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Theoretical and practical aspects for thermal treatment of waste vegetable oils

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Abstract. The study of pyrolysis of vegetable oils in the laboratory extends over a period of almost a century, its main purpose being to observe the behavior of vegetable oils during thermal decomposition. In the 1940s, the nature of pyrolysis products (hydrocarbons) was discovered, and the liquid yields reaching up to 80%, and even got industrial exploitation, thus producing form tung oil the fuel for vehicles, under the conditions of the fuel crisis. This review presents an overview of the present status of thermochemical and thermocatalytic processes for the production of olefins and liquid products from waste vegetable oils, used in chemical and petrochemical industry. The variety of techniques, operating conditions, type of catalysts and reaction mechanisms will be analysed. During the process a lot of changes occurs in the molecular structures of composition considered as important indicators of the quality of the biofuels produced. These considerations will be used to give a synopsis of the thermochemical processes of different feedstocks. The properties of the products derived from waste vegetable oils are compared with petroleum based fuels as the benchmark [1].

Keywords: vegetable oil, pyrolysis, reaction mechanism.

1. Introduction

Waste triglycerides such as waste cooking oil and waste fish oil, and also fatty acids salts from soap stock are important renewable feedstocks for fuel production

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[2]. These feedstocks have no competition from human consumption or agriculture so, their use can also solve environmental issues associated with disposal of waste organic materials [3]. Pyrolysis technique has recently shown to be a potential alternative to convert waste oils into potentially useful fuel products and chemical feedstock, though the use of this technology is not widespread as yet [4].

In the past decades, there have also been researches on the use of conventional pyrolysis process for recovery of waste oil of a biomass nature (i.e. waste cooking oil, waste vegetable oil) [5]. It has been reported that the waste oils contained long-chain, saturated, and unbranched hydrocarbons and they showed a nearly similar hydrocarbon contents to diesel fuels [6]. Consequently, efforts have been made to produce fuel products from the pyrolysis of different types of waste vegetable oil, e.g. the conversion though pyrolysis of sun flower oil into bio-fuels such as bio-diesel and bio-gasoline [7].

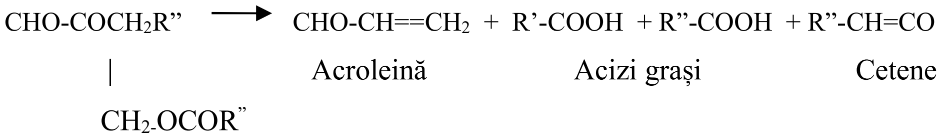
Pyrolysis is a thermal process during which a substance heats and decomposes at high temperature (300–1000°C) in an inert environment, in absence of oxygene. The thermal process has nowadays been utilized to convert waste materials into useful pyrolysis products [8]. In general, pyrolysis produces three classes of products: solid char residues, waxy liquid oils and non-condensable gases. The process can be optimized to maximize production of any of these constituents by altering parameters such as process temperature and residence time [9] e.g. a high temperature and high residence time promotes the production of gases; a high temperature and low residence time (termed “flash pyrolysis”) results in increased yield of condensable liquid oil products, and a low temperature and heating rate leads to increased char production [10] or to no chemical reactions taking place at all.

2. Mechanism of pyrolysis reactions

Following a large thermal cracking study of hydrolyzed/saponified vegetable oils, Chang and Wan [11] proposed a reaction scheme for the pyrolysis of saturated triglycerides, critically adopted by other researchers [12], based on the analysis the products resulting from the process. The first reaction is the breakdown of triglycerides (1), with the formation of fatty acids, acrolein and ketones. It is assumed that most of the acids, acrolein and cetens formed in reaction (1) decompose rapidly, according to reactions (2) and (3), and reactions (6) - (11) are mainly responsible for the formation of hydrocarbons which constitute liquid fractions, in particular petrol and kerosene fractions, as folows:

1. decomposition of triglycerides:

$CH_2\text{-}OCOR'$



$$\underset{\underset{CH_2\text{-}OCOR''}{|}}{CHO\text{-}COCH_2R''} \longrightarrow \underset{\text{Acroleină}}{CHO\text{-}CH{=}{=}CH_2} + \underset{\text{Acizi grași}}{R'\text{-}COOH + R''\text{-}COOH} + \underset{\text{Cetene}}{R''\text{-}CH{=}CO}$$

2. decomposition of fatty acids:
   $RCOOH \longrightarrow CO_2 + RH$
   $2RCOOH \longrightarrow CO_2 + H_2O + RCOR$
3. decomposition of ketenes and acrolein:
   $2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR$
   $CH_2{=}CHCHO \longrightarrow CO + C_2H_4$
   $RCOCH_2R \longrightarrow R\text{—}R + CH_2CO$
   $2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_2$
4. decomposition into elements (C,H):
   $C_nH_{2n+2} \longrightarrow nC + (n+1)H_2$
5. dehydrogenation of paraffins:
   $C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2$
6. splitting decomposition of parrafins:
   $C_nH_{2n+2} \longrightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m}$
7. alkylation of paraffins, the reverse of 6 :
8. isomerization of paraffins:
   $n\text{-}C_nH_{2n+2} \longrightarrow iso - C_nH_{2n+2}$
9. aromatic cyclization of parrafins:
   $C_{(n+6)}H_{(2n+12)} \longrightarrow C_{n+6}H_{2n+6} + 3H_2$
10. polymerisation of olefins:
    $2C_nH_{2n} \longrightarrow nC_{2n}H_{4n}$
    $C_nH_{2n} + C_mH_{2m} \longrightarrow mC_{(n+m)}H_{2(n+m)}$
11. depolymerization of olefins, reverse of 10
12. decomposition of olefins to diolefins
13. decomposition of olefins to acetylenic hydrocarbons
14. aromatization or cyclization of olefins
15. hydrogenation of olefins:
    $C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2}$
16. isomerization of olefins:
    $n\text{-}C_nH_{2n} \longrightarrow iso\text{-}C_nH_{2n}$

3. Thermal treatments of triglycerides

In the last two decades, research on pyrolysis processes has been carried out using conventional heating sources (combustible gases, electricity) for tubular furnaces or fixed bed reactors [6]; the thermal energy is applied to the outside of the reactor by heating the substances in the reactor, the reactor chamber itself but also the environment in the immediate vicinity of the reactor. In this case, the energy is not fully oriented to the heating material, and this leads to significant energy losses, reducing the energy efficiency of the entire process. However, several of these processes have been developed in pilot-scale installations. These pyrolysis processes are generically referred to "conventional pyrolysis".

- Simple pyrolysis of vegetable oils in a batch reactor

Many experiments were carried out in a batch reactor, operating in discontinuous system. In the study [11], the reactor was provided with an autoclave using soybean oils and their methyl esters as raw materials at temperature reaction between 350- 440 °C. The experimental micropilot plant for vegetable oil in a batch pyrolysis reactor is shown in Fig. 1 [12, 13].

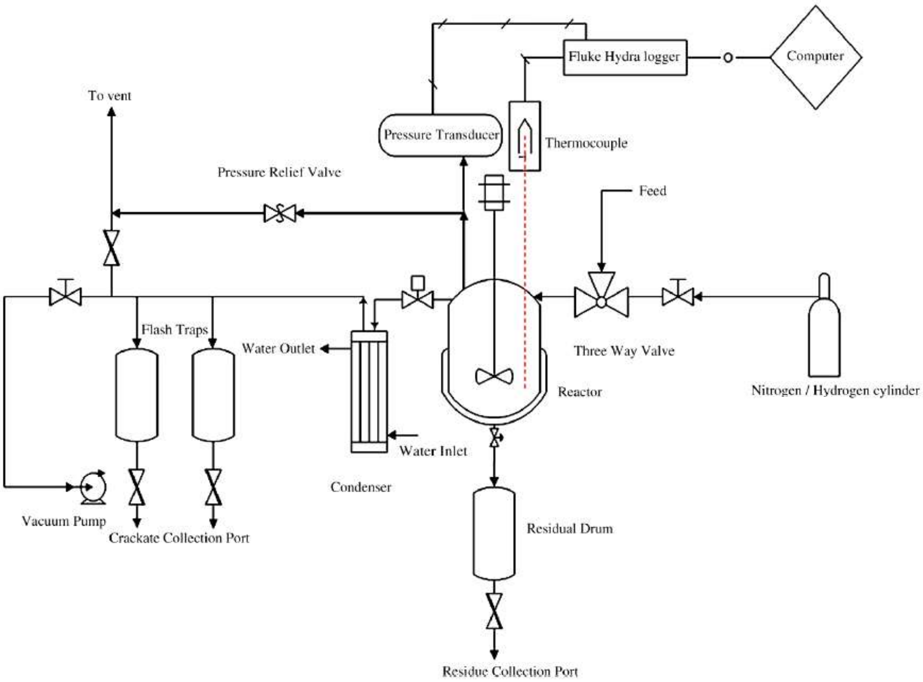


Fig 1. Experimental micropilot plant for vegetable oils batch pyrolysis [12, 13].

The effect of temperature and pressure on the yields of gaseous and liquid products was studied [12]. The gas introduced into the reactor (nitrogen or hydrogen) was used exclusively for pressurization and not for dilution, the quantities of gas being negligible in relation to the mass of the raw material and the obtained products. Hydrogen does not react with any compound from the reaction mass, under the conditions (relatively low temperature and absence of a catalyst).

The aim of this study is to use the liquid product from pyrolysis as fuels (C_7-C_{16} hydrocarbons, identified by GC-FID). The results of the thermal cracking of soybean oil, compared to those obtained from pyrolysis of its methyl esters, are presented in Table 1 [12].

It is observed that pyrolysis gives good yields at temperatures above 400°C, and the conversion increases consistently when cracking occurs near the boiling point of the raw material (at 440°C), thus suggesting that pyrolysis in vapor phase is more effective. The C7-C16 hydrocarbon yields, and alkanes yields confirmed by GC-FID analysis, also increase by decreasing pressure and increasing temperature but this increase is stopped at 420-440ºC, indicating that formation of alkanes is faboured in liquid phase. Another study [13] concluded that from rapeseed oil, soybean oil and also from their methyl esters, a kerosene-like material can be manufactured, with a yield of up to 85% , through thermal cracking in autoclave, in one step, without recirculation, and the cracking temperature is the most important factor influencing the yield.

Table 1**.** The results of soybean thermal cracking.

Reactor temperature, ºC	Conversion, (%)		Hydrocarbons yield (C_7-C_{16}), (%)		C_7-C_{16} n-alkanes yield, (%)	
	Vacuum, 3 kPa	H_2 pressure, 2200 kPa	Vaccum, 3 kPa	H_2 pressure, 2200 kPa	Vaccum, 3 kPa	H_2 pressure, 2200 kPa
350	0	0	0	0	0	0
380	18	3	0	17	2	2
400	20	17	38	37	10	8
420	49	45	36	40	11	10
440	76	64	45	39	12	10

- **Microwave pyrolysis**

Pyrolysis of vegetable oils using microwaves is a different approach than conventional pyrolysis using the electric oven. Microwave pyrolysis has recently been developed as an alternative for converting waste oils into valuable products [14,15]. This thermochemical process transforms biomass into bio-oil faster, more efficiently, selectively, controllably and flexibly. With the benefits it offers, microwave-assisted pyrolysis has a promising future in the production of bio-oils that can effectively reduce the energy gap and reduce the negative impact on the environment [16].

The main differences between microwave assisted pyrolysis and classical pyrolysis consist of the heating source and the different heat transfer mode from the heating source to the reaction mass. At conventional pyrolysis, electricity is transferred through conduction and convection mechanisms to the surface of the pyrolysable material, and then transferred by conduction into the material; the temperature of the process being limited by the temperature at the surface of the material, as well as by its physical properties, such as density and calorific value. On the contrary, in microwave assisted pyrolysis, heating is the effect of the interaction between the

electromagnetic waves and the dipoles inside the material; thus, the heating originates inside of the material, reaching higher temperatures, and the efficiency of the conversion of electricity is high: 80-85%. Waste vegetable oils have proved poor dielectric properties due to their non-polar nature, as well as hydrocarbons [17], therefore, they require heating through contact with microwave-adsorbing materials to complete the pyrolysis process. Thus, the radiant heat flux is used indirectly, by contacting the pyrolysis material with a heat-absorbing material (bed) which rapidly heats from the microwaves and subsequently transfers the heat to the reaction mass. The adsorbants used in microwave assisted pyrolysis of biomass mainly include SiC, activated carbon, graphite but sometimes ash, tire waste, etc.
In Fig. 2 is shown a microwave installation for vegetable oils pyrolysis [18].

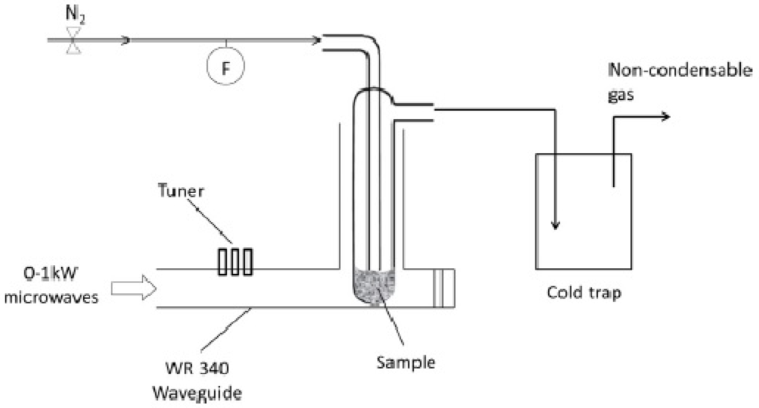


Fig. 2. Microwave installation [18].

Microwave pyrolysis in a particle layer is faster than direct heating of the raw material. Following this mechanism, a different products range is obtained, compared to the direct heating. In general, microwave-assisted pyrolysis results in higher bio-oil yields (50.18-64.74% mass) than microwave pyrolysis and direct heating (48.16- 62.91% mass) at the same temperature. reaction (400ºC-600 ºC) and more alkanes, aromatics and oxygenated compounds, but also less alkenes, cycloalkenes, cycloalkanes and alkadienes [18].

- Pyrolysis of tryglicerides in presence of steam and nitrogen

A group of researchers [1] investigated the conversion by pyrolysis of a vegetable oil from frying foods, called VEGETAMIXOIL taken from Ecogras Company (France), with the elemental composition: C = 73.6%; O = 9.7%; H = 12.2%. The reactor was a continuous one. At the end of each experiment, the amount of coke formed during the reaction was determined by air oxidation at 850 ° C. Liquid and gaseous products were analyzed by GC-MS and GC with a capillary column, while CO and CO_2 were quantified by IR infrared analyzer.
The effect of the different parameters on the pyrolysis products was investigated [1]:

- Reactor temperature. An increase in temperature leads to high conversions of the raw material and the production of small molecular species (H_2, CH_4, C_2H_4), as theory says.
- Residence time. An increase in the residence time is expected to increase in the conversion of raw materials and to have a significant effect on the chemical nature and yields of products
- Nature of the diluent. The influence of the nature of the diluent on the distribution of the products was investigated by using water or an equimolecular mixture of water and nitrogen.
- The reaction initiator. Hydrogen peroxide (H_2O_2), added in small amounts to the reaction mixture decreases the pyrolysis temperature, so conversion is expected to start at lower temperature.
- Reaction inhibitor. Thiophene (C_4H_4S) added at very low concentration to the feedstock (300 ppm) would reduce the catalytic effect of the wall which could occur at high temperatures (800 ° C) leading to a decrease in the yield of coke.

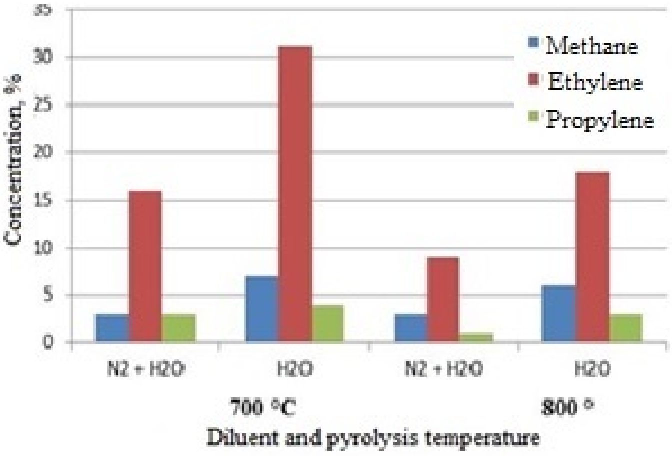


Fig. 3. Effect of temperature and nature diluent in the production of methane, ethylene and propylene during pyrolysis [1].

The high temperature of pyrolysis favors the formation of methane, ethylene and propylene (Fig.3). At 800 °, C, CO, CO_2 and H_2 are formed in higher yields than at 700 ° C, to the detriment of light hydrocarbons (methane, ethylene and propylene). Water favors the formation of light hydrocarbons at the two temperatures investigated here (700°C and 800°C), reducing the formation of CO and CO_2. H_2 formation, however, is disadvantaged by increasing the temperature from 700°C to 800°C.

It was also observed that the addition of thiophene (Fig. 4) drives the pyrolysis reaction towards the production of light hydrocarbons (especially ethylene) to the detriment of hydrogen and CO (whose production is three times lower). The addition of thiophene leads to a decrease in the yield of CO (6.3% instead of 18.8%) and CO_2 (5.4% instead of 8.1%).

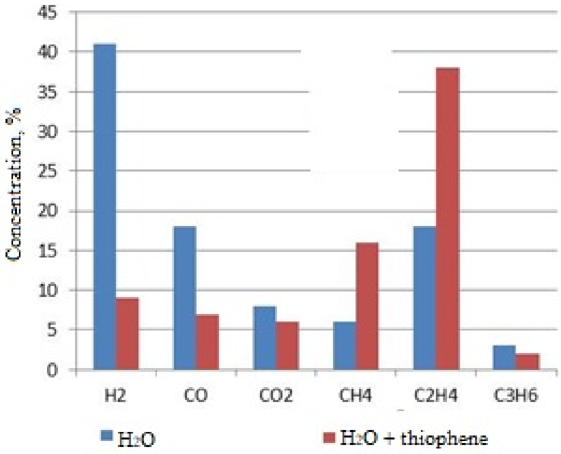


Fig. 4. Effect of inhibitor additions (thiphene) on the product concentration obtain from pyrolysis at 800°C [1].

4. Catalytic cracking of vegetable oil

The literature on catalytic cracking of vegetable oils comprises four main types of catalysts: (1) zeolites and in particular molecular sieves (2) activated alumina catalysts and other oxides, (3) transition metal catalysts, and (4) carbonate carbonate. sodium. These processes result in a fuel-like product for diesel engines, composed of linear hydrocarbons.

Activated alumina catalysts and sodium carbonate have also been shown to be efficient in the production of diesel fuels, however studies are limited and there is room for more work in this area. They have been shown to have the ability to convert fatty acids and triglycerides into almost oxygen-free liquid products. In addition, sodium carbonate as such or as an addition to other catalysts neutralizes the acidity of the products, which would otherwise be a major drawback to using bio-oil as Green Diesel. A separate type of oxide catalyst is represented by the ash obtained from the burning of solid biomass [22], which would constitute an ecological catalyst, but the results have been inferior to those obtained with other catalysts (lower liquid yield, for the time being). higher coke yield), on the other hand, the oil obtained has a very low oxygen content and a low acidity index.

The use of molecular sieves in the thermo-catalytic cracking of oils has been the natural consequence of numerous studies on alumino-silicates.

The HZSM-5 catalyst was first used in the 1970s by Weisz et al. [19] to convert vegetable oils into hydrocarbons. On this typical catalyst for the catalytic cracking of heavy oil fractions, they have succeeded in completely converting Jojoba oil to 400 °C, and castor oil to 500 °C in hydrocarbons.

The mechanism of the catalytic cracking is carboionic without excluding reactions with a radical mechanism for the non-absorbed molecules away from the catalyst.

In this regard, Katikaneni proposed [20] a hybrid mechanism (catalytic and radical) for thermo-catalytic cracking using the HZSM-5 catalyst:

(1) Canola Oil $\rightarrow$ Heavy Oxygenated C_xH_y ***(thermal)***

(2) Heavy Oxygenated $C_xH_y \rightarrow$ Heavy $C_xH_y + H_20 + CO_2 + CO$ ***(thermal and catalytic)***

(3) Heavy $C_xH_y \rightarrow$ Paraffins + Olefins (short and long chain) ***(thermal and catalytic)***

(4) Light Olefins $\rightleftarrows$ C_2-C_{10} Olefins ***(catalytic)***

(5) C_2-C_{10} Olefins $\rightleftarrows$ Aromatic C_xH_y + Aliphatic C_xH_y ***(catalytic)***
(6) Canola Oil $\rightarrow$ Coke ***(thermal)***
(7) *n*(Aromatic C_xH_y) $\rightarrow$ Coke ***(catalytic)***

In paper [21] are presented the results of a study carried out in a fluidized layer catalytic cracking plant (FCC), shown in Fig. 5, on a mixture of commercial catalysts (molecular sites) used in FCC installations for hydrocarbons. These catalysts were: CORH (which is composed mainly of Ultra-Y zeolite) and LTB-2 which was developed to maximize propylene yield in FCC industrial plants, mainly containing ZSM-5 zeolite.

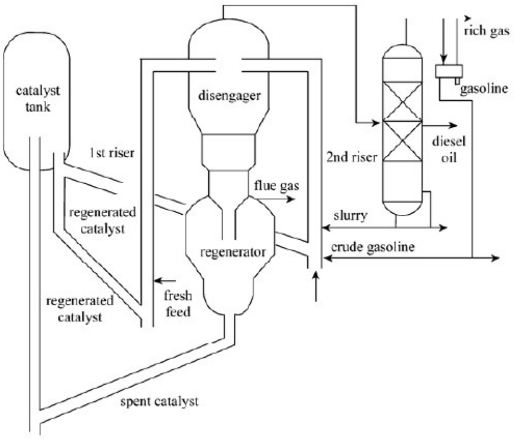
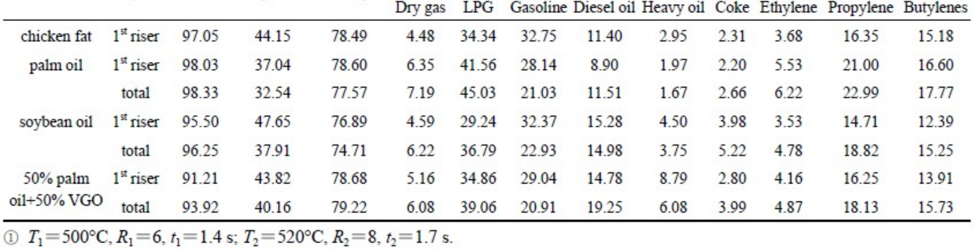


Fig. 5. Micropilot plant of FCC for pyrolysis of vegetable oils [21].

Fresh feed is injected into the riser in the first reaction step and the recirculated oil from the fractionator is injected into the second riser. The two risers share the same expansion vessel and the same regenerator. In this way, the fresh raw material and the heavy oil adsorbing on the catalyst and reacting differently, will contact the regenerated catalyst separately, ensuring the most favorable reaction conditions. Tests were made on soybean oil and palm oil, but also on animal fat and a mixture of vacuum oil distillate (50%) and palm oil (50%).

The yields of the obtained products and the experimental conditions are presented in Table 2.

Table 2. Products yields and experimental conditions at the fluid catalytic cracking of different raw materials.



Feed	Style	Conversion	Light oil	Total liquid	Product distribution						Yields of C_2–C_4 olefins		
					Dry gas	LPG	Gasoline	Diesel oil	Heavy oil	Coke	Ethylene	Propylene	Butylenes
chicken fat	1st riser	97.05	44.15	78.49	4.48	34.34	32.75	11.40	2.95	2.31	3.68	16.35	15.18
palm oil	1st riser	98.03	37.04	78.60	6.35	41.56	28.14	8.90	1.97	2.20	5.53	21.00	16.60
	total	98.33	32.54	77.57	7.19	45.03	21.03	11.51	1.67	2.66	6.22	22.99	17.77
soybean oil	1st riser	95.50	47.65	76.89	4.59	29.24	32.37	15.28	4.50	3.98	3.53	14.71	12.39
	total	96.25	37.91	74.71	6.22	36.79	22.93	14.98	3.75	5.22	4.78	18.82	15.25
50% palm oil+50% VGO	1st riser	91.21	43.82	78.68	5.16	34.86	29.04	14.78	8.79	2.80	4.16	16.25	13.91
	total	93.92	40.16	79.22	6.08	39.06	20.91	19.25	6.08	3.99	4.87	18.13	15.73

① $T_1=500°C, R_1=6, t_1=1.4$ s; $T_2=520°C, R_2=8, t_2=1.7$ s.

where, R_1 and R_2 represent the mass catalyst ratio / m.p. in the two rises, T_1 and T_2 temperatures and t_1 and t_2 reaction times.

From the analysis of the data contained in table 2, it was concluded that vegetable and animal fats can be used individually as raw materials in FCC plants, resulting in high yields of LPG and olefins. The best results were obtained from palm oil (yield LPG-45%, propylene-23%, butylene 17.8% in total gas produced, and total liquid products-77.6%). The yield of C_2-C_4 gaseous olefins is much higher (47%) than that reported by Katikaneni [20] (25.8%) in the case of catalytic cracking of canola oil in fixed layer of potassium-impregnated ZSM-5 catalyst. This is due to the two-step FCC technology that allows good selectivity for light olefins. On the other hand, fat cracking along with the conventional raw material for FCC (vacuum diesel) also leads to good LPG yields (39.1%) and light olefins (38.7%), so that vegetable and animal fats can be mixed with conventional raw materials in industrial plants.

5. Conclusions

Due to political, economic and social factors, there is a growing need to develop renewable fuels and to obtain chemicals from biomass to supplement conventional petroleum products. Currently, two processes are of importance in research about the conversion of biomass into useful products: pyrolysis of lignocellulosic biomass (to produce bio-oil) and transesterification of triglycerides (to produce olefins and pyrolitic oils). The researches in the field of pyrolysis of vegetable oil are not as numerous as the previous studies, but recent studies indicate the potential of producing liquid hydrocarbon mixtures, with possible applications as fuels or as a raw material in the chemical industry for the production of lubricants, solvents or varnishes. The disadvantages associated with both the production and the final properties of bio-oils and bio-diesel have led to further research in this field.

A less investigated aspect was the economic potential of gaseous products containing high concentrations of olefins, with high commercial value. In the literature, the terms pyrolysis, thermal cracking and catalytic cracking, regarding vegetable oils, are not always very clear. Early researchers made distinction between liquid product from solid biomass pyrolysis (called pyrolytic oil or bio-oil) and liquid product obtained from thermal or thermocatalytic decomposition of vegetable oil, which is regarded only as a mixture of hydrocarbons, and the fractions are called gasoline-like, kerosene-like, Diesel-like / Green Diesel, etc. There is no reason for the liquid product obtained from the thermal / thermocatalytic processing of vegetable oils not to be considered bio-oil, and the one obtained from the pyrolysis of the oils not to be called also pyrolytic oil. The present work started from the definition of pyrolysis of solid biomass, as a process of transformation of biomass that is thermally decomposed at high temperatures, in the absence of oxygen and considered that it applies equally well to biomass in any state of aggregation, so also to vegetable oils. The decomposition mechanism is also of radical type. Thus, the processes of decomposition of vegetable oils can be classified into thermal decomposition processes and thermocatalytic decomposition processes. The thermal decomposition at high temperature and in the absence of oxygen is called pyrolysis or thermal cracking; this can be conventional pyrolysis (which takes place for tens of minutes or even hours), rapid pyrolysis (with a reaction time of the order of seconds or minutes) and even instant pyrolysis (flash, of the order of fractions of a second). Rapid and instant pyrolysis can be achieved by means of intensifying the process (in the microwave field, in the electric arc). Thermal decomposition reactions in the presence of catalysts (thermo-catalytic processes) can be called, in short, catalytic cracking.

The results of the thermal cracking studies in literature show that the products are complex mixtures. Differences in distribution of final products appear among different studies. However, all studies show that the distribution of the products is strongly dependent on the reaction variables such as the reactor type, the residence time of the material in the reactor, the reaction temperature, as well as the collection procedure and the analytical techniques used. It is obvious that liquid mixtures with high percentages of hydrocarbons can be obtained, but in many of them oxygenated compounds are still present, such as carboxylic acids and ketones. The effect of the reaction conditions on the final distribution of the product should be studied in detail, so that the reaction can be optimized to obtain the desired product. Research is needed to optimize reaction conditions to obtain specific reaction products, to understand pyrolysis reaction mechanisms and to fully evaluate the properties of the finished product.

The use of molecular sieve catalysts (especially the HZSM-5 catalyst) is also very promising for converting vegetable oils into high aromatic gases.

In conclusion, both processes: pyrolysis or catalytic cracking of vegetable oils are worth studying for obtaining products of high commercial value: fuels or raw material for petrochemical industry.

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