Challenges associated with choosing operational conditions for triglyceride thermal cracking aiming to improve biofuel quality

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HIGHLIGHTS

▶ Thermal cracking of waste cooking oil was used to produce renewable fuels.
▶ Product distribution was influenced by temperature and residence time.
▶ Higher temperature and residence time increased the benzene content.
▶ Paraffins, isoparaffins and naphthenes remained constant under all conditions.
▶ Olefin hydrocarbons varied considerably with residence time.

ARTICLE INFO

ABSTRACT

Thermal cracking experiments were carried out to promote the conversion of waste cooking oil into a biofuel which is similar to gasoline (light-naphtha). Temperature and residence time were varied in order to analyze their effects on the light-naphtha characteristics in terms of acid value and chemical composition, (paraffins, i-paraffins, olefins, naphthenes, oxygenates and aromatics). The PIONA analysis was used to determine the composition of chemical groups in the light naphtha obtained and its benzene concentration. The results show that at higher temperatures and with longer residence times the benzene concentration increases, but the values obtained are close to the limits of the regulatory specifications of European and Brazilian laws.

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1. Introduction

Research studies on the thermal/catalytic conversion of biomass have intensified in recent years due to the possibility of obtaining high yields of liquids that can be used as fuels or chemicals. In this context, the thermal cracking process is one of the most promising techniques available to convert biomass into bio-oil [1–3]. Bio-oil can be summarized as a liquid fuel produced by the thermal/catalytic conversion of biomass [2,3]. The composition and the main characteristics of bio-oil are dependent on the biomass source and the operational conditions used in its production [4]. It is possible to divide the biomass source for fuel production into two main groups: lignocelluloses (LCs) and triglycerides (TAGs) [5–21]. The liquid fractions obtained in both cases are called bio-oil, but the products present differences in their physical properties and chemical composition.

The LC bio-oil is a dark brown viscous corrosive fuel with a high proportion of water from the original moisture and the reaction product [1,6]. Generally, it has a poor-medium heating value, and it has a complex chemical composition of oxygenated hydrocarbons such as aliphatic compounds, alcohols, aldehydes, furanoids, pyranoids, and benzenoids [1–8]. Also, the bio-oil produced from LCs is unstable and difficult to distill, with only around 50% being recovered [1,4].

On the other hand, the TAG-derived thermal cracking liquids have quite different composition and characteristics. The water content is low and the heating value is high, being similar to that of the petroleum-based fuels. The TAG bio-oil has good distillability and the liquid fuels recovered are comparable with petroleum fuels [18,20–24]. Also, it does not contain sulfur and metal contaminants [24]. The drawbacks of TAG bio-oil are the high acid value and the high concentration of olefins making it a corrosive and unstable fuel, respectively.

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Some pathways are being investigated to minimize the high acid value and the high concentration of olefins in TAG bio-oil. As examples, the use of sodium carbonate in moving bed reactors [25] and catalysts [26] provides good results in terms of reducing the acid-value; the reactive distillation using short chain alcohols is another approach to reducing the acid value through the esterification of the carboxylic acids [19,27,28]; and mild hydro-treatment processes can be applied to promote the saturation of olefins [13].

The high benzene content in TAG bio-oil, mainly produced by catalytic cracking, is another drawback due to its carcinogenic characteristics. Benzene has use restrictions and its concentration in fuels is limited by national legislation. European and Brazilian regulations, for example, limit its concentration in gasoline to 1% (v/v). The United States has relatively new regulations that lower the limit for benzene content in gasoline to 0.62% [29]. Once benzene is formed it is very difficult to remove it from the products. The hydrogenation of aromatic processes can be applied to perform the aromatic saturation, but benzene does not react easily and requires severe operational conditions and a specific catalyst.

Generally speaking, the triglycerides cracking process presents two trends: thermal cracking and catalytic cracking. The liquid fuels produced in these two processes present a significant difference in chemical composition due to the complex mechanism of TAG cracking [30].

Katikaneni et al. [31,32] investigated the influence of catalysts in the formation of aromatics in canola oil cracking. The benzene concentration varied from 0.8% to 6.6% as a function of temperature and catalyst presence and catalyst type. The authors also presented a reaction scheme for the catalytic cracking of canola oil. Idem et al. [33] performed the thermal cracking of canola oil and proposed a reaction pathway for its degradation. In both reaction schemes it is possible to note that the aromatic formation (especially of benzene) appears at the end of the reaction scheme, i.e., the longer the cracking is applied under severe conditions, the higher the possibility of benzene formation.

Idem et al. [34] analyzed the influence of the residence time and the catalyst characteristics on the liquid products of the canola oil cracking process. The results showed that the benzene concentration of the liquid products increased with temperature and residence time. Li et al. [35] compared the thermal and catalytic cracking of cotton oil and concluded that the aromatic hydrocarbon concentration increased with temperature. Wisniewski et al. [36] conducted the chemical analysis of liquid fuels from waste fish oil pyrolysis at a process temperature of 525 °C, with 17 s of residence time, and the benzene concentration obtained was 1.7% (v/v). Kubátová et al. [19] explored the reactions involved in the thermal cracking of canola and soybean oil with specific focus on the pathways of TAG cracking on changing the operational conditions. The authors detailed a new route for TAG cracking reactions.

A review of the literature reveals that many studies have been carried out on the conversion of TAG into a liquid fraction rich in hydrocarbons. These publications demonstrate that the feedstock characteristics, temperature, residence time, and presence of water and/or catalysts have a significant influence on the product composition. In relation to benzene, it is possible to conclude that catalytic cracking tends to be more favorable for the formation of aromatic compounds compared with thermal cracking.

In this context, the effect of temperature and residence time on the concentration of chemical groups in light-naphtha obtained from the thermal cracking of waste cooking oil was investigated in this study. The aim was to improve the operational conditions in order to produce biofuels from TAG with lower acid value, lower oxygenated and olefins contents, and lower benzene concentration, as a first step in producing better quality renewable fuels.

2. Material and methods

The experimental procedures employed in the characterization of the feedstock and products, as well as the flow diagram showing the steps followed to produce the light-naphtha by thermal cracking and distillation, can be seen in Fig. 1. After the thermal cracking of waste cooking oil a simple distillation apparatus was used to obtain purified products in the range of light-naphtha with a final boiling point of less than 180 °C.

The waste cooking oil was received from local restaurants and conditioned in a decanter to separate the water phase. This oil was analyzed in terms of acid value (ASTM D 974), iodine index (pr EN 14111) and FAME content. For the FAME analysis a droplet of oil was esterified with 1 mL of methanol and 1 droplet of H_2SO_4 [37]. The mixture was agitated and then left to stand for 30 min at 60 °C and 1 mL of heptane and 2 mL of NaCl (10% solution) were then added. The analysis was performed in a GC–MS CP 3800 using a CP-Sil 5 Cb capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was used as the carrier gas; the oven temperature program was 60 °C ramped at 5 °C min^{-1} to 270 °C (10 min); the injector temperature was 250 °C and injection volume 0.5 μL. The other conditions applied were transfer line 240 °C, manifold 60 °C, ion trap 170 °C and electron energy 70 eV.

The thermal cracking experiments were carried out in a continuous pilot plant described in detail in previous studies by Wiggers et al. [23,24]. A total of 33 experiments were carried out in duplicate for the operational temperatures of 475, 500 and 525 °C, with feed mass flow ranging from 0.78 to 3.65 kg h^{-1}. The residence time for each experiment is calculated through product density as a function of the average temperature of the reactor and the composition of the products, and ranged from 15 to 70.5 s.

The GC-FID analysis of light-naphtha was performed in a CP-Sil PONA capillary column (100 m × 0.25 mm i.d., 05 μm film thickness) and processed with the aid of DHA (Detailed Hydrocarbon Analysis) software. Helium (99.999%) was used as the carrier gas; the oven temperature program was 35 °C (held for 15 min) ramped at 1 °C min^{-1} to 60 °C (held for 20 min) and then ramped at 2 °C min^{-1} to 200 °C (held for 10 min). The injector temperature was 250 °C, detector temperature 280 °C and injection volume 0.3 μL.

3. Results

The chemical composition of the waste cooking oil used as the feedstock in the thermal cracking experiments is presented in Fig. 2. The fatty acids content comprised palmitic (11.79%), linoneic (50.30%), oleic (30.33%) and stearic (3.13%) acids as major chemical compounds, typically originating from soybean and corn oils used for cooking in Brazil. Almost 80% of these compounds are unsaturated fatty acids with one and two double bonds as weak points in the molecules where the thermal cracking is most favorable.

The acid index (AV) and iodine index (IV) values for the waste cooking oil were quantified as 23.8 mg KOH/g and 137.22 cgI$_2$/g, respectively. These results are in agreement with the reference values presented in the literature [38–40]. The acid index value shows that the triglyceride material was partially degraded into free fatty acids before the thermal cracking. This appears to be favorable to the process since, according to the reaction mechanisms [33], this step is one of the first steps in the thermal cracking. The iodine index value indicates total unsaturation (double and triple bonds) in the TAG, complementing the feedstock characterization. Therefore, as a preliminary conclusion, the high values of AV and IV found in the waste cooking oil make it a suitable material for the thermal cracking process.
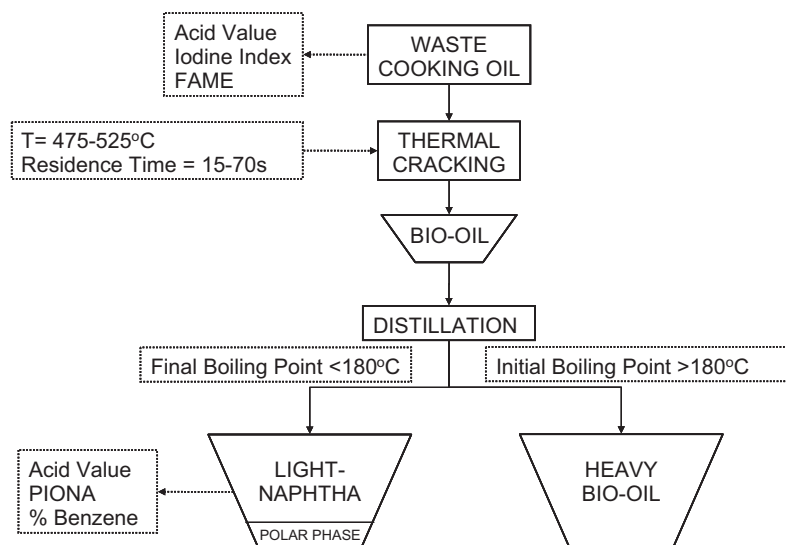
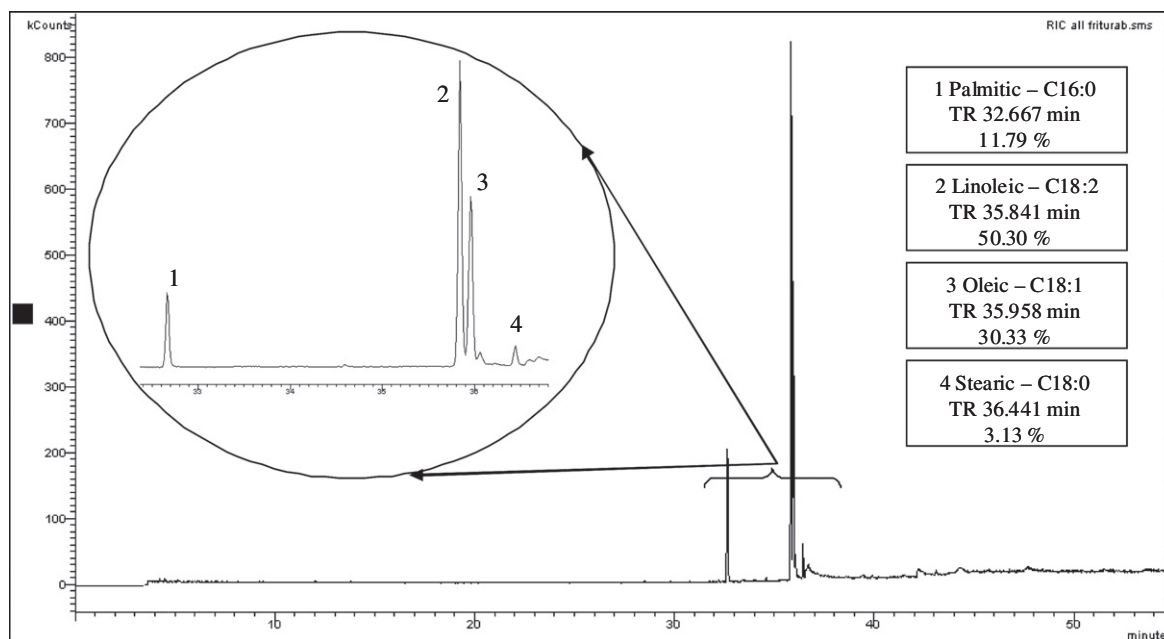Fig. 1. Light-naphtha production and characterization scheme.

Fig. 2. Chemical composition of waste cooking oil (GC–MS).

Table 1 presents the liquid yield obtained in the thermal cracking experiments and the mass balance for the simple distillation procedure. After distillation the condensate obtained before the boiling point of 180 °C was reached formed two phases and the bottom polar phase was spontaneously separated.

Tables A1, A2 and A3 in Appendix A detail the results for the hydrocarbon analysis of the light-naphtha samples obtained in the thermal cracking experiments of this study and those for a pure gasoline for comparison.

The products obtained in all experiments were yellow, clear and without impurities, with acid values ranging from 113.8 to 175.9 mgKOH g^{-1}. Minimum values can be obtained with a residence time longer than 40 s for all temperatures. Nevertheless, an increase in the temperature reduces the residence time required to close to 30 s. This effect can be attributed to the more effective cracking of large chain carboxylic acids at high temperatures, favoring decarboxylation and, consequently, deoxygenation reac-

tions. Fig. 3 presents, in detail, the dependence of the AV of the light-naphtha on the residence time for the experiments of this study.

The olefin hydrocarbons show a pronounced variation with residence time, but the values tend to be in the same range with changes in the temperature, as can be seen in Fig. 4. The olefins make fuel unstable and their concentration thus needs to be controlled. A hydro-treatment process can be applied to promote olefin saturation in order to improve the fuel stability [41].

It can be noted in Fig. 5 that the paraffin, isoparaffin and naphthene contents practically remain constant for all residence times and thermal cracking temperatures. The average values and the standard deviation are: % paraffins = 6.4699 ± 0.5561; % isoparaffins = 5.4836 ± 0.2243; and % naphthenes = 3.9093 ± 0.2689. In the TAG thermal cracking reaction scheme proposed by Idem et al. [33] these types of compounds are formed at the end of the reaction scheme through several irreversible and reversible
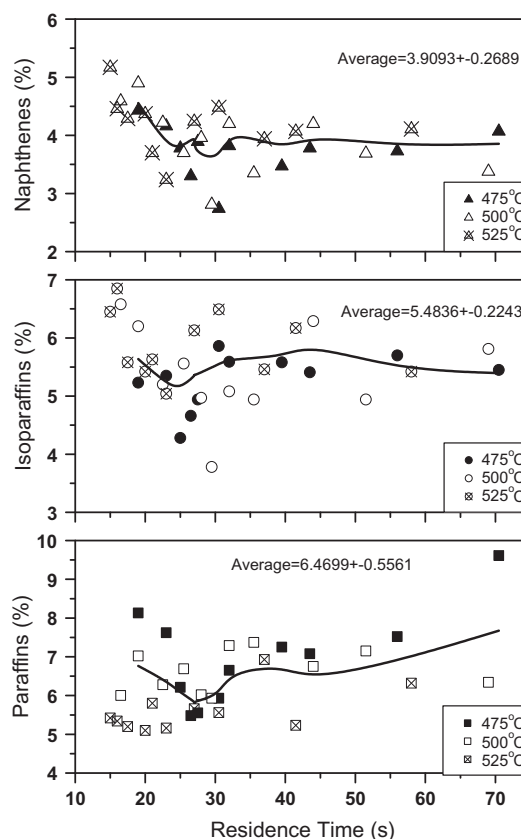
Table 1
Liquid yield of thermal cracking experiments and yields of the distillation.

Mass flow (kg/s)	Residence time (s)			Reaction yields			Distillation yields								
							FBP < 180 °C						IBP > 180 °C		
				Bio-oil (%)			Polar phase (%)			Light bio-oil (%)			Heavy bio-oil (%)		
	Thermal cracking temperature (°C)														
	475	500	525	475	500	525	475	500	525	475	500	525	475	500	525
0.78	70.5	69.0	58.0	68.6	60.2	49.5	9.8	8.2	3.0	63.7	48.5	78.4	12.0	28.9	0.0
1.08	56.0	51.5	41.5	69.3	66.4	52.1	7.5	10.3	4.1	45.9	59.5	53.1	30.7	13.3	22.2
1.31	43.5	44.0	37.0	65.0	69.5	56.5	6.0	6.0	5.0	36.0	36.2	73.9	41.5	37.3	0.0
1.61	39.5	35.5	30.5	72.7	67.7	57.8	7.3	9.3	4.9	33.6	59.4	48.9	38.1	16.1	24.2
1.88	32.0	32.0	27.0	64.7	70.3	59.8	6.8	13.2	4.7	35.4	43.8	44.1	34.3	29.4	28.4
2.14	30.5	29.5	23.0	72.0	72.9	58.4	12.6	10.0	6.9	30.2	39.2	48.5	30.5	37.4	36.7
2.45	27.5	28.0	21.0	67.9	69.7	63.4	6.5	7.5	3.4	30.0	29.0	41.7	44.6	45.4	30.9
2.62	26.5	25.5	20.0	73.8	82.1	64.7	12.2	4.4	1.2	28.3	52.5	43.2	34.8	22.3	31.0
2.86	25.0	22.5	17.5	75.2	71.0	56.1	3.7	8.5	5.2	26.4	38.1	43.3	52.4	38.8	36.0
3.21	23.0	19.0	16.0	73.5	67.3	59.7	4.8	8.4	3.2	26.3	34.9	44.5	49.3	42.5	32.2
3.65	19.0	16.5	15.0	68.2	65.6	69.4	8.1	7.0	5.1	29.3	35.2	35.2	47.2	42.0	38.9
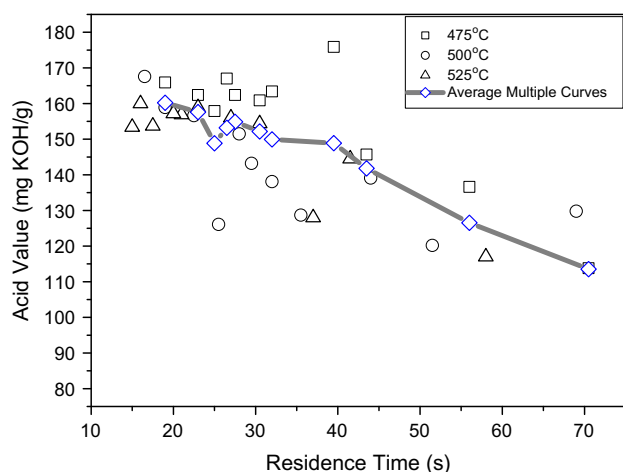
Fig. 3. Acid value versus residence time and thermal cracking temperature.
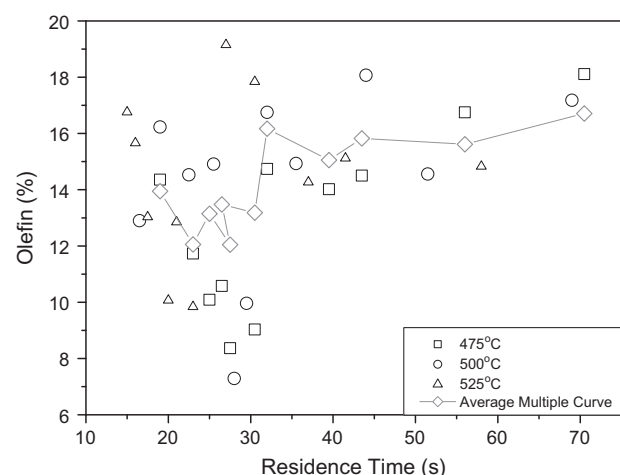
Fig. 4. Olefins content versus residence time and thermal cracking temperature.

Fig. 5. Paraffin, isoparaffin and naphthene contents versus residence time and thermal cracking temperature.

It can be seen in Fig. 6 that the aromatics content has greatest dependence on the temperature, the highest value being observed at 525 °C, but the values obtained are relatively lower than others reported in the literature [14,42,43]. The thermal cracking reactions are developed through free radicals forming preferentially saturated and unsaturated compounds, which can explain the low content of aromatics.

However, some authors have reported a very low content of aromatics (<2.5%) [15,16] or their non-detection [21] in the liquid fraction. In fact, the differences between the results obtained in the cited studies and those reported herein can be attributed to the
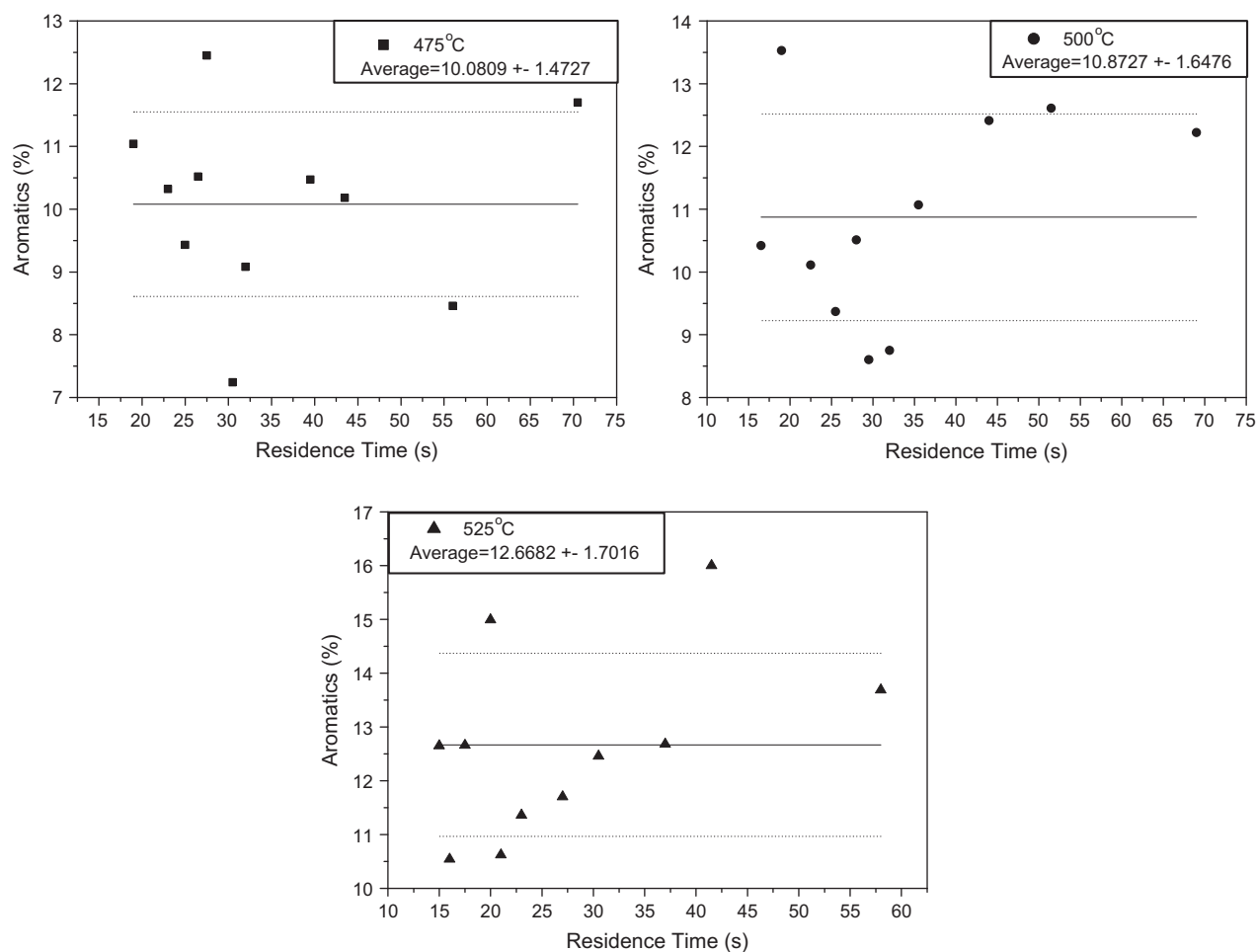
reactions in series and in parallel. Thus, the constant values obtained for these compounds suggest that the residence time and temperature employed in the experiments were sufficient to reach the maximum equilibrium concentration. In fact, these equilibrium concentrations could be modified by using catalysts.

Fig. 6. Aromatic contents as a function of the residence time and temperature.

operational conditions used, for instance, slow pyrolysis in a batch system and low temperature (350–440 °C) in the cited studies and fast pyrolysis in a continuous system and high temperature (475–525 °C) in this study. According to the thermal cracking reaction scheme [33] the aromatic formation appears at the end of the reaction and it requires a more severe cracking process which explains the results reported herein.

Fig. 7 shows the dependence of the benzene content on temperature and residence time, and two tendencies can be noted: the first is that the concentration increases with temperature, since the formation of aromatic compounds involves low-molecular olefins (ethylene and propylene) and dienes (butadiene), mainly formed at higher temperatures [33,34]; the second is that the benzene concentration is higher for longer residence times (>30 s), and at short residence times the benzene concentration varies considerably.

In relation to the oxygenated compounds, the bio-oil obtained from TAGs has lower values than from LCs. In the light-naphtha the average content of oxygenated compounds was 0.1%. There is no evidence of a correlation between the oxygenated compounds and the residence time or temperature. In fact, the characterization shows a minimal presence of oxygenated compounds.

The chemical analysis revealed a high concentration of unidentified substances for all cases, with values in the range of 40%. This is attributed to these compounds not being included in the database of the DHA software. However, based on the retention index of these compounds they must be isomers and are included in the PIONA classification.

The hydrocarbons grouped in C14+ have a tendency to decrease at higher temperatures due to the severity of the process and their presence in the light-naphtha is due to the simple distillation process applied to produce the light-naphtha.

Fig. 8 presents the GC-FID chromatograms for a light-naphtha obtained in the experiment conducted at 525 °C with 37 s of residence time compared with those for gasoline A.[1] It can be noted that the light-naphtha obtained in this study contains a wide range of chemical compounds that are present in petroleum-based fuels. The light-naphtha also contains a certain quantity of heavy compounds that are not present in gasoline A. Table 2 lists the main compounds identified by DHA analysis.

4. Conclusions

In this study, waste cooking oil was used as a triglyceride biomass source to evaluate the effects of the operational conditions of the thermal cracking process on the quality of the biofuel produced. Following the distillation of the bio-oil obtained through the thermal cracking of the waste cooking oil, a liquid fuel in the range of a light-naphtha with a high acid value was obtained. The acid value tended to decrease when longer residence times were applied.

The chemical analysis of the light bio-oil indicated a high concentration of olefins that varied considerably according to the

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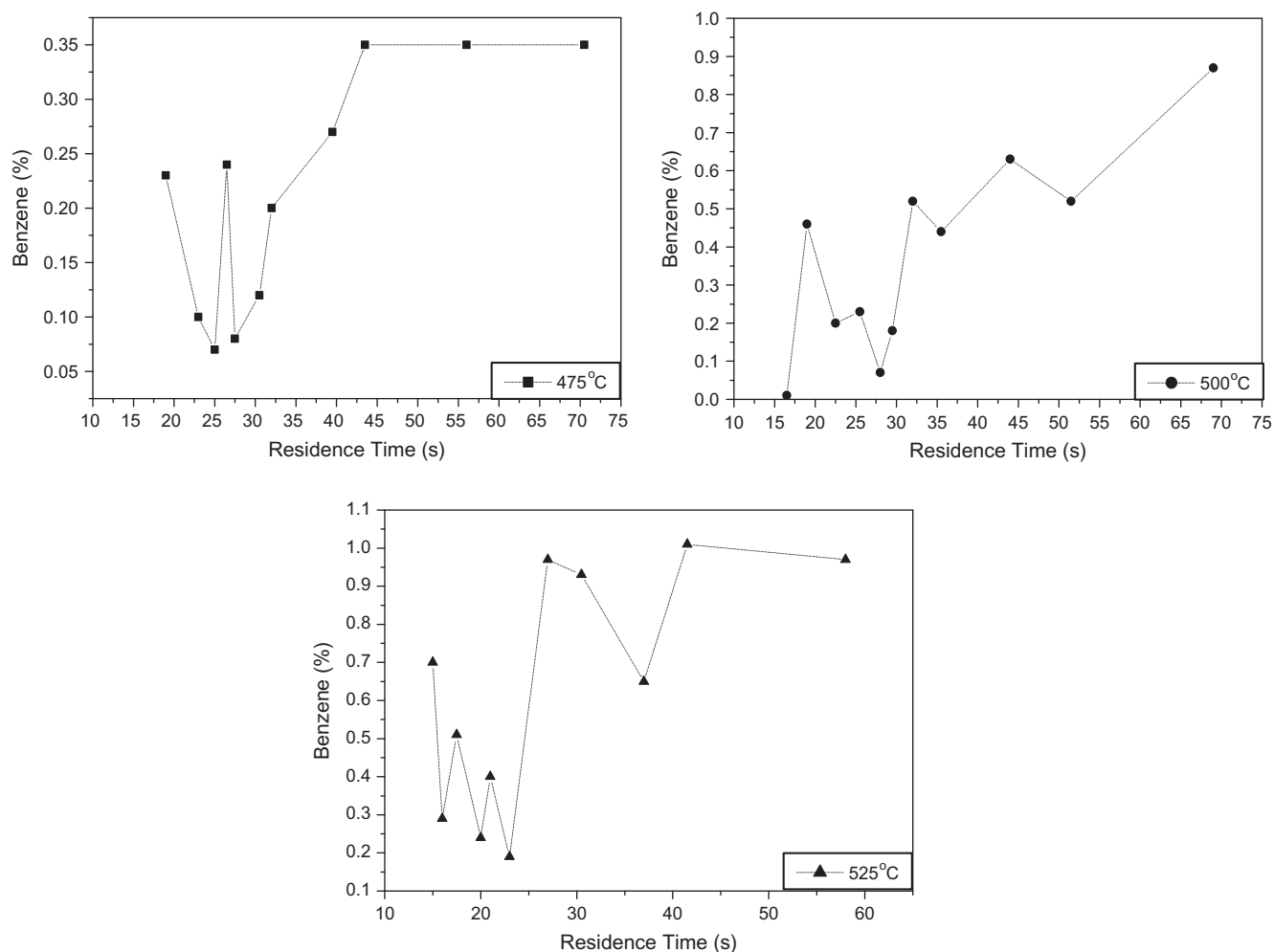[1] Gasoline A is a petroleum-based fuel without additives.

Fig. 7. Benzene content as a function of the residence time and temperature.
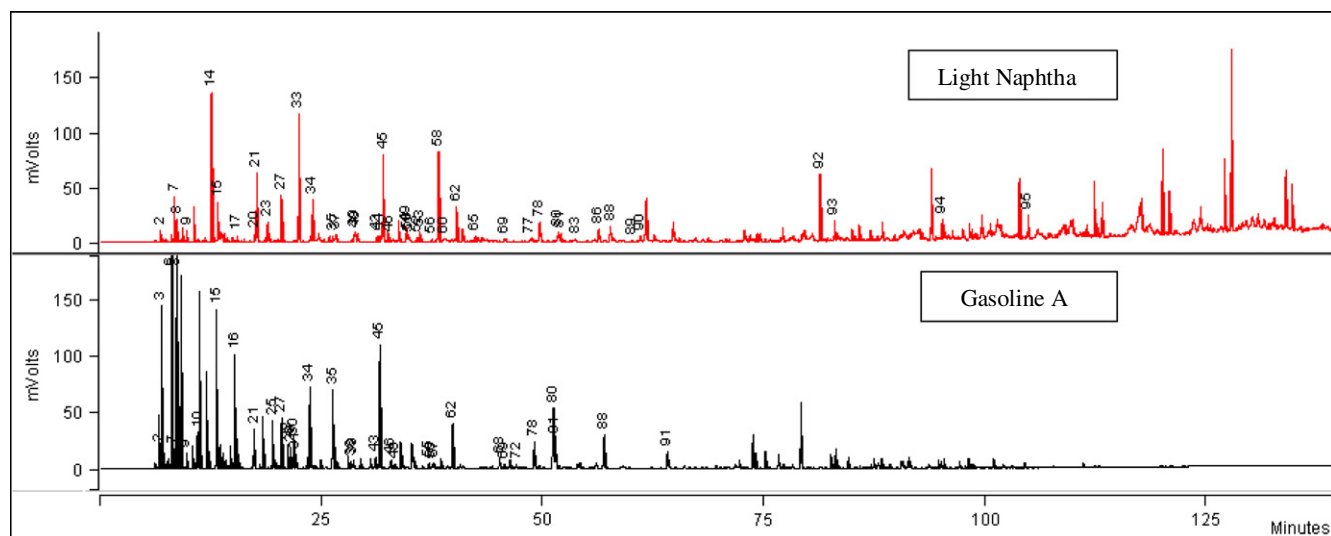

Fig. 8. GC-FID chromatogram of light-naphtha and gasoline A.

operational conditions. The content of paraffins, i-paraffins and naphthenes remained practically constant for all operational conditions. The aromatics content increased with temperature and the benzene concentration increased with both temperature and residence time, with considerable variation observed for short res-

idence times. The benzene concentration was close to the limits established by fuel regulations.

The results show that the light-naphtha obtained in this study has potential for use as a fuel, although it requires a downstream process to improve some properties such as the acid value and ole-

Table 2
Main Chemical composition of the light-naphtha and the gasoline A.

Peak	RT (min)	RI	Compound	% Relative GC-FID		% DHA	
				Gasoline	Light-naphtha	Gasoline	Light-naphtha
2	6.78	353.72	Iso-Butane	0.22	0.10	0.25	0.13
3	6.87	400.00	n-Butane	1.49	–	1.57	–
6	8.02	464.82	Iso-Pentane	5.94	–	6.25	–
7	8.36	483.26	1-Pentene	0.23	0.35	0.26	0.40
8	8.65	500.00	n-Pentane	3.97	0.19	4.14	0.22
9	9.75	525.43	2,2-Dimethylbutane	0.24	0.10	–	0.12
10	11.09		Cyclopentane	0.73	–	0.67	–
14	12.52	583.41	1-Hexene	–	1.71	–	1.85
15	13.29	600.00	n-Hexane	3.43	0.58	3.67	0.65
16	15.23	617.60	2,2-Dimethylpentane	2.87	–	2.71	–
17	15.44	619.33	Methylcyclopentane	–	0.03	–	0.08
20	17.44		1-Methylcyclopentane	–	0.07	–	0.14
21	17.65	640.17	Benzene	0.37	0.39	0.14	0.70
23	18.89	649.31	Cyclohexane	–	0.30	–	0.32
25	19.55	661.42	2,3-Dimethylpentane	1.55	–	1.57	–
27	20.45	669.62	3-Methylhexane	1.66	0.74	1.67	0.73
28	21.23	676.39	Cis-1,3-Dimethylcyclopentane	0.80	–	0.73	–
29	21.51	679.62	Trans-1,3-Dimethylcyclopentane	0.71	–	0.64	–
30	21.83	681.71	3-Ethylpentane	0.99	–	0.88	–
31	22.03	682.91	Trans 1,2-Dimethylcyclopentane	0.53	–	0.51	–
33	22.40	685.12	1-Heptene	–	2.27	–	2.36
34	23.96	700.00	n-Heptane	3.11	0.79	3.13	0.85
35	26.28	715.55	Cis-1,2-Dimethylcyclopentane	3.35	0.11	2.94	0.11
36	26.44	715.98	Methylcyclohexane	–	0.11	–	0.08
37	26.64	719.34	1,1,3-Trimethylcyclopentane	–	–	–	–
38	28.40	726.95	Ethylcyclopentane	0.33	0.15	0.33	0.21
39	28.73	729.12	2,5-Dimethylcyclohexane	0.33	0.20	0.32	0.18
43	31.27	742.52	1,2,3-Trimethylcyclopentane	0.48	0.12	0.43	0.12
44	31.49	745.60	2,3,4-Trimethylpentane	–	0.13	–	0.13
45	31.94	748.64	Toluene	5.56	1.79	4.07	1.40
46	32.74	756.41	1,1,2-Trimethylcyclopentane	0.37	0.08	0.32	0.09
48	33.30	758.16	2-Methyl-3-Ethylpentane	0.21	0.05	0.21	0.04
49	34.60	763.59	2-Methylheptane	–	0.29	–	0.31
50	34.76	765.06	4-Methylheptane	–	0.15	–	0.16
51	34.90	765.81	3,4-Dimethylhexane	–	0.13	–	0.07
53	36.11	772.44	3-Ethylhexane	–	0.25	–	0.28
55	37.10	783.42	1,3-Ethylmethylcyclopentane	0.31	–	0.27	–
56	37.45	785.72	Cis-1,3-Ethylmethylcyclopentane	0.22	–	0.19	–
57	37.80	787.02	Trans-1,2-Ethylmethylcyclopentane	0.28	–	0.24	–
58	38.17	787.25	1-Octene	–	2.15	–	2.27
62	40.24	800.00	n-Octane	2.27	0.81	2.23	0.85
65	42.37	805.20	C9 Naphthene 1	–	0.18	–	0.16
68	45.12	816.98	Cis-1,2-Dimethylcyclohexane	0.62	–	0.54	–
69	45.69	821.56	Ethylcyclohexane	0.25	0.08	0.24	0.07
72	46.99	826.17	1,1,3-Trimethylcyclohexane	0.25	–	0.25	–
77	48.57	832.21	C9 Naphthene 3	–	0.09	–	0.10
78	49.67	837.35	Ethylbenzene	1.62	0.70	1.94	0.67
80	51.75	845.75	m-Xylene	4.50	0.43	3.33	0.34
81	52.04	846.83	p-Xylene	1.72	0.25	1.27	0.20
83	53.70	853.99	4-Ethylheptane	–	0.11	–	0.09
86	56.32	864.10	3-Ethylheptane	–	0.48	–	0.48
88	57.64	868.99	o-Xylene	2.56	0.58	2.51	0.45
89	60.16	885.30	1-Nonene	–	0.08	–	0.09
91	64.27	900.00	n-Nonane	1.28	–	1.22	–
92	81.31	990.94	1-Decene	–	1.47	–	1.52
93	83.00	1000.00	n-Decane	–	0.43	–	0.43
94	95.16	1100.00	n-Undecane	–	0.39	–	0.39
95	104.87	1200.00	n-Dodecane	–	0.40	–	0.40
			Total	55.35	20.21	51.64	20.24

fins content in order to reduce the corrosiveness and improve the stability, respectively.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2012.11.011.

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