



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

V.R. Wiggers^{a,*}, G.R. Zonta^a, A.P. França^b, D.R. Scharf^b, E.L. Simionatto^b, L. Ender^a, H.F. Meier^a

^a Chemical Engineering Department, Regional University of Blumenau (FURB), SC, Brazil

^b Chemistry Department, Regional University of Blumenau (FURB), SC, Brazil

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.

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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.

* Corresponding author. Tel.: +55 47 3221 6049.

E-mail address: vrwiggers@gmail.com (V.R. Wiggers).

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 H₂SO₄ [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., 0.5 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%), linoleic (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 cgI₂/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.

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