x_2^2$	a ₀ :0.0007 a ₁ :0.0364 a ₂ :0.0009 a ₃ : 0.0071 a ₅ :0.0012	0.9980	0.150
Methane	$y = -16.66 - 0.0685 \cdot x_1 + 0.00015 \cdot x_2 + 0.000151 \cdot x_1x_2 - 0.000063 \cdot x_2^2$	a ₀ :0.0399 a ₁ :0.0018 a ₂ :0.0312 a ₃ : 0.0010 a ₅ :0.0263	0.9954	0.120
Ethane	$y = -44.0014 - 0.0222 \cdot x_1 + 0.1504 \cdot x_2 + 0.00007 \cdot x_1x_2 - 0.00026 \cdot x_2^2$	a ₀ :0.0001 a ₁ :0.0123 a ₂ :0.0002 a ₃ : 0.0020 a ₅ :0.0002	0.9987	0.066
Propane	$y = -3.72 + 0.0052 \cdot x_1 + 0.0020 \cdot x_2$	a ₀ :0.0121 a ₁ :0.0520 a ₂ :0.0079	0.7878	0.297
CO+CO ₂	$y = -225.904 + 0.0612 \cdot x_1 + 0.7992 \cdot x_2 - 0.00069 \cdot x_2^2$	a ₀ :0.0156 a ₁ :0.0028 a ₂ :0.0173 a ₅ :0.0209	0.8951	1.38

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