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Renewable Hydrocarbons from Triglyceride's Thermal Cracking

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Abstract

This chapter gives an overview of renewable hydrocarbon production through triglyceride's thermal-cracking process. The influence of feedstock characteristics and availability is discussed. It also presents issues about the reaction, the effect of operational conditions, and catalysts. A scheme of the reaction is presented and discussed. The composition and properties of bio-oil is presented for both thermal and catalytic cracking. The high content of olefins and the high acid index are drawbacks that require downstream processes. The reactor design, kinetics, and scale-up are opportunities for future studies. However, the similarity of bio-oil with oil turns this process attractive.

Keywords: waste fatty acids, triglyceride, pyrolysis, biofuels, green chemicals

1. Introduction

Nowadays, the search for processes that aims to reduce the use and the dependence of fossil fuels is imperative. Decrease in the emission of greenhouse gases might be a global effort. In this way, the biomass appears to be the logical choice to produce solid, liquid, and gaseous fuels, once it is abundant and available all over the world [1]. There are many technological processes applied to different kinds of biomass being studied and proposed by scientific community [2]. One thing is for sure, there will not be only one technology that will solve all the issues, but different technological routes taking into account the specific characteristics of the source region and the feedstock.

Besides the fact that these new technologies to produce biofuels must be environmentally friendly, they are facing some obstacles to overcome economic and technical viability, high scale, and stable production. Specifically on liquid biofuels, another technical barrier is the fact that almost every machine and vehicle was designed for fossil fuels usage. These fossil fuels have several regulations and quality parameters that must be attended for commercialization. In this way, it is a “sine-qua-non” condition that the new generation on liquid biofuels shall be compatible with actual standard of the engines. The modern electronic fuel injection systems make possible the use of different fuels maintaining a good combustion in the engine. However, how higher the similarity of the biofuel with fossil fuels, higher is the possibility for its commercial application. In this way, the organic liquid product produced by thermal cracking of vegetable oils and waste fats appears with high potential of oil substitute in the refineries [3].

The objective of this chapter is to provide a brief overview about the thermal conversion of triglycerides into a liquid fraction, called bio-oil, rich in hydrocarbons, presenting its properties.

2. Thermal cracking of triglycerides

The production of bio-oil through thermal cracking of biomass is easily found in literature [4–32]. The bio-oil is defined as a dark brown viscous corrosive fuel obtained from biomass pyrolysis [33], but it is very important to highlight that the bio-oil has different properties according to the feedstock. If it is produced from lignocellulosic materials, the bio-oil has significant amount of water and oxygen content, decreasing its gross calorific value and its stability [34, 35]. On the other hand, if the feedstock is triglycerides, the oxygen and water content is low and the high heating value is comparable to the fossil fuels [6, 36]. Another important characteristic is the similar chemical composition, based on hydrocarbons [37]. So, based on these issues, the bio-oil produced from triglycerides appears like one of the most promising technologies for biofuels production [38].

2.1. Feedstock

The triacylglycerol, also known as triglyceride (TAG) is an ester derived from glycerol and three fatty acids [38]. It can be found in edible and nonedible vegetable oils, animal fats, and used oils. The most abundant vegetable oils are soybean, palm, canola, sunflower, rapeseed, among others. From animals, the main sources are pork lard, poultry fat, fish oil, and beef tallow [39]. Waste greases or tap greases are found in cooking oils and sewage scum [40].

In general, they have similar physical properties and chemical structure. They differ in the composition of the fatty acids, in the acidity and content of saturated fatty acids [39]. The acidity of the oil is evaluated through the acid index determination (ASTM D974) which gives the free fatty acids (FFAs) content in the oil. Waste oils are classified in yellow and brown greases according to the content of FFA. Oils with lower than 15% (w/w) are classified as yellow greases, while if it has more than 15% it is brown greases.

The iodine index (pr EN 14111) provides the number of double bonds in the fatty acids. Oils with high content of unsaturated acids are liquid in ambient conditions; however, oils with high content of saturated acids are solid or semisolid in the same conditions.

The fatty acid composition is provided by the fatty acid methyl ester (FAME) determination [41]. It is a chromatographic analysis, which is a well-accepted method for its determination. The fatty acids composition of various TAGs can be found in the literature [34, 41, 42].

One fact that must be pondered over, when one talks about biofuels production using TAGs, is the feedstock availability [42]. In this way, we have two subjects to consider: the use of edible oils and the logistic to join the wasted ones.

In the first case, we need to consider the food versus fuels issues. The main concern is based on the assumption that biofuel feedstocks tend to be more profitable than food feedstocks, which may lead to food shortages. Thus, it must be carefully pondered in order to efficiently attend both markets [43].

In the second case, it is possible to consider the waste-cooking oils, the animal fats, and the sewage scum. From cooking oils, its generation varies to each country, as it depends on the vegetable oil consumption. The estimated generation in the European Union (EU) is about 700,000–1,000,000 tons/year [44]. Only the UK generates an amount of approximately 250,000 tons per year [45]. Canada produces around 135,000 tons of yellow grease every year [46]. Mexico's generation is about 840,000 tons every year, similar to Malaysia. Japan produces around 450,000–570,000 tons/year [47]. Hong Kong generates approximately 20,000 tons/year [48]. The USA's generation is about 1,000,000 tons/year [47]. Even so, it is estimated that the general worldwide generation is around 4.1 kg per habitant per year [49].

Animal fats availability is also related to the region. It is well known that China, the USA, and Brazil are large producers of meat. Only in 2013, the US industry processed 180,000 tons of meat and poultry [50]. The fish industry also plays an important role. In 2014, the world fish production was about 146 million tons of fish [51]. As the amount of oil ranges from 40 to 65% [52], it represents around 70.8 million tons of waste fish oil.

Thus, these numbers show that it is possible to use biofuels production as a final destination to these wastes. It is important to highlight the complex logistic to use it and that these amounts will not replace the oil, but they can be a viable alternative.

2.2. Process and reaction

The thermal-cracking reaction is defined as thermal decomposition of the organic chains by heat in an atmosphere free of oxygen, with or without the aid of a catalyst. **Figure 1** presents a basic scheme of the triglycerides thermal-cracking process. As one can see in the scheme, the reaction will generate always a solid fraction, generally called coke, a liquid product named as bio-oil, and a gaseous stream known as biogas.

This reaction is affected by the feedstock characteristics and the pair temperature-residence time [34]. The higher the temperature and the residence time, the higher the yield of the gas product. Lower temperatures and higher residence times improve the coke formation.

Moderate temperatures with short residence times yield the liquid product. This last operational condition is called fast pyrolysis [5]. The fast pyrolysis process is gaining attention due to the possibility to obtain high amounts of bio-oil, which can be used as fuel. **Figure 1** shows that independent of the operational conditions, the solid fraction called coke will appear, and this product will not be easily removed from the reactor. In general, this product formation is associated with clogging [53]. One possibility to remove it is to proceed a controlled burning in the heated reactor through feeding air instead of biomass, for a certain period of time, promoting the combustion of the coke.

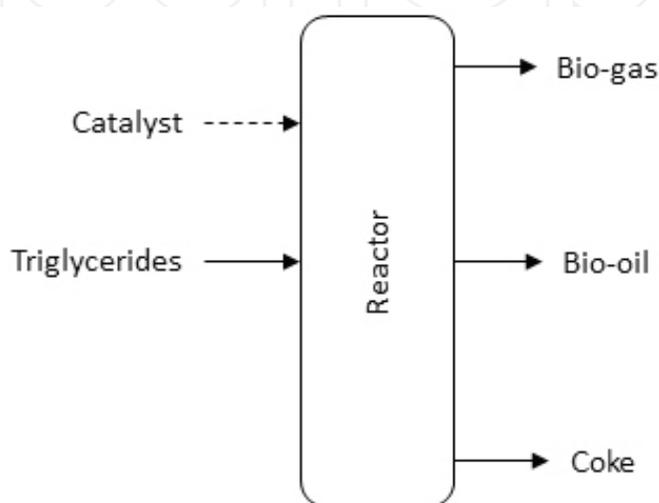


Figure 1. A general scheme of thermal-cracking process.

The reactor design is the heart of the process [54]. Different configurations have been proposed in the literature for several researches. It is possible to find batch [9, 10, 12, 16, 21, 22, 24, 31, 32] and continuous configurations [4–8, 11, 13, 17–20, 23, 25–27, 55]. In general, the batch reactors are used to evaluate the reaction mechanism, kinetics, yields, and chemical characterization. As it works with lower capacities, they are not appropriated for industrial applications. The continuous ones are in a higher sizes, bench or pilot, testing different reactor designs and operational conditions, evaluating the kinetics, yields, characterization, energy consumption, and economic evaluation, aiming the scale-up studies [26].

The irreversible reaction is highly endothermic and requires high heat transfer rates. The possibility to run the process in an autothermal operation promotes an advantage over other processes. This condition can be reached burning a fraction of the products to produce the thermal energy required for the reaction. An energy balance of the TAGs thermal cracking was presented by [5].

Due to the complexity of the organic reactions, there is no complete knowledge about all the reactions involved, just proposals for the principal ones. A simplified reaction step for the thermal cracking of triglycerides is presented in **Figure 2**. The reaction starts with the decomposition of the triglyceride molecule forming heavy oxygenated hydrocarbons. Some of the saturated fatty acids formed may not suffer any subsequent breaking. The decarboxylation

and decarbonylation reactions (2) are favored by unsaturations and compete with the C-C bond cleavage reaction (3). The CO and CO₂ are formed by the deoxygenation reactions in (2) and (4). The isomerization, polymerization, dehydrogenation, and cyclization are responsible for dienes, acetylenes, cycloparaffins, and polyolefins (5). The Diels-Alder addition of dienes to olefins also produce cyclo-olefins (8) resulting in hydrogen formation. The hydrogenation of cyclo-olefins to cycloparaffins and the reverse reaction occurs in steps (6) and (7). Hydrogen also comes from steps (9) and (10). The solid product coke is produced directly from triglyceride (12), by the polycondensation of heavy hydrocarbons and saturated fatty acids (11) and aromatics (10). The polymerization of olefins can also lead to coke (13). Considering the reaction scheme in **Figure 2**, it is very important to advance the cracking at least to the point which deoxygenation reaction occurs, eliminating the oxygen by CO and CO₂. It is also important avoid coke formation (steps 10 and 13 in the **Figure 2**). As a first conclusion, for thermal cracking, the temperature-residence time is the key factor for this process.

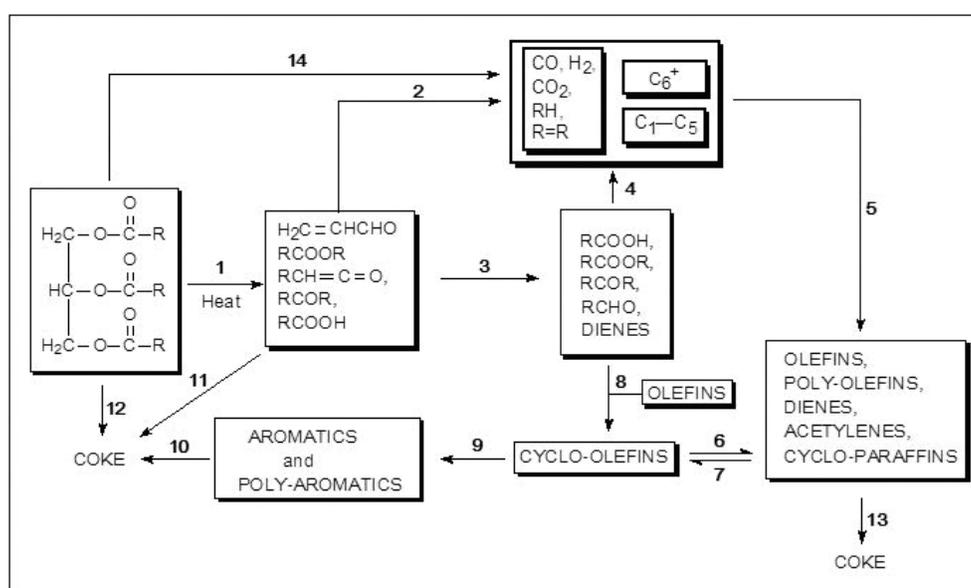


Figure 2. Proposed reaction scheme for the thermal cracking of vegetable oil and animal fats (triglyceride). Adapted from [13, 26, 38, 56]. (1) Initial cracking, thermolysis of triglyceride molecule ester bond; (2) decarboxylation/decarbonylation of long-chain oxygenated hydrocarbons; (3) C-C bond cleavage of unsaturated oxygenated hydrocarbons; (4) decarboxylation/decarbonylation of short-chain oxygenated hydrocarbons; (5) isomerization, polymerization/dehydrogenation, cyclization to form dienes, acetylenes, cycloparaffins, and polyolefins; (6) dehydrogenations of cycloparaffins to form cyclo-olefins; (7) hydrogenations of cyclo-olefins to form cycloparaffins; (8) Diels-Alder addition of dienes to olefins to form cyclo-olefins; (9) aromatization of cyclo-olefins to form aromatics and polyaromatics hydrocarbons; (10) Coking from polyaromatics; (11) coking by polycondensation of oxygenated hydrocarbons; (12) coking by polycondensation of triglyceride molecule; (13) polymerization of olefins to form coke; (14) direct route for C1-C5 hydrocarbon formation from triglyceride molecule.

The use of catalysts aims to aid the reaction and increases the products' quality [57]. As the composition of the products may vary due to catalyst material, size, and shape [58], several works evaluate the use of many types of catalysts. **Table 1** shows the different catalysts used for the cracking of triglycerides. One of the concerns involving catalysts use relies on their stability and reutilization, which directly affect the cost of the process [31]. In general, the coke

formation limits the use of heterogeneous catalysts, due to the deactivation, and this phenomenon requires a regeneration process for its reuse, making the entire process for the conversion complex. A scheme reaction for catalytic cracking was proposed by [59].

Catalyst	Reference
Fe-ZSM-5, H-Beta	[9]
H-ZSM-5	[8, 9, 17, 32, 55]
K ₂ CO ₃	[11, 17, 18, 31, 32]
Na ₂ CO ₃	[11, 17, 18, 21, 23, 31, 32]
NaY	[17, 31]
USY	[17]
Si-MCM-41	[17, 31, 32]
Alumina	[20]
ZSM-5, Ni/ZSM-5, Ni/h-ZSM-5 (12)	[8]
Al ₂ O ₃ , MCM-41	[11, 15]
SAPO-5, SAPO-11, MgAPO-36	[7]
Silicalite, silica, γ-alumina, silica-alumina	[55]
Calcium oxide, magnesium oxide	[55]
CaO	[15, 18]
NaOH, Fe ₂ O ₃	[18]
KOH	[18, 22]
ZnO	[18, 22]
CO ₃ O ₄ , MoO ₃ , NiO, V ₂ O ₅	[22]
Metallic oxides	[25]
Zeolite REY	[27]
K ₂ O/Si-MCM-41, Mg-MCM-41	[31]
K ₂ O/Mg-MCM-41	[31, 32]
Ba-MCM-41	[32]

Table 1. Main catalysts used.

2.3. Yields, properties and characterization

The yields of the products are strongly affected by the operational conditions. **Table 2** shows the range of temperature and residence time applied in published papers, presenting the average product yields obtained in thermal [4–6, 9, 10, 13–15, 17, 18, 22, 24, 26, 31, 55] and catalytic cracking [7, 9, 11, 15, 17, 18, 20, 21–23, 25, 27, 31, 55]. In thermal-cracking processes, the temperature range is higher than catalytic. One can also note that the yield of liquid and

gas products tends to be a little higher in thermal cracking. On the other hand, the coke formation is more favorable in the catalytic cracking.

Triglyceride's cracking		
Temperature range (°C)		
	Thermal	Catalytic
Max	600	550
Min	300	320
Residence time (s)		
	Thermal	Catalytic
Max	1800	1800
Min	1	10
Yields average (%)		
Liquid	63.20 ± 16.45	56.67 ± 20.55
Gas	28.77 ± 21.06	26.19 ± 15.68
Coke	8.22 ± 7.27	15.39 ± 13.01

Table 2. Average products yielding obtained with thermal and catalytic cracking of triglycerides.

The liquid fuels have fundamental importance in final energy consumption, especially due to its energy density. So, in this way, most of the researches are being conducted in the way to maximize the organic liquid product. No less important are the properties and the characterization of this product. **Table 3** presents average properties of the bio-oil presented in the literature for thermal [4, 5, 9, 10, 12–15, 18, 19, 22, 24, 31, 55] and catalytic cracking [7–9, 11, 15, 17, 18, 20–22, 55]. The elementary chemical composition for bio-oil does not vary so much and the sulfur content is low. The high heating value (HHV) is also comparable to the fossil fuels. The acidity of the bio-oil is higher for the thermal cracking compared to catalytic, but in both cases, the bio-oil requires a reduction in this property for processing and usage. The esterification reaction and reactive distillation were performed by [11] and [60] to reduce the acid index.

The content of olefins in the liquid can also be problematic, once its content is associated with poor stability, which may lead to gum or insoluble materials formation. To saturate the double bonds, the hydrorefining process can be applied [61]. The direct hydrocracking also can be an option [62–64].

Figure 3 presents typical chromatograms from two samples of bio-oil produced through fast pyrolysis of soybean oil and waste-cooking oil. For comparison, the chromatograms of an n-alkane sample and an oil sample are shown together. The samples were injected at the same conditions. The oil and bio-oil samples are complex mixtures containing hundreds of compounds and this turns difficult to determine the complete composition and physico-chemical properties.

Properties of bio-oil		
	Thermal	Catalytic
Variable		
Carbon (%)	75.15 ± 4.43	79.96 ± 5.58
Hydrogen (%)	11.46 ± 0.68	12.20 ± 0.85
Nitrogen (%)	0.29 ± 0.59	1.83 ± 0.50
Sulfur (%)	0.02 ± 0.03	0.24 ± 0.20
Oxygen (%)	13.07 ± 5.34	9.78 ± 4.96
Ash (%)	0.51 ± 0.70	0.02 ± 0.02
HHV (MJ/kg)	33.38 ± 15.34	40.75 ± 2.38
Density (kg/m ³)	865.98 ± 22.87	858.25 ± 22.69
Water content (%)	1.39 ± 1.00	2.29 ± 1.48
Acid index (mg KOH/g)	132.08 ± 35.56	59.46 ± 26.74
Iodine index (chI ₂ /g)	64.00	-
Hydrocarbon groups		
Aliphatic (%)	3.70 ± 0.88	10.87 ± 6.46
Aromatic (%)	38.99 ± 15.41	36.73 ± 18.16
Oxygenated (%)	4.83 ± 0.74	14.86 ± 8.49
Unknown (%)	50.72 ± 14.96	29.54 ± 17.81

Table 3. Average properties of bio-oil.

One way of characterizing these liquid fuels is the distillation curve, used to plot the true boiling point (TBP) versus distilled volume fraction. In general, a simple distillation is performed according to ASTM D86 and ASTM D1160 methods and data obtained are converted to TBP according to correlations outlined in [65]. Process simulators also can be used for this conversion and to predict the thermophysical properties of the oil and its fractions [66]. The bio-oil characterization using distillation curves applying the oil correlations was presented by [34]. The authors showed that it is possible to use this method, but it requires more studies to confirm the results.

A chemical characterization was performed by [37] in the distilled fractions of the bio-oil produced by [4]. The purified products, light bio-oil and heavy bio-oil, were obtained in the range of the gasoline and diesel oil, respectively. The detailed hydrocarbon analysis (DHA) performed in light fraction showed that it was composed by aromatics (16.86%), i-paraffins (8.31%), naphthenes (6.07%), olefins (26.56%), paraffins (4.48%), C14+ (5.3%), oxygenates (0.06%), and unclassified (32.38%). The main composition of heavy bio-oil was formed by olefins, aromatics, and carboxylic acid residues. In a continuation of the study [60], samples of the bio-oil were submitted to a reactive distillation process to produce light and heavy bio-oil cuts, with lower acid index.

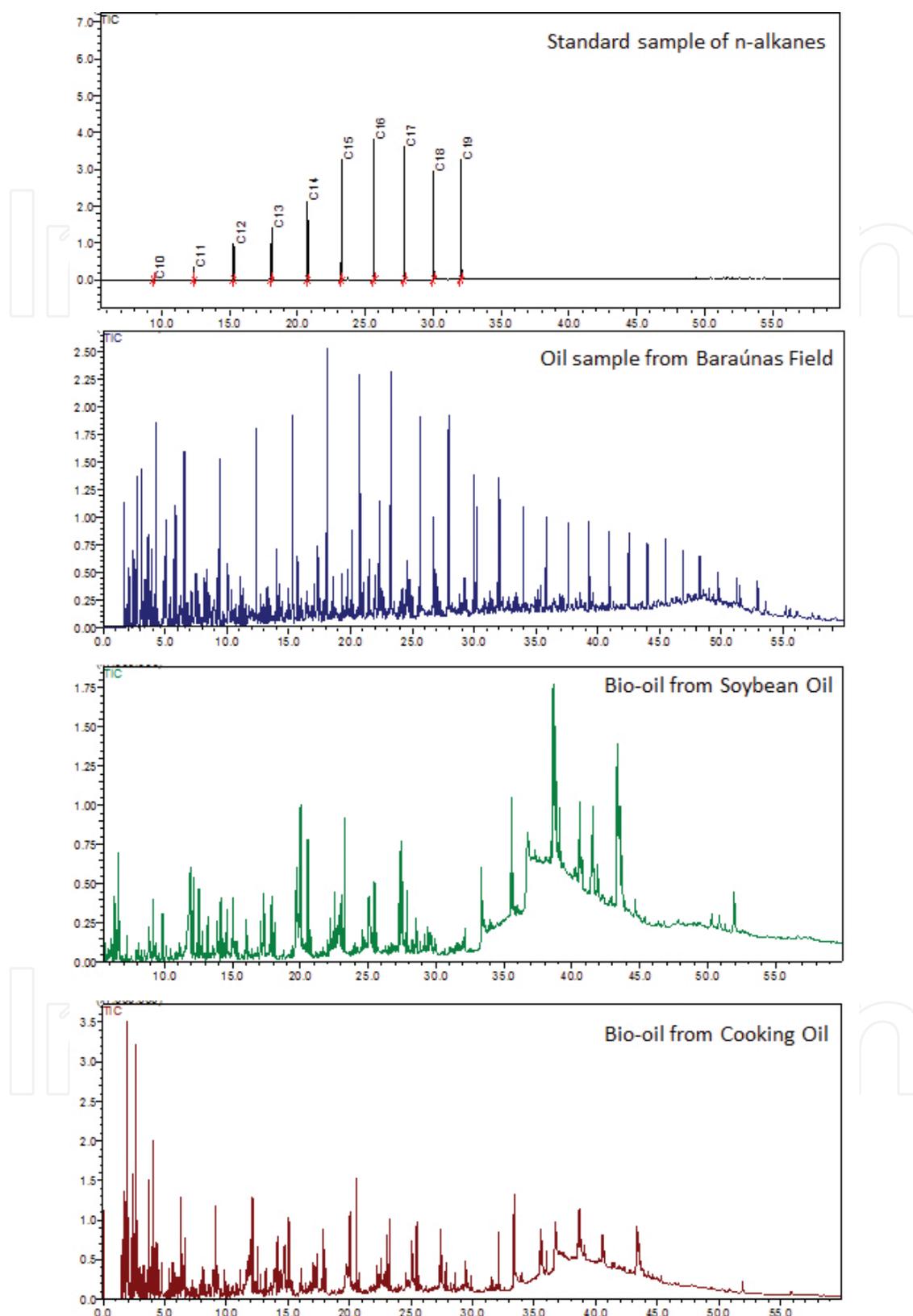


Figure 3. GC-FID chromatogram of n-alkanes sample, an oil sample, bio-oil from soybean oil, and a bio-oil from waste-cooking oil.

The gaseous products have great importance as liquids, once it has short hydrocarbons and a high HHV and it can be fuel source for the thermal energy required by the endothermic reaction. **Table 4** presents the average composition of biogas from thermal [5, 10, 13, 55] and catalytic cracking [7, 8, 17, 23, 55]. Using this average composition, the HHV is estimated in 46.6 MJ/kg (thermal cracking) and 46.3 MJ/kg (catalytic cracking). The high content of ethene also makes this product interesting for petrochemical industries.

Biogas (v/v %)		
Component	Thermal	Catalytic
CO	4.47 ± 3.58	6.02 ± 8.15
CO ₂	4.15 ± 2.74	4.42 ± 7.61
H ₂	1.88 ± 1.24	3.88 ± 5.68
CH ₄	13.40 ± 5.34	6.31 ± 4.61
C ₂ H ₄	29.32 ± 3.12	12.69 ± 10.19
C ₂ H ₆	9.64 ± 1.02	4.89 ± 2.91
C ₃ H ₈	2.82 ± 2.53	6.89 ± 7.52
C ₄ H ₁₀	10.16 ± 1.73	5.99 ± 11.55

Table 4. Average composition of the biogas produced from thermal and catalytic cracking.

2.4. Kinetics

One of the technical difficulties to scale up the process is the determination of the reaction kinetics. Once the process has hundreds, maybe thousands of reactions, it is very difficult to determine an accurate kinetic mechanism. In these cases, the first step is to use the lumping method to propose simplified mechanisms. The lumping strategy consists in join groups of products according to some similar property, the boiling range, for example. The works of [67–69] presented the first kinetic lumped models for TAG's thermal cracking. **Table 5** shows the kinetic models proposed in the literature. The model proposed by [67] is simpler than the other models once it has fewer lumps, but it can predict the solid fraction. The study of the kinetic of cracking of TAGs is increasing and soon more models shall appear.

2.5. Challenges

The continuous availability of the feedstock is an issue that requires a complex logistic to solve the high-scale collection. In certain regions, staying close to animal-rendering facilities can be an option [70].

The industrial application of the thermal/catalytic-cracking technology has some obstacles to overcome [71]. The first is related to reactor design and scale-up. With the improvement of the kinetics, the simulation using computational fluid dynamics shall help to deal with this issue. A short work presented by [72] deals with the simulation of TAG's thermal-cracking reactor aiming scale-up studies.

The products upgrading is required also, especially to deal with the acid index and olefins content. The acidity reductions, mainly caused by carboxylic acids, using the esterification reaction and neutralization, are opportunities for this issue. The reduction of alkenes content can be done through hydrotreatment reactions, widely used in oil refineries. The use of actual sites for oil refining can be suitable for this biofuel production, once most of polishing processes are present.

3. Conclusions

The thermal and/or catalytic-cracking processes are a promising technique to produce renewable source for hydrocarbon production. The product similarity with fossil fuels turns its usage and development attractive. However, some obstacles such as feedstock availability, reactor design, scale-up, and products upgrading require more studies. The thermal/catalytic cracking of triglycerides will not completely substitute the oil, but it can reduce our dependence and be a suitable environmental option.

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References

- [1] Herbert G.M.J., Krishnan A.U. Quantifying environmental performance of biomass energy. *Renewable and Sustainable Energy Reviews*. 2016;59:292–308. DOI: 10.1016/j.rser.2015.12.254.

- [2] Sharma A., Pareek V., Zhang D. Biomass pyrolysis – A review of modelling, process parameters and catalytic studies. *Renewable and Sustainable Energy Reviews*. 2015;50:1081–1096. DOI: 10.1016/j.rser.2015.04.193.
- [3] Hua T., Chunyi L., Chaohe Y., Honghong S. Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins. *Chinese Journal of Chemical Engineering*. 2008;16(3):394–400. DOI: 10.1016/S1004-9541(08)60095-6.
- [4] Wiggers V.R., Wisniewski Jr A., Madureira L.A.S., Barros A.A.C., Meier, H.F. Biofuels from waste fish oil pyrolysis: Continuous production in a pilot plant. *Fuel*. 2009;88:2135–2141. DOI: 10.1016/j.fuel.2009.02.006.
- [5] Wiggers V.R., Meier H.F., Wisniewski Jr A., Barros A.A.C., Wolf Maciel M.R. Biofuels from continuous fast pyrolysis of soybean oil: A pilot plant study. *Bioresource Technology*. 2009;100:6570–6577. DOI: 10.1016/j.biortech.2009.07.059.
- [6] Wiggers V.R., Zonta G.R., França A.P., Scharf D.R., Simionatto E.L., Ender L., Meier H.F. Challenges associated with choosing operational conditions for triglyceride thermal cracking aiming to improve biofuel quality. *Fuel*. 2013;107:601–608. DOI: 10.1016/j.fuel.2012.11.011.
- [7] Katikaneni S.P.R., Adjaye J.D., Bakhshi N.N. Performance of aluminophosphate molecular sieve catalysts for the production of hydrocarbons from wood-derived and vegetable oils. *Energy and Fuels*. 1995;9:1065–1078.
- [8] Botas J.A., Serrano D.P., García A., Ramos R. Catalytic conversion of rapeseed oil for the production of raw chemicals, fuels and carbon nanotubes over Ni-modified nanocrystalline and hierarchical ZSM-5. *Applied Catalysis B: Environmental*. 2014;145:205–215. DOI: 10.1016/j.apcatb.2012.12.023.
- [9] Giannakopoulou K., Lukas M., Vasiliev A., Brunner C., Schnitzer H. Low pressure catalytic co-conversion of biogenic waste (rapeseed cake) and vegetable oil. *Bioresource Technology*. 2010;101:3209–3219. DOI: 10.1016/j.biortech.2009.12.032.
- [10] Biswas S., Mohanty P., Sharma D.K. Studies on co-cracking of Jatropha oil with bagasse to obtain liquid, gaseous product and char. *Renewable Energy*. 2014;63:308–316. DOI: 10.1016/j.renene.2013.09.045.
- [11] Junming X., Jianchun J., Yanju L., Jie C. Liquid hydrocarbon fuels obtained by the pyrolysis of soybean oils. *Bioresource Technology*. 2009;100:4867–4870. DOI: 10.1016/j.biortech.2009.04.055.
- [12] Lima D.G., Soares V.C.D., Ribeiro E.B., Carvalho D.A., Cardoso E.C.V., Rassi F.C., et al. Diesel-like fuel obtained by pyrolysis of vegetable oils. *Journal of Analytical and Applied Pyrolysis*. 2004;71:987–996. DOI: 10.1016/j.jaap.2003.12.008.
- [13] Idem R.O., Katikaneni S.P.R., Bakhshi N.N.. Thermal cracking of canola oil: reaction products in the presence and absence of steam. *Energy & Fuels*. 1996;10:1150–1162.

- [14] Iha O.K., Alves F.C.S.C., Suarez P.A.Z., Silva C.R.P. Potential application of *Terminalia catappa* L. and *Carapa guianensis* oils for biofuel production: Physical-chemical properties of neat vegetable oils, their methyl-esters and bio-oils (hydrocarbons). *Industrial Crops and Products*. 2014;52:95–98. DOI: 10.1016/j.indcrop.2013.10.001.
- [15] Junming X., Jianchun J., Jie C., Yunjuan S. Biofuel production from catalytic cracking of woody oils. *Bioresource Technology*. 2010a;101:5586–5591. DOI: 10.1016/j.biortech.2010.01.148.
- [16] Junming X., Jianchun J., Yunjuan S., Jie C. Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst. *Bioresource Technology*. 2010b; 101:9803–9806. DOI: 10.1016/j.biortech.2010.06.147.
- [17] Li L., Quan K, Xu J., Liu F., Liu S., Yu S., et al. Liquid hydrocarbon fuels from catalytic cracking of rubber seed oil using USY as catalyst. *Fuel*. 2014;123:189–193. DOI: 10.1016/j.fuel.2014.01.049.
- [18] Junming X., Guomin X., Yonghong Z., Jianchun J. Production of biofuels from high-acid-value waste oils. *Energy Fuels*. 2011;25:4638–4642. DOI: 10.1021/ef2006723.
- [19] Ben Hassen-Trabelsi A., Kraiem T., Naoui S., Belayouni H. Pyrolysis of waste animal fats in a fixed-bed reactor: Production. *Waste Management*. 2014;34:210–218. DOI: 10.1016/j.wasman.2013.09.019.
- [20] Boocock D.G.B., Konar S.K., Mackay A., Cheung P.T.C., Liu J. Fuels and chemicals from sewage sludge 2. The production of alkanes and alkenes by the pyrolysis of triglycerides over activated alumina. *Fuel*. 1992;71:1291–1297. DOI: 0016-2361/92/111291-07.
- [21] da Mota S.A.P., Mancio A.A., Lhamas D.E.L., de Abreu D.H., da Silva M.S., dos Santos W.G. Production of green diesel by thermal catalytic cracking of crude palm oil (*Elaeis guineensis* Jacq) in a pilot plant. *Journal of Analytical and Applied Pyrolysis*. 2014;110:1–11. DOI: 10.1016/j.jaap.2014.06.011.
- [22] Yigezu Z.D., Muthukumar K. Catalytic cracking of vegetable oil with metal oxides for biofuel. *Energy Conversion and Management*. 2014;84:326–333. DOI: 10.1016/j.enconman.2014.03.084.
- [23] Junming X., Jianchun J., Zhang T., Weidi D. Biofuels production from catalytic cracking of triglyceride materials followed by esterification reaction in a scale-up reactor. *Energy & Fuels*. Forthcoming. DOI: 10.1021/ef3018173
- [24] Biswas S., Sharma D.K. Studies on cracking of *Jatropha* oil. *Journal of Analytical and Applied Pyrolysis*. 2013;99:122–129. DOI: 10.1016/j.jaap.2012.10.013.
- [25] Botton V., Riva D., Simionatto E.L., Wiggers V.R., Ender L., Meier H.F., et al. THERMO-CATALYTIC CRACKING OF THE MIXTURE OF USED FRYING OIL - TEXTILE STAMPING SLUDGE FOR THE PRODUCTION OF OIL WITH LOW ACIDITY INDEX. *Quimica Nova*. 2012;35(4):677–682.

- [26] Shirazi Y., Viamajala S., Varanasi S. High-yield production of fuel- and oleochemical-precursors from triacylglycerols in a novel continuous-flow pyrolysis reactor. *Applied Energy*. 2016;179:755–764. DOI: 10.1016/j.apenergy.2016.07.025.
- [27] Tamunaidu P., Bhatia S. Catalytic cracking of palm oil for the production of biofuels: Optimization studies. *Bioresource Technology*. 2007;98:3593–3601. DOI: 10.1016/j.biortech.2006.11.02.
- [28] Junming X., Jianchun J., Jiaping Z. Thermochemical conversion of triglycerides for production of drop-in liquid fuels. *Renewable and Sustainable Energy Reviews*. 2016;58:331–340. DOI: 10.1016/j.rser.2015.12.315.
- [29] Hilten R., Speir R., Kastner J., Das K.C. Production of aromatic green gasoline additives via catalytic pyrolysis of acidulated peanut oil soap stock. *Bioresource Technology*. 2011;102:8288–8294. DOI: 10.1016/j.biortech.2011.06.049.
- [30] Chen G., Zhang X., Ma W., Yan B., Li Y. Co-pyrolysis of corn-cob and waste cooking oil in a fixed bed reactor with HY upgrading process. In: *Energy Procedia*, editor. The 6th International Conference on Applied Energy – ICAE2014, Taipei City, Taiwan; Elsevier Ltd; 2014. p. 2363–2366. DOI: 10.1016/j.egypro.2014.12.005.
- [31] Lu L., Kejing Q., Junming X., Fusheng L., Shiwei L., Shitao Y., Congxia X., Xiaoping G. Preparation of basic mesoporous molecular sieves K₂O/Mg-MCM-41 and its catalytic performance on the cracking of soybean oils. *Journal of Analytical and Applied Pyrolysis*. 2014;110:313–317. DOI: 10.1016/j.jaap.2014.09.019.
- [32] Lu L., Kejing Q., Junming X., Fusheng L., Shiwei L., Shitao Y., et al. Mesoporous molecular sieves K₂O/Ba(Ca or Mg)-MCM-41 with base sites as heterogeneous catalysts for the production of liquid hydrocarbon fuel from catalytic cracking of rubber seed oil. *Green Chemistry*. 2013;15(9):2573–2578. DOI: 10.1039/C3GC40796A.
- [33] Bridgwater A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*. 2012;38:68–94. DOI: 10.1016/j.biombioe.2011.01.048.
- [34] Stedile T., Ender L., Meier H.F., Simionatto E.L., Wiggers V.R. Comparison between physical properties and chemical composition of bio-oils derived from lignocellulose and triglyceride sources. *Renewable and Sustainable Energy Reviews*. 2015;50:92–108. DOI: 10.1016/j.rser.2015.04.080.
- [35] Xiu S., Shahbazi A. Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews*. 2012;16:4406–4414. DOI: 10.1016/j.rser.2012.04.028.
- [36] DeOliveira E., Quirino R.L., Suarez P.A.Z., Prado A.G.S. Heats of combustion of biofuels obtained by pyrolysis and by transesterification and of biofuel/diesel blends. *Thermochimica Acta*. 2006;450:87–90. DOI: 10.1016/j.tca.2006.08.005.
- [37] Wisniewski Jr A., Wiggers V.R., Simionatto E.L., Meier H.F., Barros A.A.C., Madureira L.A.S. Biofuels from waste fish oil pyrolysis: Chemical composition. *Fuel*. 2010;89:563–568. DOI: 10.1016/j.fuel.2009.07.017.

- [38] Maher K.D., Bressler D.C. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*. 2007;98:2351–2368. DOI: 10.1016/j.biortech.2006.10.025.
- [39] Bankovic-Ilic I.B., Stojkovic I.J., Stamenkovic O.S., Veljkovic V.B., Hung Y. Waste animal fats as feedstocks for biodiesel production. *Renewable and Sustainable Energy Reviews*. 2014;32:238–254. DOI: 10.1016/j.rser.2014.01.038.
- [40] Manara P., Zabaniotou A. Towards sewage sludge based biofuels via thermochemical conversion – A review. *Renewable and Sustainable Energy Reviews*. 2012;16:2566–2582. DOI: 10.1016/j.rser.2012.01.074.
- [41] Ramos M.J., Fernández C.M., Casas A., Rodríguez L., Pérez A. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*. 2009;100:261–268. DOI: 10.1016/j.biortech.2008.06.039.
- [42] Adewale P., Dumont M.J., Ngadi M. Recent trends of biodiesel production from animal fat wastes and associated production techniques. *Renewable and Sustainable Energy Reviews*. 2015;45:574–588. DOI: 10.1016/j.rser.2015.02.039.
- [43] Hassan S.N., Sani Y.M., Abdul Aziz A.R., Sulaiman N.M.N., Daud W.M.A.W. Biogasoline: An out-of-the-box solution to the food-for-fuel and land-use competitions. *Energy Conversion and Management*. 2015;89:349–367. DOI: 10.1016/j.enconman.2014.09.050.
- [44] Supple B., Holward-Hildige R., Gonzalez-Gomez E., Leahy J.J. The effect of steam treating waste cooking oil on the yield of methyl ester. *Journal of the American Oil Chemists' Society*. 2002;79(2):175–178.
- [45] UKSBA. Written evidence submitted to the Environmental Audit Committee [Internet]. August 23, 2011. Available from: <http://www.publications.parliament.uk/pa/cm201012/cmselect/cmenvaud/1025/1025vw08.htm> [Accessed: August 1, 2011].
- [46] Kulkarni M.G., Dalai A.K. Waste cooking oils an economical source for biodiesel: A review. *Industrial & Engineering Chemistry Research*. 2006;45:2901–2913.
- [47] Sheinbaum-Pardo C., Calderon-Irazoque A., Ramírez-Suarez M. Potential of biodiesel from waste cooking oil in Mexico. *Biomass and Bioenergy*. 2013;56:230–238. DOI: 10.1016/j.biombioe.2013.05.008.
- [48] Karmee S.K., Patria R.D., Lin C.S.K. Techno-economic evaluation of biodiesel production from waste cooking oil – a case study of Hong Kong. *International Journal of Molecular Sciences*. 2015;16:4362–4371. DOI: 10.3390/ijms16034362.
- [49] Maddikeri G.L., Gogate P.R., Pandit A.B. Improved synthesis of sophorolipids from waste cooking oil using fed batch approach in the presence of ultrasound. *Chemical Engineering Journal*. 2015;263:479–487.

- [50] North American Meat Institute (NAMI). The United States Meat Industry at a Glance [Internet]. Available from: <https://www.meatinstitute.org/index.php?ht=d/sp/i/47465/pid/47465> [Accessed: August 10, 2016].
- [51] FAO. The State of World Fisheries and Aquaculture 2016. [Internet]. Available from: <http://www.fao.org/3/a-i5555e.pdf> [Accessed: August 8, 2016].
- [52] Arruda L.F., Borghesi R., Oetterer M. Use fish waste as silage – A review. *Brazilian Archives of Biology and Technology*. 2007;50(5):879–876.
- [53] Yang Y., Brammer J.G., Ouadi M., Samanya J., Hornung A., Xu H.M., et al. Characterisation of waste derived intermediate pyrolysis oils for use as diesel. *Fuel*. 2013;103:247–257. DOI: 10.1016/j.fuel.2012.07.014.
- [54] Bridgwater A.V. Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*. 2003;91(2–3):87–102. DOI: 10.1016/S1385-8947(02)00142-0.
- [55] Idem R.O., Katikaneni S.P.R., Bakhshi N.N. Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution. *Fuel Processing Technology*. 1997;51:101–125.
- [56] Kubátová A., Luo Y., Štavová Y., Sadrameli S.M., Aulich T. New path in the thermal cracking of triacylglycerols (canola and soybean oil). *Fuel*. 2011;90:2598–2608. DOI: 10.1016/j.fuel.2011.04.022.
- [57] Fréty R., da Rocha M.G.C., Brandão S.T., Padilha J.F., Borges L.E.P., Gonzalez W.A. Cracking and hydrocracking of triglycerides for renewable liquid fuels: Alternative processes to transesterification. *Journal of the Brazilian Chemical Society*. 2011;22(7): 1206–1220. DOI: 10.1590/S0103-50532011000700003.
- [58] Doronin V.P., Potapenko O.V., Lipin P.V., Sorokina T.P. Catalytic cracking of vegetable oils and vacuum gas oil. *Fuel*. 2013;106:757–765. DOI: 10.1016/j.fuel.2012.11.027.
- [59] Katikaneni S.P.R., Adjaye J.D., Bakhsh N.N. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *The Canadian Journal Of Chemical Engineering*. 1995;73:484–497.
- [60] Wisniewski Jr A., Wosniak L., Scharf D.R., Wiggers V.R., Meier H.F., Simionatto E.L. Upgrade of biofuels obtained from waste fish oil pyrolysis by reactive distillation. *Journal of the Brazilian Chemical Society*. 2015;26(2):224–232. DOI: 10.5935/0103-5053.20140251.
- [61] Pstrowska K., Walendziewski J., Stolarski M. Hydrorefining of oil from rapeseed cake pyrolysis over NiMo/Al₂O₃ catalyst. *Fuel Processing Technology*. 2014;128:191–198. DOI: 10.1016/j.fuproc.2014.07.035.
- [62] Zandonai C.H., Yassue-Cordeiro P.H., Castellã-Pergher S.B. Production of petroleum-like synthetic fuel by hydrocracking of crude soybean oil over ZSM5 zeolite – Improve-

- ment of catalyst lifetime by ion exchange. *Fuel*. 2016;172:228–237. DOI: 10.1016/j.fuel.2015.12.059.
- [63] Ishihara A., Fukui N., Nasu H., Hashimoto T. Hydrocracking of soybean oil using zeolite – alumina composite supported NiMo catalysts. *Fuel*. 2014;134:611–617. DOI: 10.1016/j.fuel.2014.06.004.
- [64] Hanafi S.A., Elmelawy M.S., Shalaby N.H., El-Syed H.A., Eshaq G., Mostafa M.S. Hydrocracking of waste chicken fat as a cost effective feedstock for renewable fuel production: A kinetic study. *Egyptian Journal of Petroleum*. 2015. Article in press. DOI: 10.1016/j.ejpe.2015.11.006.
- [65] API – American Petroleum Institute. *Technical Data Book – Petroleum Refining*. Washington, DC: American Petroleum Institute; 1993.
- [66] Fahim M.A., Al-Sahhaf T.A., Elkilani A.S. *Fundamentals of Petroleum Refining*. 1st ed. Elsevier B.V. Amsterdam, The Netherlands; 2010. 516 p.
- [67] Frainer B.L.M., Wiggers V.R., Sharf D.R., Meier H.F., Ender L., Simionatto E.L. Thermal cracking of frying oil: A proposal for a kinetic mechanism based on groups of compounds. In: American Institute of Chemical Engineers, editor. 2014 Annual Meeting, November 20, 2014; Atlanta, GA: American Institute of Chemical Engineers; 2014.
- [68] Meier H.F., Wiggers V.R., Zonta G.R., Scharf D.R., Simionatto E.L., Ender L. A kinetic model form thermal cracking of waste cooking oil based on chemical lumps. *Fuel*. 2015;144:50–59. DOI: 10.1016/j.fuel.2014.12.020.
- [69] Periyasamy B. Reaction pathway analysis in thermal cracking of waste cooking oil to hydrocarbons based on monomolecular lumped kinetics. *Fuel*. 2015;158:479–487. DOI: 10.1016/j.fuel.2015.05.066.
- [70] Baladincz P., Hancsók J. Fuel from waste animal fats. *Chemical Engineering Journal*. 2015;282:152–160. DOI: 10.1016/j.cej.2015.04.003.
- [71] Butlera E., Devlina G., Meierb D., McDonnella K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews*. 2011;15(8):4171–4186. DOI: 10.1016/j.rser.2011.07.035.
- [72] Jacomel C.R.R., Bastos J.C.S.C., Ender L., Wiggers V.R., Meier H.F., Noriler D. Numerical simulation of a thermal cracking continuous reactor. In: American Institute of Chemical Engineers, editor. 2015 Annual Meeting, November 9, 2015; Salt Lake City, UT: American Institute of Chemical Engineers; 2015.