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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.

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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.
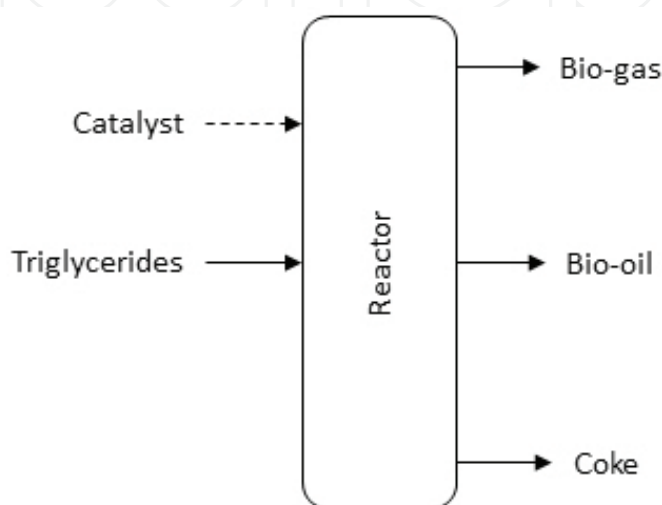

Figure 1. A general scheme of thermal-cracking process.

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 CO_2 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.
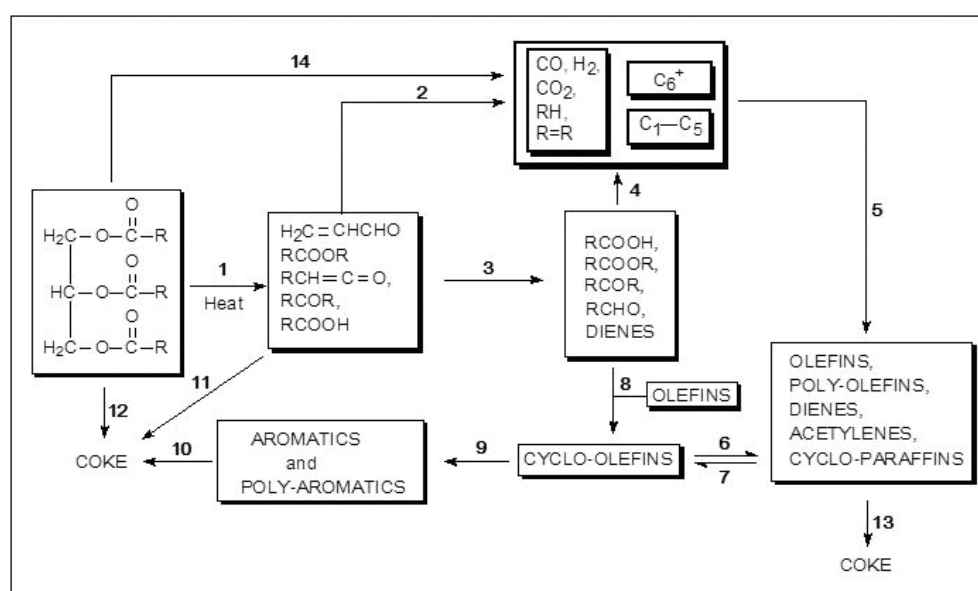
Figure 2. Proposed reaction scheme for the thermal cracking of vegetable oil and animal fats (triglyceride). Adapted from [13, 26, 38, 56]. (1) Initial cracking, thermolysis of triglyceride molecule ester bond; (2) decarboxylation/decarbon-ylation of long-chain oxygenated hydrocarbons; (3) C-C bond cleavage 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 polyconden-sation 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

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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_2CO_3	[11, 17, 18, 31, 32]
Na_2CO_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_2O_3, MCM-41	[11, 15]
SAPO-5, SAPO-11, MgAPO-36	[7]
Silicalite, silica, y-alumina, silica-alumina	[55]
Calcium oxide, magnesium oxide	[55]
CaO	[15, 18]
NaOH, Fe_2O_3	[18]
KOH	[18, 22]
ZnO	[18, 22]
CO_3O_4, MoO_3, NiO, V_2O_5	[22]
Metallic oxides	[25]
Zeolite REY	[27]
K_2O/Si-MCM-41, Mg-MCM-41	[31]
K_2O/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 physicochemical 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.
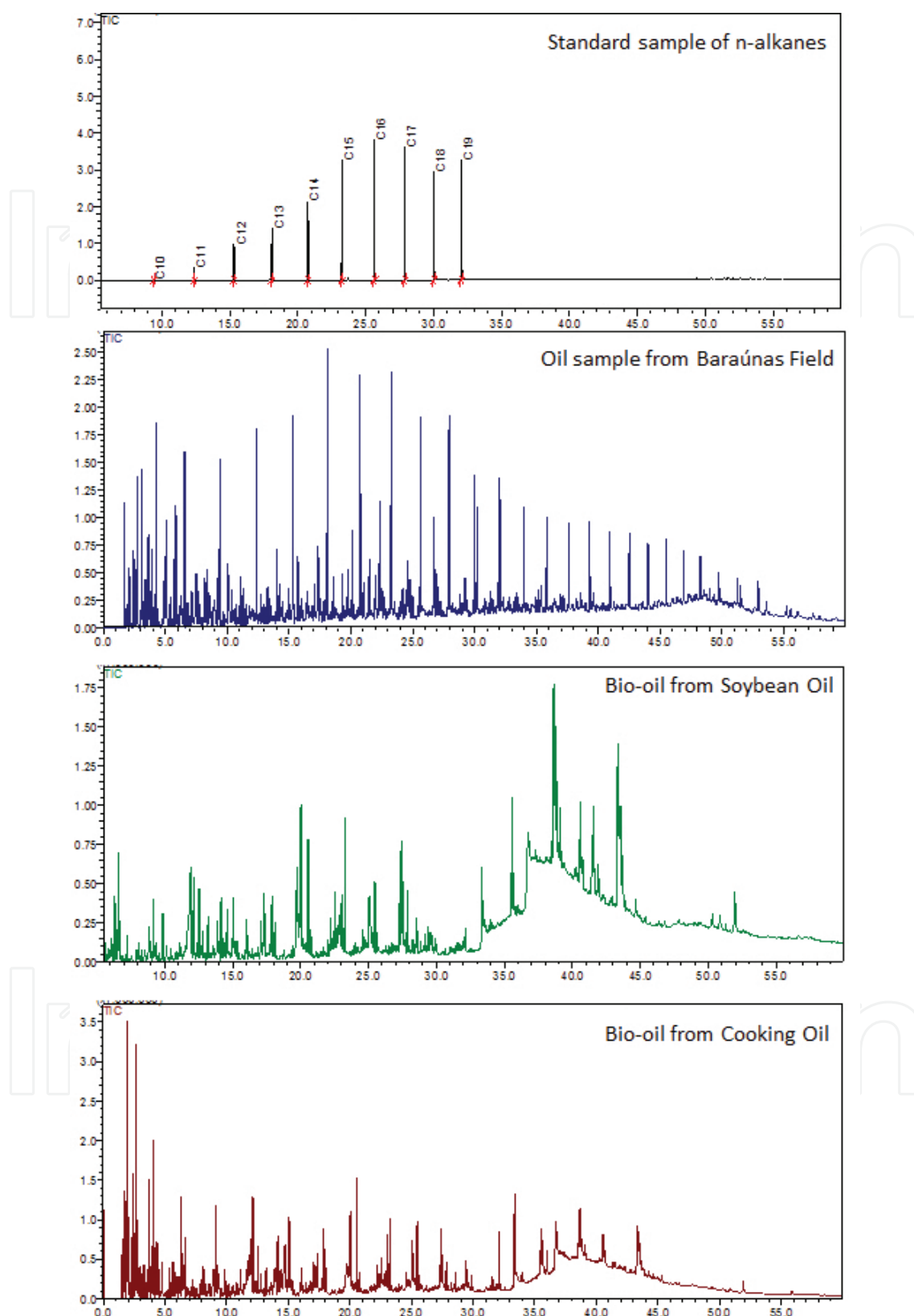
Figure 3. GC-FID chromatogram of n-alkanes sample, an oil sample, bio-oil from soybean oil, and a bio-oil from waste-cooking oil.

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_2H_4	29.32 ± 3.12	12.69 ± 10.19
C_2H_6	9.64 ± 1.02	4.89 ± 2.91
C_3H_8	2.82 ± 2.53	6.89 ± 7.52
C_4H_{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.

Kinetic-lumped models

Mechanism	Constant rate (min^{-1})	500°C	525°C	550°C	Activation energy (J/mol)	Frequency factor (min^{-1})		Reference
WCO $\xrightarrow{k_1}$ L $\xrightarrow{k_2}$ G $\xrightarrow{k_3}$ C	k_1	1.900E-02	2.810E-02	6.880E-02	5.84E+04	k_{10}	2.20E+04	[67]
	k_2	1.900E-02	2.810E-02	5.880E-02	5.14E +04	k_{20}	4.14E+03	
	k_3	9.070E-03	7.150E-03	3.380E-03	4.47E+04	k_{30}	4.73E+06	
WCO $\xrightarrow{k_1}$ L $\xrightarrow{k_2}$ G ; L $\xrightarrow{k_3}$ C	k_1	1.780E-02	3.680E-02	4.740E-02	4.51E+04	k_{10}	9.79E+02	[67]
	k_2	5.670E-03	5.970E-03	7.810E-03	1.45E+04	k_{20}	5.62E+00	
	k_3	1.730E-03	2.740E-03	3.050E-03	2.62E+04	k_{30}	1.01E+00	

Mechanism	Constant rate (s^{-1})	475°C	500°C	525°C	Activation energy (J/mol)	Frequency factor (s^{-1})		Reference
WCO $\xrightarrow{k_1}$ HBO $\xrightarrow{k_2}$ LBO $\xrightarrow{k_3}$ BG ; WCO $\xrightarrow{k_4}$ LBO	k_1	2.681E-02	2.783E-02	4.441E-02	4.96E+04	k_{10}	7.27E+01	[68]
	k_2	1.410E-02	1.426E-02	1.513E-02	6.97E+03	k_{20}	4.29E-02	
	k_3	9.580E-03	4.400E-03	1.037E-02	6.17E+03	k_{30}	1.98E-02	
	k_4	2.697E-02	3.906E-02	8.035E-02	1.08E+05	k_{40}	8.76E+05	
WCO $\xrightarrow{k_1}$ HBO $\xrightarrow{k_2}$ LBO $\xrightarrow{k_3}$ BG ; k_5 (WCO→BG), k_6 (HBO→BG), k_4 (WCO→LBO)	k_1	1.831E-02	3.342E-02	5.874E-02	1.16E+05	k_{10}	2.20E+06	[69]
	k_2	4.425E-03	8.504E-03	1.569E-03	1.26E+05	k_{20}	2.63E+06	
	k_3	1.058E-03	2.175E-03	4.274E-03	1.38E+05	k_{30}	5.05E+06	
	k_4	2.418E-02	4.374E-02	7.624E-02	1.14E+05	k_{40}	2.20E+06	
	k_5	2.473E-03	4.816E-03	8.994E-03	1.28E+05	k_{50}	2.20E+06	
	k_6	1.952E-03	3.852E-03	7.285E-03	1.31E+05	k_{60}	2.63E+06	

Table 5. Kinetic-lumped models.

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.

Acknowledgements

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