



# Thermal processing of soybean oil to obtain bio-based polymers and bio-oil



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## ABSTRACT

In this study we evaluated the use of triacylglycerides to produce bio-based resins and bio-oils suitable to be used, respectively, as a binder in printing inks (offset) and as diesel-like fuel. Soybean oil was kept under nitrogen atmosphere at temperatures ranging from 260 °C to 370 °C up to 12 h in the presence or absence of a nickel complex as a catalyst precursor. It was observed that the reaction occurs in two steps. In the first one, occurs the consumption of the double bonds via Diels–Alder to form a polymer increasing the viscosity of the material. In a second step, the pyrolysis of ester groups and the alkyd chains takes place, reducing a viscosity of the polymers. Besides, using Nickel complex as a catalyst precursor it was observed a high activity to produce polymers with higher viscosity in a shorter time than when comparing with reactions without catalyst. It was also analyzed the bio-oil formed during the reaction. It was observed that without catalyst the pyrolysis leads to the formation of high amounts of carboxylic acids with short chain. However, the presence of Nickel complex increased the formation of hydrocarbons and reduced the amount of formed carboxylic acids, strongly indicating its activity in the deoxygenation.

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## 1. Introduction

With the petroleum supply crisis in the 1970s, researchers were encouraged to develop products using biomass as raw materials. Particularly, the treatment of triacylglycerides at high temperatures proved to be an important way to produce new bio-products, such as fuels, lubricants, inks, additives and others (Suarez et al., 2007).

In the early 1980s, American Newspaper Publishers Association reported the development of printing inks using a high viscosity bio-based polymer obtained from vegetable oils as a binder (Moynihan, 1985). When mixing this polymer with pigments and additives were obtained inks suitable to be used to print newspapers and magazines with very advantageous properties. Indeed, when compared these bio-based inks with traditional petroleum-based inks, was observed a better affinity with the carbon black pigment, making possible to reduce its amount in the formulation, a better degradation by fungi and a easier recycling of the paper, as well as a lower price (Moynihan, 1985; Erhan and Bagby, 1991, 1992, 1993, 1994, 1995). Because of these

characteristics these bio-based inks were quickly accepted in the printing market and are still in use.

Nowadays, the search for renewable feedstock to produce materials and fuels is pointed out as an elegant solution to address environmental behaviors related to the petroleum industry as well as to address the increasing demand for organic materials and fuels. In this context, biobased polymers have received increasing attention and their use as binder in inks, paints, coatings and adhesives has proved to be viable from both economic and technical points of view (Suarez et al., 2007; Moynihan, 1985; Erhan and Bagby, 1991, 1992, 1993, 1994, 1995).

However, there are few studies in the literature relating the thermal polymerization of vegetable oils (Archer Daniels Midland Company, 1938; Sims, 1957). It is well accepted that the reaction starts around 200 °C, when the isomerization and the conjugation of double bonds to form trans conjugated dienes take place. Thus, the polymerization starts after 260 °C when the formed dienes react by Diels–Alder to achieve tetra substituted cyclohexenes, forming a cross-link between chains (Sims, 1957), or via free radicals combination (Arca et al., 2012). Usually, the use of catalysts proved to diminish the reaction time, achieving higher viscosities in shorter times (Mello et al., 2013a). Thus, because of the high temperatures associated with thermal polymerization the use of catalyst are claimed to reduce energy consumption.

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Above 350 °C occurs a thermal cracking of triacylglycerides. In this process, the decomposition of the ester groups take place, converting the triacylglycerides into a mixture of different compounds, mainly hydrocarbons, carboxylic acids and other oxygenated compounds (Lima et al., 2004; Quirino et al., 2009). The composition of this mixture, known as bio-oil, varies according to the source of triacylglyceride used as a raw material, reaction conditions (temperature and time) and the catalyst used in this process (Lima et al., 2004; Quirino et al., 2009; Tami et al., 2011; Ramya et al., 2012; Botas et al., 2012). Because of their interesting physical and chemical properties (density, flash point, kinematic viscosity, calorific value and copper corrosion), the bio-oils have been pointed out as suitable to be used as liquid fuels (Lima et al., 2004; Quirino et al., 2009).

In the literature several reports describe the use of triacylglycerides to produce bio-polymers and bio-oils (Moynihan, 1985; Erhan and Bagby, 1991, 1992, 1993, 1994, 1995). These studies are carried out at low temperatures (around 300 °C) when aiming to obtain polymers and at high temperatures (above 400 °C) when liquid fuels are desired. For instance, we have demonstrated the catalytic activity of different metal compounds to obtain polymers from different oils at low temperatures (Mello et al., 2013a) and the possibility to produce diesel-like fuels from different vegetable oils at high temperatures with (Quirino et al., 2009) or without (Lima et al., 2004) catalysts. For instance, we have recently published the use of bio-polymers obtained from soybean oil and frying oil in printing inks formulation (Mello et al., 2013b; Montenegro et al., 2013) and the production and storage stability of diesel-like fuel from soybean oil in a continuous pilot-plant (Barreto et al., 2012).

However, as far as our knowledge, it was not yet studied simultaneously both processes, as well as the influence of the temperature and the use of catalyst in order to tune the selectivity. The aim of this work was to study the influence of temperature, in presence and absence of a nickel-based catalyst, in the bio-polymer and bio-oil yield.

## 2. Experimental

### 2.1. Materials

Alkali-refined soybean were obtained from Bunge Alimentos (Valparaíso, GO, Brazil) and used as received. Nickel complex used as catalyst precursor was synthesized utilizing  $\text{Ni}^{2+}$  and carboxylate ligands derived from palm oil fatty acids, with the generic structure of  $\text{Ni}(\text{carboxylate})_2$ , as previously described by Mello et al. (2013a,b).

### 2.2. Thermal reaction procedures

Alkali-refined soybean oil (650 g) was added into a 1.0 L five necked round bottom flask equipped with a condenser, a nitrogen inlet, a thermocouple and a heating mantle. The experimental apparatus can be depicted from Fig. 1. When evaluating the catalytic activity of  $\text{Ni}(\text{carboxylate})_2$ , the complex (0.65 g) was directly dissolved in soybean oil without any activation procedure.

During the reaction, polymer samples were taken at different times. In order to take samples one of the flask neck was opened under a nitrogen flux and 20 mL were taken with a syringe. Thus, the sample was analyzed by FT-IR and its kinematic viscosity and acid index were determined. The FT-IR spectra were obtained using a Shimadzu Prestige-21 equipped with ATR (Attenuated Total Reflectance, from Pike Technologies), optical way 7 mm and 10 reflections, using nominal spectral resolution of  $4 \text{ cm}^{-1}$  and average of 32 interferograms. The kinematic viscosity was determined using an Ubbelohde viscosimeter according to ASTM D445 standard

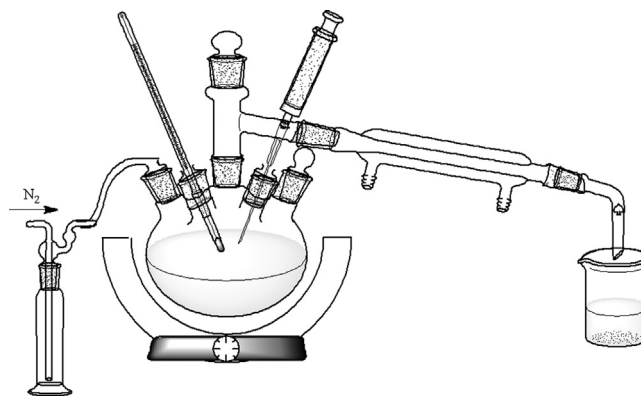


Fig. 1. Experimental apparatus used for thermal decomposition of soybean oil.

method. The acid index of the samples was obtained according to AOCs Cd 3d-63 standard method.

Condensed Bio-oil samples were collected and analyzed by GC-MS in a CG-EM-QP5050 equipment from Shimadzu using a fused silica capillary column CBPI PONA with 50 m of length, 0.25 mm of diameter and 0.50  $\mu\text{m}$  width. The temperature of the injector was kept at 250 °C, and the column temperature varied from 60 to 250 °C, with 10 °C/min heating rate, 39 min in total. Note that according to the experiment different time intervals were used to collect the bio-oil.

The presence of nickel in the products was measured using an iCAP 6300 Duo ICP optical emission spectrometer (Thermo Fisher Scientific, Cambridge, England) equipped with axially and radially viewed plasma. The spectrometer was equipped with a simultaneous charge injection device detector allowing measurements from 166.25 to 847.00 nm and the Echelle polychromator was purged with argon. The introduction system was composed of a cyclonic spray chamber and a Meinhard nebulizer. The injector tube diameter of the torch was 2.0 mm.

The precipitates in the polymeric product were analyzed by X-ray diffraction powder using a Bruker diffractometer, model D8 Focus. The detection range (2Theta) was 10–90° with the step size of 0.05° ( $1^\circ \text{min}^{-1}$ ).

## 3. Results and discussion

### 3.1. Mass relationship between polymer and bio-oil

Initially, it was evaluated the mass relationship between the polymer and bio-oil formed at different temperatures during 1 h, with and without catalyst. It was observed that in a reaction without catalyst bio-oil was formed only above 350 °C (Fig. 2A) and that in the presence of Nickel complex it was formed above 330 °C, reducing the initial temperature by 20 °C, clearly indicating a catalytic activity in pyrolysis. In sequence, it were analyzed the viscosities of the obtained bio-polymers, observing an increase in the viscosity values when increasing the temperature. Note that above 300 °C the viscosity of the polymer is always higher when using  $\text{Ni}(\text{carboxylate})_2$  than in the absence of catalyst. (Fig. 2B).

### 3.2. Polymer

To evaluate the reaction parameters in the bio-polymer produced, soybean oil was kept at different temperatures during 12 h. It were taken samples at the times 0.0, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 h. The viscosities of the different samples are shown in Fig. 3. As can be depicted from Fig. 3, in the presence or absence of catalyst, it was not observed any increase in the viscosity during

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