



## Full Length Article

## Effect of degree of triglyceride unsaturation on aromatics content in bio-oil

R.F. Beims<sup>a</sup>, V. Botton<sup>a</sup>, L. Ender<sup>a</sup>, D.R. Scharf<sup>b</sup>, E.L. Simionatto<sup>b</sup>, H.F. Meier<sup>a</sup>, V.R. Wiggers<sup>a,\*</sup><sup>a</sup> Chemical Engineering Department, University of Blumenau, Blumenau SC, Brazil<sup>b</sup> Chemistry Department, University of Blumenau, Blumenau SC, Brazil

## ARTICLE INFO

## Keywords:

Bio-oil  
Thermal cracking  
Triglycerides  
Degree of unsaturation  
Aromatic compounds

## ABSTRACT

In this study, the influence of the degree of unsaturation of the triglyceride on the composition of the products of the thermal cracking process, in particular the formation of aromatic compounds, was investigated. Experiments were performed using triglyceride sources with different degrees of unsaturation, maintaining the same operational conditions. Analysis of the products revealed that a greater amount of aromatic compounds is formed during the thermal cracking of biomass with a higher degree of unsaturation. The aromatics content in the liquid product decreased by 14% in the cracking of biomass with the lowest unsaturated content. A correlation between the aromatics content and the iodine index of the sample was proposed, as a simple way to estimate the aromatics content in bio-oil. It was also observed that the reactions for carboxyl removal were favorable in the case of saturated compounds, the acidity index reducing from 210.9 to 139.0 gKOH/g in the biomass with the lowest unsaturated content. However, long-chain paraffinic compounds were present in the products, which suggests that a catalyst or more severe conditions might be necessary for the biomass cracking.

## 1. Introduction

The increasing demand for energy in recent decades has led to the search for alternative energy sources. Moreover, several concerns regarding petroleum usage, e.g., crude oil shortages and greenhouse gas emissions, have increased the interest in renewable energy sources [1]. In this context, fuels and chemicals produced from biomass thermal conversion are a promising option [2,3].

Thermal cracking, also called pyrolysis, is one of the main processes used to convert biomass into liquid fuels. It consists of the thermal degradation of biomass at a given temperature, in the absence of oxygen, with or without catalysts [4]. The use of catalysts is aimed at improving the reaction and product quality [5], which can vary according to the catalyst composition and format [6,7]. The products obtained are bio-oil (liquid fraction), bio-gas (non-condensable fraction) and coke (solid, co-product). The composition of the products is highly dependent on the operational conditions, especially the temperature-residence time combination. A high temperature with a long residence time will promote the formation of gas products while a low temperature and long residence time will promote the formation of coke. Lastly, a moderate temperature with a short residence time will give higher yields of the liquid product [8,9].

Bio-oil is a dark brown viscous fuel, comprised by aliphatic and olefinic hydrocarbons, aromatics, several types of organic compounds (e.g. acids, ketones, aldehydes, and esters), nitrogen, water and solid

particles [4]. In terms of the presence aliphatic hydrocarbon, bio-oil resembles crude oil, however, the olefinic and oxygenated compounds reduce the possibilities for the application of bio-oil as a fuel source. Notably, bio-oil compositions can vary according to the biomass source.

For thermochemical conversions, the biomass source can be divided in two main groups: lignocellulose (LC) and triglyceride (TAG) sources [10]. Lignocellulosic biomass comprises plant matter derived from crops, bark and other agro-industrial residues, such as rice husk and sugarcane bagasse. Forestry residues are very attractive due to their abundance and low cost [11]. In comparison to bio-oil from TAG sources, bio-oil from LC tends to have high water and oxygen contents, leading to a lower gross calorific value and poor stability [12–14], and occasionally an additional step is required prior to thermal cracking, such as torrefaction [15], which makes TAG technically more favorable than LC [16]. TAG sources include vegetable oils, animal fat and other residues. There are several studies reported in the literature concerning the use of soybean oil [8,17–20], palm oil [21,22], jatropha oil [23], sunflower oil [24], canola oil [25], rubber seed oil [26], residues from grease traps [27,28], waste cooking oil [29–34], sewage sludge [35], fish waste [36–39], chicken fat and skin [40] and other animal fat wastes [41].

Nevertheless, bio-oil from TAG also has drawbacks associated with its use as an alternative fuel source. Olefinics, oxygenated compounds and carboxylic acids are commonly present in bio-oils obtained from TAG, and thus they require an upgrading process for their refinement

\* Corresponding author.

E-mail address: [vwiggers@furb.br](mailto:vwiggers@furb.br) (V.R. Wiggers).

and to allow their use in modern machines and vehicles [13,42–44]. Aromatic compounds are also present in bio-oil obtained from TAG. These are widely used in the petrochemical industry and are responsible for increasing the octane number of light fuels, such as gasoline [45], however aromatics are toxic and their content is restricted by regulations, notably benzene. Furthermore, the removal of aromatic compounds can be complicated as it requires complex processes and catalysts [13], and thus avoiding their formation is the best strategy.

The composition of the feedstock, in particular the types and distribution of fatty acids, strongly affects the composition and characteristics of the products [46]. Moreover, there are innumerable reactions occurring simultaneously during the thermal cracking of TAG. In order to better understand the formation of compounds, several publications in the literature propose reaction schemes for the thermal cracking of triglycerides. One of the first examples is proposed by [47]. The authors studied the thermal cracking of tung oil and proposed a 16-step scheme focused on the decomposition of saturated fatty acids. The main objective of the work was to obtain liquid products in the gasoline range. According to the authors, aromatic compounds are formed from either paraffin or olefin cyclization reactions.

Following the studies of [47–49] proposed a further modification of the reaction scheme of saturated fatty acids based on the thermal cracking of palm, babassu and pequi oils. Triglyceride thermal cracking generates two types of substituents: RCOO and RCH<sub>2</sub>CO. Successive reactions of ethylene molecules in the former substituent leads to the formation of odd *n*-alkanes and 1-alkenes. Regarding the latter substituent, due to disproportionation and other successive eliminations, *n*-alkanes and 1-alkenes are generated, all with an even number of carbon atoms in the chain.

Nevertheless, the greater part of fatty acids in vegetable oils are unsaturated. Thus, [50] suggested a reaction pathway considering unsaturated fatty acids in the thermal cracking of soybean oil. The formation of compounds such as alkanes, alkenes, dienes, aromatics and carboxylic acids was observed in their study. In particular, the formation of aromatics occurs through the Diels-Alder reaction between a diene and an alkene, forming a cyclic alkene with no intermediates [51–53]. The dehydrogenation of the cyclic alkene leads to aromatics formation in the thermal cracking of triglycerides. Detailed steps of this reaction are well-described in the studies from Idem et al. [25] and Kubátová et al. [54].

Ref. [25] proposed a 30-step reaction scheme for canola oil thermal cracking considering more complex pathways and including many other intermediates, such as heavy oxygenated compounds. The scheme suggests intermediate reactions involving saturated and unsaturated fatty acids, after the initial cracking of the triglyceride molecule. The main steps of this scheme, based on this study, are discussed below.

Initially, oxygenated compounds (esters, aldehydes, ketones and long chain carboxylic acids) are formed from the decomposition of the triglyceride molecule. Subsequently, these compounds may follow different pathways. One involves decarbonylation and decarboxylation reactions, producing carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), respectively. Subsequent reactions involving CO and CO<sub>2</sub> proceed until small hydrocarbons in the range of C<sub>1</sub>–C<sub>5</sub> are produced. Cyclic compounds were reported due to cyclization reactions in which C–C bonds (from unsaturated fatty acids) undergo bond cleavage to form initially a conjugated diene, followed by Diels-Alder addition.

The formation of aromatic compounds is related to hydrogen elimination from C<sub>6</sub> or longer cycloolefins at elevated temperature. Linolenic acids are also able to derive aromatic compounds after their decarboxylation. [25] reported that the majority of aromatics are in the range of benzene and toluene. They suggested that the dienes and olefins involved were in the C<sub>4</sub>–C<sub>5</sub> and C<sub>2</sub>–C<sub>3</sub> ranges, respectively. Phenolics were not reported by [25]. Although it represents a large fraction on bio-oil produced by LC sources [55], it is not reported on studies using TG sources. The key point regards in the molecular composition of LC, which is quite different from TG. Phenolics are

derived from chemical compounds from cellulose, hemicellulose, and mainly from lignin, which are the typical LC polymers [41,55].

Notably, [25] proposed that saturated and unsaturated compounds follow different routes during thermal cracking and that the reactions involved are in competition. Although one route can lead to a saturated fatty acid producing an aromatic compound, the authors report that this route is longer and more complex than that involving an unsaturated compound. This suggests that the formation of aromatic compounds from unsaturated compounds is a more favorable route.

The study carried out by [25] is still one of the most comprehensive in terms of the thermal cracking reaction scheme. Other previous studies worth mentioning are those by [54,56,57]. All of these authors agree that aromatics are formed by the Diels-Alder reaction between a diene and an alkene, with further hydrogen elimination to give cycloolefins. In a recent study, [58] investigated the effect of the degree of unsaturation by means of the microwave-assisted pyrolysis of fatty sodium stearate, sodium oleate and sodium linoleate. Although the experiments were performed with fatty acid salts, the authors also noted that the formation of aromatic compounds increased with a higher degree of unsaturation.

In reports in the literature the formation of aromatics is attributed to unsaturated compounds in the triglycerides; however, it still appears to be unclear if different amounts of unsaturated triglyceride compounds can alter the aromatic content in the bio-oil produced by thermal cracking. Thus, the purpose of this study was to investigate the influence of the unsaturated compounds on the aromatics content in the bio-oil. Thus, thermal cracking experiments were carried out with three biomass samples with different contents of unsaturated compounds. Soybean oil is widely used for biofuel production and it was employed in the previously mentioned studies. Therefore, by blending with hydrogenated fat we could obtain a common feedstock with different degrees of unsaturation. Subsequently, by comparing the data obtained, the influence of unsaturated chains on the presence of aromatics in bio-oil could be investigated. The results highlighted the possibility for the use of more severe operational conditions (temperature-residence time pair), resulting in higher liquid product yields.

## 2. Material and methods

Experiments were performed using three biomass samples with different degrees of unsaturation in order to investigate the effect of this parameter on the formation of aromatic compounds in bio-oil. The samples employed in this study are shown in Table 1.

The SO 100 sample is 100% soybean oil, while SH 90:10 and SH 80:20 are blends of soybean oil with hydrogenated fat (derived from soybean oil) in the proportions shown in Table 1. Both the commercial soybean oil and hydrogenated fat were donated by a local company. Hydrogenated fat is solid at room temperature and thus it cannot be fed into the reactor. Therefore, all blends were prepared at higher temperatures. By heating the hydrogenated fat on a hot plate, it was found that it becomes liquid at approximately 75 °C. Thus, the blends were prepared at 90 °C to ensure the liquid state and avoid clogging in the reactor and the decomposition of the soybean oil or hydrogenated fat.

The iodine index (II) of the raw material decreases with the addition of hydrogenated fat and compared with SO 100 the values were 12% and 15% lower for SH 90:10 and SH 80:20, respectively. This confirms

**Table 1**  
Samples used in thermal cracking experiments.

Sample name	Soybean oil (%, weight)	Hydrogenated fat (%, weight)	Iodine index (gI <sub>2</sub> /100 g)
SO 100	100	–	134.6 ± 4.6
SH 90:10	90	10	117.7 ± 3.0
SH 80:20	80	20	113.1 ± 3.9

Download English Version:

<https://daneshyari.com/en/article/6632003>

Download Persian Version:

<https://daneshyari.com/article/6632003>

[Daneshyari.com](https://daneshyari.com)