



Bosting an Oil Refinery into a Biorefinery

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The use of biofuels is increasingly important in order to mitigate the consumption of petroleum and increase the energy use of renewable sources. The estimative is that in 2040 the demand for oil will intensify by 26% and part of it will have to be supplied by renewable energy. Biofuels offer a reliable alternative and among the process associated to biofuels production, thermal cracking results on a liquid product (bio-oil) with similar characteristics to the fossil fuels, particularly when performed with triglyceride sources (TG). In this sense, the main goal of this work is to propose an alternative sequence of chemical processes aiming to boost an oil refinery chain into a green refinery by producing, co-processing and improving bio-oil characteristics obtained from triglyceride source. Some bio-oil characteristics like density, acidity (AI), iodine index (II), oxygen content (OC), carbon number distribution and chemical compositions are presented. The properties of bio-oil obtained from the thermal cracking of triglycerides might be compared to petroleum and its derivatives. Although the characteristics are similar between them, the bio-oil requires upgrading to reduce its high acid index, until achieve levels acceptable for its processing at a refinery.

1. Introduction

Energy plays a vital role in our society; we depend on it for the maintenance of life, as we know it: services, transportation, telecommunications, sanitation, water supply, electricity, fuels, among others. Energy demand in Brazil 2018 was largely attended by oil, natural gas and coal, fossil and non-renewable energy sources^[1]. Overuse of fossil fuels for power generation has a direct impact on our environment, changes range from small events to major disasters. No matter how much investment governments and productive sectors make around the efficient use of energy, production must be increased more and more, mainly due to the natural process of reducing inequality, income distribution and access to new technologies.

The use of biofuels is increasingly important in order to mitigate the consumption of petroleum and increase the energy use of renewable sources. The estimative is that in 2040 the demand for oil will intensify by 26% and part of it will have to be supplied by renewable energy^[2]. The need for diversification and expansion of renewable sources in energy production and chemical inputs renewed the interest in the thermal conversion processes of biomass. Biomass is probably the only renewable energy source that can completely replace the use of fossil fuels. Several alternatives were created to increase the insertion of biofuel in a country's energy matrix, thereby reducing the consumption of petroleum fuels. The proposed alternatives are bio-oil^{[3]–[6]}, biodiesel^{[7]–[11]}, bioethanol^{[12]–[15]}, hydro-processed esters^{[16]–[18]}, among others. These fuels might be used pure or blended with fossil ones. In this sense, thermal and catalytic cracking processes are presented as options for the production of hydrocarbons that can be fractionated for use as biofuels, petrochemical inputs and substitutes for petroleum derivatives^{[19]–[21]}. It is in this direction that the cracking or pyrolysis process stands out, because the low dependence on the quality of the raw material, the absence of reagents, the wide range of products and the possibility of auto-thermal operation, points to a good economic viability.

Despite all initiatives, the oil economy and logistics are strong and well spread, so this work wants to show that is possible to use the actual infrastructure for oil refining adding new processes to produce bio-oil and slowly turning an oil refinery. The main goal of this work is to propose an alternative sequence of chemical processes aiming to boost an oil refinery

chain into a green refinery by producing, co-processing and improving bio-oil characteristics obtained from triglyceride source.

2. Bio-oil from triglyceride thermal cracking

In search of replacing fossil fuels, one of the conversion techniques is the thermal cracking process, also known as pyrolysis, which is the biomass degradation at high temperatures (300 to 600°C) in the absence of oxygen, also known as pyrolysis, is an alternative process for converting biomass into liquid fuels^[22]. Biofuels offer a reliable alternative and among processes associated to its production, thermal cracking results on a liquid product (bio-oil) with similar characteristics to the fossil fuels, particularly when performed with triglyceride sources (TG). TG have been widely studied as biomass for thermal cracking processes^[23],^[24], also due to its large availability^[25],^[26]. Soybean it is the most common, from 2012 to 2014 130,736,882 tonnes of soybean oil were produced worldwide, the top region producer is America with 53% and Asia with 34.3%. More specifically, the top three producers countries are China with 10,935,400 tonnes, followed by United States of America and Brazil with 9,288,333.33 and 7,176,666.67, respectively^[27]. Pyrolysis's studies using soybean are commonly in the literature^[4],^[26],^[28],^[29]. Other oilseeds' works like castor oil^{[30]–[32]}, sunflower oil^[33],^[34], palm oil^[28] and canola oil^[35,36] were also studied. Besides that, waste oils like fish oil^[24],^[37], poultry fat^[38], beef tallow^[39], lard^[40], cooking oil^[23],^[26],^[41],^[42] and sewage sludge^[43] also are reported.

Bio-oil from thermal cracking can be obtained from different raw materials, e.g. Beims et al.^[44] performed thermal cracking of soybean oil and blends of soybean oil with hydrogenated fat, 80:20 and 90:10, respectively. The temperature was 525°C with residence time from 6.7 to 7.6 s and the bio-oil production was from 61.3 to 67.8% with acidity from 210.9 to 139.0 mg KOH g⁻¹. While Araújo et al.^[45] had 78.6% bio-oil yield from thermal cracking with sunflower oil at 425°C. Waste oils can also be used in thermal cracking process, e.g. Wiggers et al.^[37] used waste fish oil producing 72 to 73% bio-oil at 525°C with 17 s of residence time. Frainer et al.^[46] employed waste cooking oil for thermal cracking at 550°C from 4.2 to 12.5 s and Trabelsi et al.^[41] at 800°C with the same material achieving 80% bio-oil with high acid index of 126.8 mg de KOH g⁻¹.

The amount of bio-oil generated depends on the raw material and operating conditions used, specially the temperature and the residence time (t_R). When the reactor temperature is high with an extended

residence time, the formation of gaseous products will increase. While if the temperature is low and the residence time is longer, coke formation will increase, but if the temperature is moderate and the residence time is short, higher yields will be obtained in the liquid fraction^[4]. Table 1 presents averaged operational conditions, yields and products' properties based on 20 works and 16 different feedstocks used. The sulfur content is rarely reported, once its content in biomass is extremely low.

There are basically four known pyrolysis processes: gasification, slow, intermediate and fast pyrolysis. They can be identified by looking at the product rates obtained, e.g. the slow pyrolysis generates significant portions of solids, while intermediate and fast pyrolysis use higher temperatures and shorter reaction times, favoring the liquid production, being able to reach up to 75% bio-oil^[19]. The maximum and minimum values reported place the works in the range of slow, intermediate and fast pyrolysis. Gasification works were not selected to be reported here. One can note that the range of temperature is not so wide. Temperatures below 300°C will not promote cracking reactions, and temperatures above 600 °C might result in an excessive cracking leading to a high bio-gas yield. However, the residence time range reported are spread, this can be associated to the reactors models used (batch and continuous) or to the different ways to estimate the residence time.

The pair temperature and residence time has direct impact over products yields. The char is an undesirable product, once its presence is associated with coke formation, clogging and catalyst deactivation^[47]. The bio-oil yield average value reported in the literature was around 63% with the

maximum value of 92%. Bio-oil presents acid index from 2.9 to 210.96 mg KOH g⁻¹ according to Table 1, and the regulations establish the maximum value of 0.5 mg KOH g⁻¹ for Brazilian diesel and biodiesel^[2]. The high acidity is related to high carboxylic acid content and when used under these conditions can cause corrosion in the refining equipment and motors, narrowing its use^[41].

The average value for iodine index was 107.35 g₂/100g and it is associated with the unsaturations bonds in the material. High content of olefins compounds reduces the chemical stability of the derivate. The presence of water in fuels can damage burners, clog filters and reduce their calorific value. The average water content in the bio-oil was around 0.84% but, it can be removed by centrifugation, while the bio-oil density average value was 866 kg/m³. For comparison purpose the Brazilian diesel has water content specification of 200.0 mg/kg, average density of 850 - 900 kg/m³ according to resolution number 45 from Brazilian National Agency of Petroleum, Natural Gas and Biofuels - ANP^[48].

3. Bio-oil for Oil Refining

Peláez Samaniego^[49] studied the challenges of using crude bio-oil in traditional combustion systems. The direct use of crude bio-oil as a fuel still presents some difficulties; the author listed the most important ones: changes in physical and chemical properties during storage; complexity of multiphase properties; corrosivity; presence of solid particles; very low lubricating properties and cold ignition difficulties.

Table I: Averaged conditions, yields and properties of 20 pyrolysis' works reported in the literature

Conditions	Average ^{±s-d}	Values	
		Maximum	Minimum
Temperature (°C)	475.75 ^{±57.18}	600	300
Residence time (s)	143.51 ^{±360.69}	1800	1
Yields	Average ^{±s-d}	Values	
		Maximum	Minimum
Bio-oil (%)	62.98 ^{±15.61}	92.00	14.80
Bio-gas (%)	26.85 ^{±18.19}	75.00	6.80
Char (%)	11.72 ^{±7.24}	27.40	0.00*
Properties	Average ^{±s-d}	Values	
		Maximum	Minimum
Acid index (mg KOH/g)	85.70 ^{±76.60}	210.96	2.90
Iodine index (g ₂ /100g)	107.35 ^{±30.34}	134.60	64.00
Density (kg/m ³)	866.98 ^{±24.90}	910.00	818.40
Water content (%)	0.84 ^{±0.22}	1.00	0.68

Sequential steps are required to improve and refine the bio-oil according to specific fuel regulations^{[50], [51]}. The proposal of this work is divided in four steps (Fig. 1): the first is to produce bio-oil through triglyceride's thermal cracking in a continuous mode of operation; the second process is to promote the esterification of bio-oil to reduce its acid index (AI); the third stage is co-processing bio-oil in a distillation unit being fractionated into desired fractions; however, the olefins and the oxygen content will remain in the fractions, the fourth step involves hydrotreatment to reduce both iodine index (II) and oxygen content. The advantage of first thermal cracking rather than direct hydrocracking is that it removes part of the oxygen from the TG molecules in an auto thermal process and reduces hydrogen consumption in the hydrotreatment step, providing products in a wide range of carbon chain.

Since after thermal cracking process the bio-oil presents high acid index, one of the alternatives is the esterification reaction that can be considered a route to improve product quality. This is a reversible process of ester formation (Fig. 2). Fisher's esterification method, 1985, is the catalytic reaction of a carboxylic acid with an alcohol under certain heating.

Ramos et al.^[52] performed 6 experiments of thermal cracking of soybean oil at 525 °C with mass flow rate of 350 g/h and an average residence time of 4 seconds. Afterwards, the esterification reaction of the crude bio-oil was carried out in laboratory scale using ethyl and methyl alcohols and sulfuric acid as catalyst. Ethyl esterification reaction temperatures of 60, 70 and 75 °C and for methyl esterification reactions of 50, 60 and 65 °C were defined, both at 90 min. The results showed that the acidity index reduction was higher when methanol was used, since the initial acidity index of the bio-oil was 133.33 and reduced to 3.35 mg KOH/g, resulting in a 97.5% of reduction. Xu et al.^[53] performed the esterification of the bio-oil from the catalytic cracking of the frying oil. The reaction occurred in the presence of methanol and sodium bisulfate catalyst. The results showed

that the bio-oil acidity index decreased 93.0% from 28.8 to 2.0 mg KOH/g after the esterification reaction at 65°C for 2 h.

Li et al.^[54] obtained bio-oil from the thermal cracking process of rubber seed oil. The esterification reaction of bio-oil using ZrO₂/SBA-15 as solid acid catalyst was used to improve product quality. The initial acidity index was 97.0 mg KOH/g and decreased 98.9% to 1.2 mg KOH/g after the esterification reaction at 100 °C at 4 h.

The fractioning can be performed with distillation processes. Wiggers et al.^[37] used a simple distillation to obtain purified products such as gasoline and diesel from rapid and continuous pyrolysis of soybean oil in a pilot plant, alternating temperature from 450 to 600 °C and water concentration from zero to 10%. The authors showed that physical, chemical and chromatographic analysis from biofuels were similar to fossil fuels. Wisniewski et al.^[24] converted waste fish oil into bio-oil by rapid pyrolysis with yields above 70% and the reactive distillation process was used to separate light and heavy fractions, aiming not only separation but bio-oil acidity reduction. The crude bio-oil obtained from Suota et al.^[55] with the thermal cracking of used cooking oil was distilled, producing light and heavy fractions with yields of approximately 30 and 50%, respectively.

According to Venderbosch^[56] the high levels of oxygen in the bio-oil are reported to be the main cause for the unstable character. The oxygen atoms from TG can be removed through decarbonilation and decarboxylation reactions producing CO and CO₂ in the first step. The catalytic treatment of bio-oil is one of the most promising options and the catalysts are noble metals, transition metals or metal sulphides^[16]. The hydrotreatment can be divided in two steps with the first called stabilization, when the carbonyl and carboxyl functional groups are transformed into alcohols. The most common catalysts used in this first step are Pt, Ru and Pd. The second step occurs the cracking and hydro-deoxygenation with most common catalysts Ru, Ni and sulfided CoMo^[57].

Among the noble metals, the potential of homogeneous Ru catalysts for the catalytic upgrading of fast pyrolysis oil fractions was showed by

Venderbosch^[56]

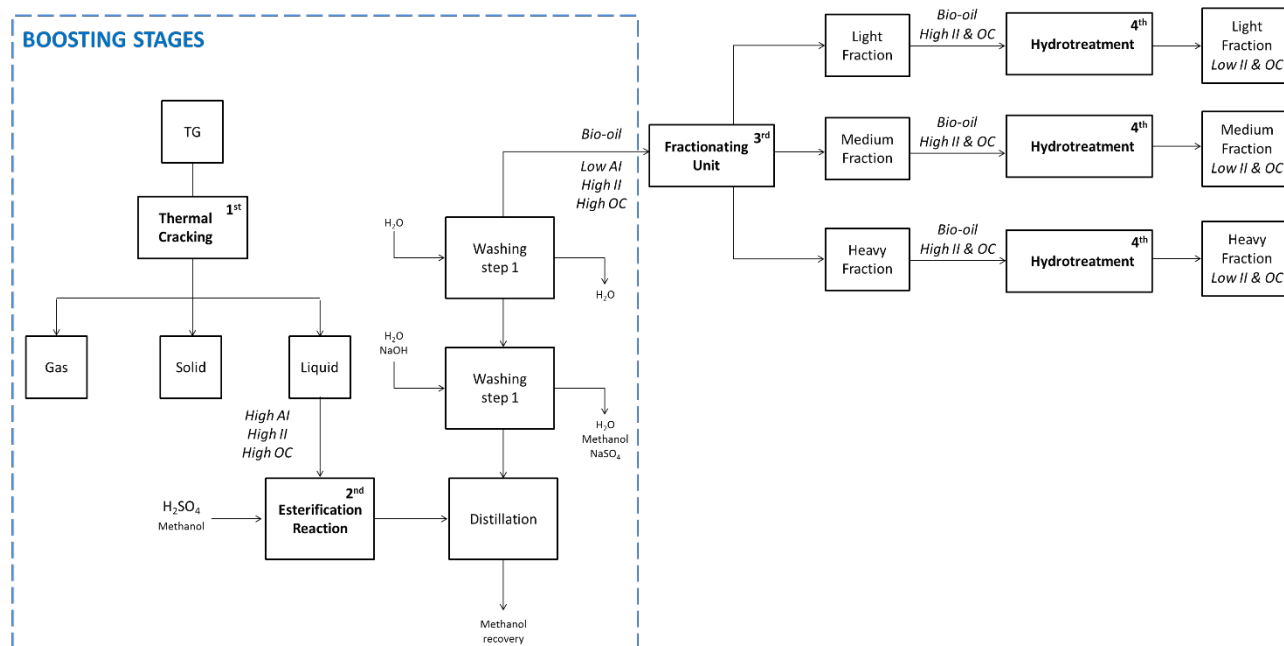


Fig. 1. Schematic 4 step proposal

4. Mundial and Brazil Scenario

Bioeconomy refers to an economy that relies on renewable natural resources to produce food, energy, products and services. It is related to the use of biomass as a renewable energy source and consequent reduction in the consumption of fossil fuels that result in greenhouse gas emissions. It also focuses on the use of raw materials and application in research, development and innovation and can be understood as an economy in which renewable biomass is produced and converted into value added materials, chemicals, food and feed, fuels and energy^{[60], [61]}.

Allied to the great need for energy supply, there is also the exponential generation of waste from the most diverse anthropic activities. Regions that do not properly dispose their waste will find it difficult to provide and maintain adequate health, education, transportation, and other services. The heterogeneity of waste means that several combined or individual technological solutions must be used. The lack of technical data on the impacts of the use of a particular technology for waste treatment makes it difficult to decide on the authorization of its use and, in most cases, leads to a postponement, making the current scenario increasingly critical.

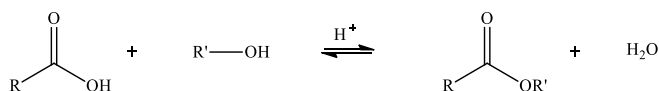


Fig. 2. Fisher's esterification reaction acid catalyzed

Ingrao et al.^[62] highlighted the contributions of bioeconomics in research themes, such as: biomass, biomaterials and bioenergy; agriculture; forestry; production and packaging of food and feed; and diverse applications. The authors point out that all societies must take seriously the responsibilities and actions to accelerate the transition to sustainable post-carbon fossil economies by sustainable use of renewable biomass in place of fossil sources for biomaterials and bioenergy production. It is noteworthy that the bioeconomy is related to the circular economy, which is designed to optimize materials and energy efficiency through technological development and industrial symbiosis, and to the green economy that is designed to enhance the functionality and resilience of socioecological systems, taking advantage of natural capital; and complementing technical corrections with nature-based solutions.

According to Finnish Bioeconomy Strategy^[63], the bioeconomy will reduce dependence on fossil natural resources, prevent loss of biodiversity and

create new economic growth and employment in line with the principles of sustainable development.

Brazil, in 2017, instituted law number 13.576 establishing the national biofuels policy, known as *RenovaBio*, which aims to provide subsidies to the commitments made by the country in the Paris Conference on Climate Change in 2015, to expand the participation of biofuels in the national energetic matrix. In general, the goal is to develop the Brazilian bioenergetic sector, allowing companies to seek resources and to encourage the expansion of their investments. The program provides for the establishment of compulsory individual targets to be met by fuel distributors that promote industry compensation and target decarbonization. Targets were set gradually for short, medium and long term. National Energy Policy Council (CNPE) resolution number 5 seeks to reduce projected carbon intensity, reduce target carbon intensity, decarbonizations credits (CBIO) and delimit the tolerance ranges. Thus, the *RenovaBio* reflects a Brazilian policy that encourages the increase of biofuel production by promoting its insertion in the energetic matrix.

5. Conclusion

Co-refining of bio-oil appears to be a promising approach to increase the biofuels content in an oil refinery, to reduce sulfur and to maintain the quality parameters of commercial fuels. Use the actual infrastructure of oil refineries can reduce significantly the investments for biofuels productions and fastly introduce large amounts of biofuels facilitating the transition to a sustainable energy matrix. It is important to highlight that studies are still required for upscaling thermal cracking, acidity reduction process, co-refining and hydrotreatment of bio-oil and its fractions.

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