THERMAL CRACKING OF WASTE VEGETABLE OIL – A PRELIMINARY RESEARCH

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This article proposes a renewable raw material, in this case is used waste palm oil for obtaining valuable products which are usually resulted from crude oil, a limited resource. The main goal of the research work is to produce high yield of olefins through thermal cracking processes using waste vegetable oils from different uses. A preliminary research was designed for the thermal cracking of waste palm oil in a micropilot plant composed by a metallic, tubular and electrically heated reactor. The process operated at 2 bar, in a temperature range of 450-630º C and different residence time (120-180-240s). Mass balance allowed us to calculate the products yields. The products obtained from the process were analyzed using Gas-Chromatography. The study concluded that significant olefins yields (up to 10% wt for ethylene and 7 % wt for propylene) can be obtained by increasing temperature and residence time in the reactor.

Keywords: thermal cracking, waste vegetable oil, ethylene yield, propylene yield, olefins

1. Introduction

Vegetable oils represent an alternative to the mineral oils and fuels for their ecological friendliness. Vegetable oils used as lubricants, individually or in combinations with mineral ones, have limited applications due to their low oxidative stability and poor performances at low temperature [1]. The same reasons stand against the use as Diesel-like fuel for engines, adding at this low calorific power by comparison with mineral Diesel. This is why, chemical modifications are required to vegetable oil composition. The most important types of vegetable oil used for the chemical conversion are soybean and sun-flower oil which "was synthesized under different reaction condition" [2] in some

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experiments. The widespread application is the transesterification of triglycerides and production of so called „biodiesel" [3]. But chemical transformation can also be reached by hydroprocessing which involves hydrogenation and decarboxylation of fatty acids [4] with the beneficial effect of alkanes formation; this process is rather expensive and a cheaper alternative would be the thermal cracking at moderate temperature (430-440 ^{o}C), for the improvement of cold-flow properties [5]. Upgrading of oxidation stability was also obtained when working in hydrogen atmosphere. Also, some research studies "were used to obtain predictive equations for biodiesel blends" [6].

Pyrolysis gives a wider range of products: gas, high octane gasolines and Diesel-like fuels [7], but gas compounds are different from those obtained in gasification. Olefins production [8] along Diesel-like fuel is possible through oil pyrolysis, a less expensive method than gasification. The pyrolysis can be conducted slowly, at long residence times and lower temperature or faster, at higher temperatures and shorter residence times. The pyrolysis can take place through direct heating or over an inert material, in absence or in presence of an inert fluid [9-12]. Use of catalysts was also considered by researchers: zeolites for catalytic cracking [13,14] or catalysts tailored for improving the conversion in hydrocarbons by deoxygenating / decarboxylating triglycerides [15,16]. The reactions can be performed in batch systems at pressures ranging from vacuum to dozens of bar [17,18], or in flow reactors [10,11,17]. One of the similitudes consists in the long chains of hydrocarbon present in crude oil as well as in the vegetable oils [19].

In this work is presented a study on thermal cracking of waste vegetable oil (palm oil) in a flow reactor operated at pressure of 2 bar and temperature over 400 ^{o}C, in absence of catalyst or inert gas.

2. Experiment

2.1 Materials and methods

The aim of thermal cracking of waste palm oil was to produce renewable olefins for petrochemical industry such as polymers. This feedstock was selected due its availability and low cost. In this preliminary study, the waste palm oil collected from a restaurant was used. The thermal cracking of waste palm oil was studied in the micropilot plant installed at Ovidius University in Constanta. The process is operated in a continuous flow system at temperature ranging from 450 to 630°C. The experimental method involved the gas chromatography for determination of ethylene, propylene, methane, hydrogen and carbon mono and dioxide concentration. The composition of the cracked gas was determined by

chromatographic analysis methods: Refinery Gas Analysis developed by Wasson on Agilent 6890 N.

2.1.1 Equipment and test procedure

The thermal conversion was carried out in a micropilot plant. A schematic diagram of the reactor setup can be seen in Figure 1.

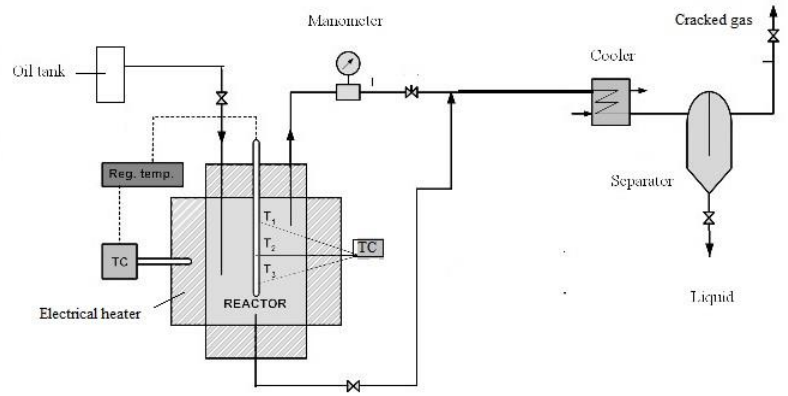

Fig. 1. Micropilot plant for thermal cracking of waste palm oil

The installation shown in figure 1 is equipped with a tubular reactor with an inside diameter of 1.9 cm and a height of 47 cm. The reactor is electrically heated from the outside with three electric resistors, the reactor is isolated with chamotte to minimize the heat loss and maintain uniform temperature distribution. The feedstock was injected into reactor by a piston pump with adjustable flow rate whence different resident times. The inside temperature of the reactor is controlled by thermocouple to provide accurate temperature control with a temperature variance of ±5 ^{o}C. The reactor effluent was condensed in the water-cooled heat exchanger and entered in the separator to separate gases from liquid. The pressure was constant (2 bar) and monitored to prevent pressurization and possible explosion hazard. The gas product was collected in samples and analyzed by gas chromatography and the excess was evacuated. The yields of different compounds in gas were determined by material balance combined with the composition determined by gas-chromatography.

2.1.2 Analytical methods

The gas products were analyzed by chromatographic analysis Refinery Gas Analysis developed by Wasson on Agilent 6890 N apparatus with multiple columns and different detectors. The method detected and measured with high

accuracy the concentration of individual hydrocarbons, hydrogen, carbon monoxide and carbon dioxide.

The liquid samples were analyzed for viscosity, density and flash point, as for heating fuel utilization. Also, iodine number was determined, as an indication of its unsaturated character. The measurements were performed according to standard methods in use. Density was measured by pycnometer with standard method ASTM D1298-99. Kinematic viscosity was determined at 40 °C by Ubbelohde viscometer according to ISO 3104 method. Flash points were determined by Marcusson apparatus using DIN12785. The iodine number standard method for oil fatty acids, ASTM D5768-02, was adapted for the pyrolysis oil analysis.

2.1.3 Characteristics of waste vegetable oil

The main physical-chemical properties of raw palm oil were shown in Table 1. It should be noted that the feedstock for this technology was collected from the restaurant and was filtered before using it in process.

Table 1

Characteristics 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
Iodine value	5.07	g I2/ 100g
Flash Point	240	°C

3. Results and discussion

The tests were performed in a temperature range of 450-630ºC, residence time: 120, 180 and 240 s and pressure of 2 bar. Initial test at low temperature (380 ºC) with frying palm oil feedstock demonstrated that thermal cracking occurred slightly and only cracking liquids were obtained.

In each case, the gas yields were calculated by material balance, taking into account the feedstock and the liquid products weight, shown in equation 1.

$$\text{Yield of cracking gas} = \frac{\text{mass}_{\text{feedstock}} - \text{mass}_{\text{liquid}}}{\text{mass}_{\text{feedstock}}} \text{x} 100 \quad (1)$$

The gas yield correlates with the temperature and the residence time, wherefrom with the severity of the process. The variation of the gas yield with temperature and the residence time is shown in figure 2. As expected, increasing temperature leads to high conversion of the feedstock and gas yields. Temperature over 600 ºC leads to gas yield over 50%. Also the residence time has a significant effect on the yield of cracking gases, in the same sense, so that at 620ºC and residence time of 240 s, the gas yield gets 63.3% wt.

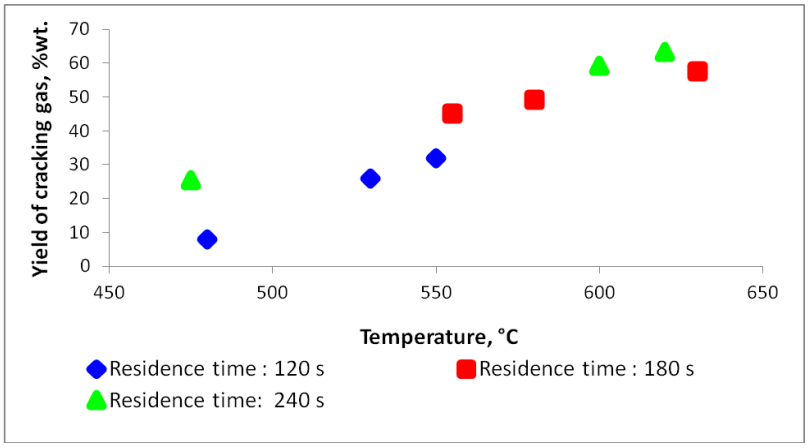

Fig. 2. Yield of cracking gas

The liquid product, also named pyrolytic oil or cracking oil, has some characteristics like the mineral light fuel oil. In table 2, the characteristics of the pyrolysis oil obtained at 120 s residence time and different temperature are presented.

Table 2

The characteristics of pyrolysis oil obtained at 120 s residence time

Parameter	Value			Unit
Cracking temperature	480	530	550	°C
Density at 20 ˚C	879	866	875	kg/m³
Kinematic viscosity at 40 ˚C	$8.2 \cdot 10^{-6}$	$4.3 \cdot 10^{-6}$	$5.88 \cdot 10^{-6}$	m²/s
Iodine value	4.619	7.475	7.545	g I_2/100 g
Flash Point	47	47	48	°C

As seen in Table 2, the characteristics of the pyrolysis oil are similar to those of the light mineral fuel oil, the differentiating characteristics being the

iodine value which denotes a highly unsaturated product; this doesn't prevent anyone from using it as a fuel oil.

In the gas, valuable compounds were obtained for petrochemical and chemical industry use and for energy consumption. The yield of ethylene in cracked gas was obtained with equation 2 as shown:

$$\textit{Yield of ethylene} = \textit{Yield of cracking gas} * \textit{Ethylene concentration, [\%]} \quad (2)$$

The gas was collected in a special aluminum bag and analyzed by gas chromatography. Many individual components were obtained and the list included: methane, hydrogen, carbon monoxide and carbon dioxide, alkanes, olefins, benzene, etc. Some of compounds were obtained in insignificant concentration but the interesting compounds (ethylene, propylene, methane, hydrogen, carbon monoxide and dioxide) showed high concentrations. The compounds yield mentioned above was calculated taking into account the total gas yield and mass concentration. The results are plotted in the figures 3-7.

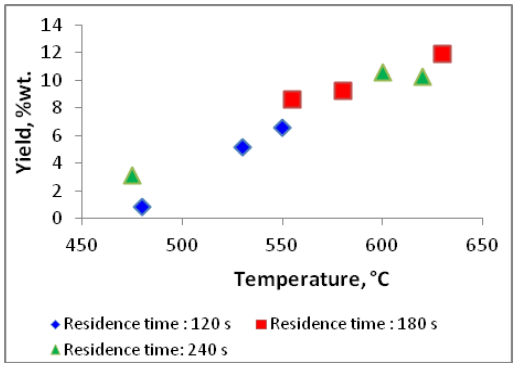

Fig. 3. Yield of ethylene in cracked gas

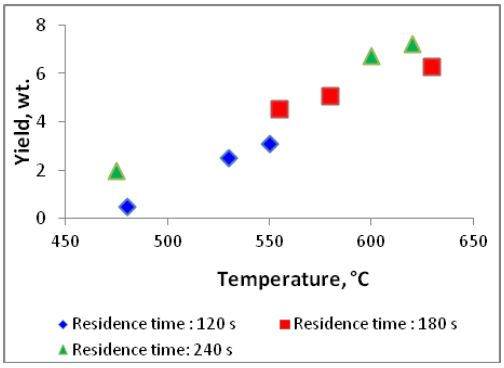

Fig. 4. Yield of propylene in cracked gas

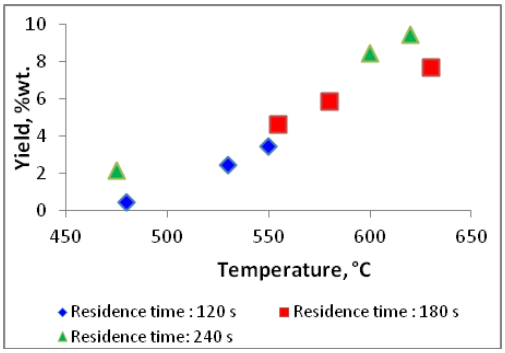

Fig. 5. Yield of methane in cracked gas

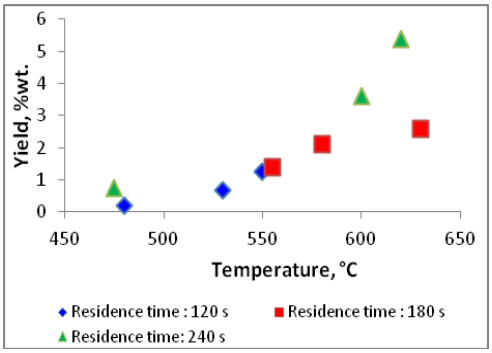

Fig. 6. Yield of hydrogen in cracked gas

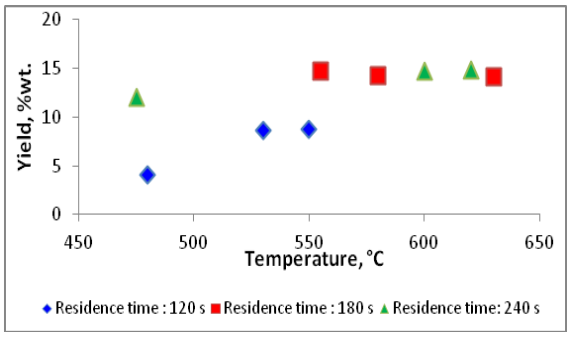

Fig. 7. Yield of carbon monoxide + dioxide in cracked gas

Increasing the temperature and the residence time will have effect on yields increased for ethylene, propylene, methane and hydrogen, and other valuable compounds to be obtained. The effect of the same parameters on the carbon monoxide + dioxide yield is weaker, especially at higher temperature (550-630 ^{o}C), where yield is maintained nearly constant, around 15% wt, the difference to 100% consisting in hydrocarbon.

4. Conclusions

Comparatively to hydrocarbon pyrolysis, the olefins yields are smaller although cumulated hydrocarbon can represent over 85 % wt. yield. For example, yield of ethylene (the main product of the thermal cracking) in the gas was 12% comparatively with 26-28% at the cracking of naphtha.

The yields are strongly affected by temperature and residence time so that temperatures over 600 ^{o}C and residence time over 180 s are desired. At these conditions, yield of ethylene in cracked gas was 12 % and yield of propylene was 6 %. Also yield of methane was 7.6 % and hydrogen resulted in a good yield (2.6%) comparatively with 0.8-2.2% for naphtha cracking. The gas obtained at the cracking of vegetable oil contains more CO_2 (14% wt) than that obtained at the steam cracking of hydrocarbon (0.1-0.2% wt), which is a disadvantage because it requires a larger absorber for the gas purification, and a higher impact on the environment.

According to the results, it is obvious that waste palm oil can be a very promising feedstock for olefins production.

REFERENCES

[1]. *S. Z. Erhan, S. Asadauskas*, Lubricant basestocks from vegetable oils, Industrial Crops and Products, **11** (2-3), 2000, pp. 277-282;

[2]. Ivanoiu I.A. (Basa), Bandur G., Rusnac L. M., Thermal Analysis of biosiesel from soybean and sunflower oils, Rev. Chim. (Bucharest), **61** (9), 2010, pp.876.
[3]. *A.C, Pinto, L.L.N. Guarieiro, M.J.C. Rezende*, Biodiesel: an overview. J. Brazil. Chem. Soc., **16** (6B), 2005, pp. 1313–1330;
[4]. *P. Šimacek, D. Kubicka, G. Šebor, M. Pospišil*, Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel, Fuel, **88** (3), 2009, pp. 456–460;
[5]. *W. Seames, Y. Luo, I. Ahmed, T. Aulich, A. Kubatova, J. Stavova, et al*., The thermal cracking of canola and soybean methyl esters: improvement of cold flow properties, Biomass & Bioenergy, **34** (7), 2010, pp. 939–46;
[6]. *Geacai S., Niţă I., Iulian O., Geacai E.*, Refractive indices for biodiesel mixtures, U.P.B. Sci. Bull., Series B, **74**, Iss. 4, 2012, pp. 158;
[7]. *K.D. Maher, D.C. Bressler*, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology **98** (12), 2007, pp. 2351–2368;
[8]. *S.M. Sadrameli and A.E.S. Green*, Systematics of renewable olefins from thermal crackin of canola oils, Journal of Analytical and Applied Pyrolysis, **78** (2)**,** 2007, pp. 445–451;
[9]. *R.O. Idem, S.P.R.Katikaneni, N.N.Bakhshi*, Thermal cracking of canola oil: Reaction products in the presence and absence of steam, Energy Fuels, **10** (6), 1996, pp. 1150-1162;
[10]. *Koncsag CI,, Sterpu AE., Dumitru AI, Chis T*., Olefins production by steam cracking of waste vegetable oil. Preliminary study, 14 th GeoConference on Energy and Clean Technology, Varna, Bulgaria, Conference Proceedings ISSN 1314-2704, **2**, SGEM 2014, pp. 183-190;
[11]. *P.Zamostny, Z.Belohlav and J. Smidrkal*, Production of olefins via steam cracking of vegetable oils, Resources, Conservation and Recycling, **59**, 47-51 (2012);
[12]. *P.C.Nichols, R.T.Holman*, Pyrolysis of saturated triglycerols, Lipids, **7** (12), 1973, pp. 773-779;
[13]. *X. Dupain, D.J. Costa, C.J. Schaverien, M. Makkee, J.A. Moulijn*, Cracking of a rapeseed vegetable oil under realistic FCC conditions, Applied Catalysis B: Environmental, **72** (1-2), 2007, pp. 44–61;
[14]. *F.A. Twaiq, N.A.M. Zabidi, S. Bhatia*, Catalytic conversion of palm oil to hydrocarbons: performance of various zeolite catalysts. Industrial & Engineering Chemical Research, **38**, 1999, pp. 3230–3237;
[15]. *I. Kubickova, M. Snare, K. Eranen, P. Maki-Arvela, D.Y. Murzin*, Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catalysis Today, **106 (1-4)**, 2005, pp. 197–200;
[16]. *P Maeki-Arvela, I Kubickova, M.Snre, K. Eraenen, D.Y. Murzin*, Catalytic deoxygenation of fatty acids and their derivatives, Energy&Fuels, **2**, 2007, pp. 30–41
[17]. *Y. Luo, I. Ahmed, A. Kubátová, J. Štavova, T.Aulich, S.M. Sadrameli, W.S. Seames*, The thermal cracking of soybean/canola oils and their methyl esters, Fuel Processing Technology, **91 (6)**, 2010, pp. 613–617;
[18]. *A. Kubatova, Y. Luo, J. Štavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames*, New path in the thermal cracking of triacylglycerols (canola and soybean oil), Fuel, **90 (8)**, 2011, pp. 2598–2608;
[19]. *Cioroiu D.R., Koncsag C.I (2014)*, Prediction of products yield at the thermal cracking of vegetable oil, Ovidius University Annals of Chemistry, Ovidius University of Constanta, Department of Chemical Engineering and Technology ISSN-1223-7221, **25(2)**, pp.81-84.