CO-PROCESSING OF THERMAL CRACKING BIO-OIL AT PETROLEUM REFINERIES

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ABSTRACT

The aim of this study is to investigate the viability of implementing bio-oil co-processing in an oil refinery. The physical properties of bio-oil obtained from the thermal cracking of triglycerides are compared to those of petroleum. Although the oil characteristics are similar, bio-oil requires upgrading to reduce its high acid index to levels acceptable for its processing at the refinery. The hydrotreatment unit of the refinery can deal with the olefin and oxygen contents of the upgraded bio-oil. This study indicates that bio-oil can be co-refined in the distillation, fluid catalytic cracking, and delayed coking units. Thus, the co-processing of bio-oil appears to be a promising approach to increasing the use of bio-oil. However, some challenges related to the technical issues need to be studied in greater depth.

KEYWORDS

bio-oil; oil; biofuels; co-refining; co-processing; bio-refinery

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1. INTRODUCTION

Most liquid fuels currently in use are derived from fossil hydrocarbons. Typically, vehicles are powered by internal combustion engines propelled by gasoline and diesel. In 2015, the total world liquid fuel consumption was around 94 million barrels per day, a volume that is expected to rise to 97 million in 2017 (**Energy Information Administration, 2016**). There are several concerns associated with the use of fossil fuels, including availability and environmental issues, which prompt the search for new alternative sources of energy to replace them. According to Rudolf Diesel, the use of vegetable oil as a fuel has drawbacks due to its unfavorable properties, notably viscosity, which can lead to engine wear, poor combustion, and high emission levels. These negative characteristics have motivated research that aimed at finding other compatible fuels (**Misra & Murthy, 2010; Bergthorson & Thomson, 2015**). Liquid fuels obtained from biomass (i.e. bioethanol, biodiesel, and biogasoline), known as biofuels, are considered sustainable energy sources and being probably the best candidates to replace fossil fuels (**Bergthorson & Thomson, 2015**).

Bioethanol has been used to power vehicles for some time, demanding modifications to the engine and other parts. Nowadays, in Brazil, almost every new car is able to run on both gasoline and bioethanol. However, since the bioethanol is usually made from starch or sugar, it creates concerns. The fuel production competes with the food industry for the crops that are used for food supply which can lead to food price increases. Thus, the investigation of non-edible fuel sources is of great interest (**Demirbas, 2011; Adewale et al., 2015**). In the production of bioethanol from non-edible sources, known as “second generation bioethanol,” lignocellulosic materials (i.e. cereal straw, sugar cane bagasse, and forest residues) generally are used (**Scaife et al., 2015**). However, making second-generation bioethanol economically viable still presents a considerable challenge (**Demirbas, 2011; Aditiya et al., 2016**).

Alternatively, the thermal cracking process offers a promising opportunity to convert biomass into liquid fuels and chemicals. Basically, the biomass is subjected to high temperatures (around 500°C), in the absence of oxygen, with or without the aid of catalysts, to promote the decomposition

of organic compounds into three streams: bio-oil, bio-gas, and coke. Although undesired products are generated, thermal cracking can be managed to produce greater fractions of the desired products (**Bridgwater & Peacocke, 2000; Xiu & Shahbazi, 2012**).

Despite the numerous research studies carried out in this area, barriers associated with the design of an industrial plant to produce exclusively this type of biofuels still hinder its economic viability (**Maity, 2015**). It is clear that a large investment would be needed to design new structures and create an achievable market for biofuels. One way to avoid this capital investment in new structures is to use an oil refinery to produce compatible fuels from bio-oils (**Maity, 2015; Hassan et al., 2015**). In this context, the development of a product that is similar to petroleum would be the easiest way to insert biofuels into the existing refinery infrastructure (**Ringer et al., 2006**).

Most refineries can receive petroleum from different origins, thus, with properties that might differ slightly. In addition, some units in the refinery (i.e. fluid catalytic cracking, delayed coking, and hydrocracking units) give flexibility to the refining. Furthermore, because the refining process has passed through several modifications over the years, due to changes in product specifications or environmental concerns, such as operations to reduce the sulfur content of products and to replace octane-boosting, facilitates the development of new methods for bio-oil processing in a standard petroleum refinery (**Walls, 2010**).

However, a carefully analysis is required to identify all of the changes that are necessary to enable the co-processing of a bio-oil blend in a standard oil refinery and produce biofuels that adhere to current regulations. Each type of fuel is regulated by various specifications and standard parameters to ensure its quality and safety. The Reid vapor pressure (RVP), the distillation curve, the sulfur and oxygen contents, and the acid index (AI) are parameters that affect engine operation and gaseous emissions directly (**Rodríguez-Antón et al., 2015**). Any potential modifications should maintain or improve the product characteristics. The co-processing of bio-oil and petroleum in an oil refinery could offer a chance to increase biofuel production while maintaining the fuel quality

standards. In addition, this would reduce society's dependence on liquid fuels from fossil sources, as bio-oil would become part of the refinery's feedstock.

This paper addresses the viability of bio-oil co-processing in an existing oil refinery infrastructure, presenting some properties of petroleum and bio-oil produced by the thermal cracking of triacylglycerols (TAGs).

2. PETROLEUM AND BIO-OIL

Currently, fossil hydrocarbons are the principal material source for the production of liquid fuels and petrochemicals. The main hydrocarbons (HCs) in crude oil are aliphatic and aromatic compounds. Some HCs contain heteroatoms (sulfur, nitrogen, oxygen, and metals) forming asphaltenes and resins (Roussel & Boulet, 1995). Crude oil is extracted from different areas around the world, and the physical and chemical properties of oil vary according to its origin (Fahim et al., 2010). To safeguard the entire refining process, it is necessary to ascertain crude oil properties, such as API gravity, distillation curve, kinematic viscosity, pour point, Al, and water content. The API gravity is used to measure petroleum density. In fact, this value is the main factor in setting oil prices (Fahim et al., 2010). Distillation curves are used to measure the volatility of a hydrocarbon mixture, plotting the boiling temperature against the distilled volume fraction (Ott et al., 2008). The distillation curve is the start point for predicting several physical properties of the oil (Fahim et al., 2010). The oil viscosity, along with the pour point, which is the lowest temperature at which the crude oil would flow, is another property required for its classification. It is also an indicator of the difficulty involved in pumping the oil.

Crude oils are also classified by their sulfur content, which is possibly the main petroleum contaminant. In general, the terms 'sweet' and 'sour' are applied in an oil refinery for a quick reference to the sulfur content. If an oil contains less than 1% sulfur it is referred to as sweet and when this value is greater than 1% it is considered as sour (Fahim et al., 2010). The oxygen content of crude oil is usually under 2 wt.% and this element can be present in innumerable forms (i.e. alcohol, carboxylic acids, and ketone). Oxygen can bring an

acid character to the oil, which can lead to processing problems (Quelhas, 2012).

Bio-oil, a dark brown liquid, is a mixture of hydrocarbons of different chemical groups with molecules of varying size. It is primarily derived from depolymerization and fragmentation reactions that occur during thermal cracking. This technique is becoming progressively popular due to its simplicity and the possibility to directly increase liquid fuel production (Bridgwater & Peacocke, 2000; Maher & Bressler, 2007; Qiang et al., 2009; Mubofu, 2016).

Bio-oils are comprised of several types of organic compounds (acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, and furans), nitrogen and multifunctional compounds, water, and solid particles (Bridgwater & Peacocke, 2000; Qiang et al., 2009). The specific composition varies according to the biomass source and the process parameters (Maher & Bressler, 2007). There are two main sources of biomass for bio-oil production: lignocelluloses (LCs) and triacylglycerols (TAGs) (Stedile et al., 2015a). Since biomass properties vary significantly, they must be well known prior to developing a new option for processing in refineries.

Lignocellulose, a source material for bio-oil production, is comprised of carbohydrates such as simple sugars, cellulose, hemicellulose, and starch and lignin, both present in the biomass. According to Stedile et al. (2015a), bio-oils produced from LC sources usually have higher oxygen content (around 30%). This leads to a poor high heating value (HHV), low stability and immiscibility with hydrocarbon fuels (Ringer et al., 2006; Czernik & Bridgwater, 2004). Water is also present in bio-oils produced from LCs due to the moisture in the feed material and as a product of the chemical reactions (Ringer et al., 2006; Bridgwater, 2012). Water can have a negative effect, as it reduces the HHV and the flammability, but positive effects include reducing the viscosity and benefiting combustion (pumping and atomization) (Czernik & Bridgwater, 2004; Lehto et al., 2014).

As an alternative to LCs, biomass based on fats and vegetable oils can be used for bio-oil production. This type of biomass is known as triacylglycerol (or triglycerides) and it is composed of one mole of glycerol and three moles of fatty acids (Demirbas, 2009). The use of TAGs for fuel

production also raises issues related to competition between food market and fuel. Several feedstocks for bio-oil production are comprised of edible vegetable oil, which brings some concerns related to land use for fuel instead of food. This could have an adverse effect mainly in the least developed countries, decreasing the food supply. However, it is possible to obtain similar results for bio-oil produced from non-edible oils (**Taufiqurrahmi & Bhatia, 2011**). Also, well-grounded political decisions regarding the allocation of land for food or for fuel might solve this question (**Tomei & Helliwell, 2016**).

TAG sources are promising, as they do not have the same drawbacks as LCs. They contain less oxygen, which makes them high-energy liquids (**Junming et al., 2016**). Bio-oil produced from TAGs has a high HHV and low water and oxygen contents, and it is distillable, which makes it similar to petroleum (**Oliveira et al., 2006; Lima et al., 2004; Wang et al., 2012**). However, bio-oil from TAGs also has drawbacks, specifically due to its high acid value and high concentration of olefins (**Wiggers et al., 2013; Yue et al., 2014**). Although this can increase the octane rating, a high olefin content might also lead to the production of gum deposits (**Wisniewski et al., 2010**) and make the fuel unstable (**Wiggers et al., 2013; Trivedi et al., 2015**). Thus, this is a property that needs to be controlled. In the remainder of this paper, bio-oil refers to the product obtained from TAG sources.

Bio-oil can contain short and long chain carboxylic acids (**Shirazi et al., 2016**), resulting in a high acid index. Acidity is a barrier to the operational steps since special construction materials need to be used in the processing vessels and pipework (**Bridgwater, 2012; Qi et al., 2007**). Fossil oils usually have low acid content (**Quelhas, 2012**) and thus an upgrading process is required prior to bio-oil co-processing in a standard refinery (**Qi et al., 2007**).

The viscosity of the bio-oil varies according to the biomass origin and the pyrolytic process (**Qi et al., 2007**). A higher viscosity value increases the operational costs and makes it difficult to pump and manage the oil (**Bridgwater, 2012**). The density also plays an important role in the bio-oil combustion performance and fraction yields (**Lehto et al., 2014**). In general, crude oils are heavier than bio-oils and the density can be reduced by blending

them.

Several authors have studied bio-oil production from the thermal cracking of TAGs, using different feedstocks, types of reactors and catalysts according to the feedstock feasibility, and the results of research on more efficient processes (**Fréty et al., 2011; Mancio et al., 2016; Mancio et al., 2017**). Generally, the bio-oil obtained is characterized to determine the composition in terms of the carbon number in the carbon chain, acid index, and chemical composition. In addition, in some cases, the bio-oil was distilled to produce light and heavy fractions in the range of gasoline and diesel (**Junming et al., 2016; Wiggers et al., 2013; Wisniewski et al., 2010; Wiggers et al., 2009a; Wiggers et al., 2009b; Yigezu et al., 2014; Junming et al., 2010; Junming et al., 2013; Mota et al., 2014; Tamunaidu & Bhatia, 2007**). Also, the distillation curve can be obtained to characterize the distillation behavior (**Stedile et al., 2015b**).

Soybean oil is a feedstock commonly employed in studies (**Lima et al., 2004; Wiggers et al., 2009a; Junming et al., 2009**), but several other TAGs have also been researched, e.g., canola oil (**Boocock et al., 1992; Idem et al., 1997; Katikaneni et al., 1995**), rubber seed oil (**Lu et al., 2014**), waste cooking oil (**Junming et al., 2011; Botton et al., 2012**), waste fish oil (**Wiggers et al., 2009b; Fadhil et al., 2017**), fatty poultry waste, fatty swine waste (**Adebanjo et al., 2005; Hassen-Trabelsi et al., 2013**), coconut oil (**Boocock et al., 1992**), and palm oil (**Yigezu and Muthukumar, 2014; Mota et al., 2014**).

These types of studies have been carried out in both batch (**Yigezu & Muthukumar, 2014; Mota et al., 2014**) and continuous (**Wiggers et al., 2009b; Shirazi et al., 2016**) reactors.

Based on data available in the literature, it is possible to compare the physical and chemical properties of fossil oils and bio-oils (Table 1) and the density values are relatively similar. The range of viscosity values reported for bio-oils lies within the range observed for fossil oils. The sulfur content of bio-oils should be highlighted due to its low value when compared to fossil oils. The pour point is generally lower for bio-oils, although in some cases the values for petroleum are even lower. The acid index of bio-oils is higher than that of fossil oils and is too high for processing bio-oil in an oil refinery, due to the corrosion potential. The

Table 1. Comparison between fossil oil and bio-oil.

PROPERTIES	Fossil oil		Bio-oil	
	Range	Reference	Range	Reference
API Gravity	19.6 - 62.3	A	24.8 - 27.1	I
Density	772.1 - 936.0	B	818.4 - 923.6	J
Viscosity (cSt) @50°C	0.55 - 73.9	C	2.7 - 37.1	J
Sulfur content (%)	0 - 3.63	A	0 - 0.013	K
Pour Point (°C)	30.0 - 62.0	D	-31.7 - 4.0	L
Acid content (mg KOH/g)	0.04 - 2.0	E	116.2 - 207.5	M
Iodine Index (cgl/g)	n.a.	-	64.0	N
Water content (v/v %)	0.05 - 0.17	F	0.36 - 0.68	O
Carbon	83.0 - 87.0	G	73.6 - 85.6	P
Hydrogen	10.0 - 14.0	G	11.4 - 13.9	P
Nitrogen	0.10 - 2.0	G	0.07 - 2.7	P
Oxygen	0.05 - 1.5	G	7.88 - 14.9	P
HYDROCARBON GROUPS	Range	Reference	Range	Reference
Aliphatic (%)	47.0 - 56.2	H	73.6 - 91.0	Q
Aromatic (%)	32.6 - 53.0	H	20.4 - 60.5	R
Oxygenated (%)	n.a.	-	4.30 - 5.35	S
Olefin content (%)	n.a.	-	26.56	S
Unknown (%)	n.a.	-	29.1 - 67.8	S
A. Odebunmi et al., 2002; Capline, 2004; Capline, 2015; Chevron, 2015; ExxonMobil, 2015; Statoil, 2015; TOTSA, 2015.				
B. Statoil, 2015; TOTSA, 2015.				
C. Odebunmi et al., 2002; Capline, 2015; Chevron, 2015; ExxonMobil, 2015; TOTSA, 2015.				
D. Capline, 2004; Capline, 2015; Chevron, 2015; ExxonMobil, 2015; Statoil, 2015; TOTSA, 2015.				
E. Odebunmi et al., 2002; Capline, 2015; Chevron, 2015; ExxonMobil, 2015; Statoil, 2015; TOTSA, 2015.				
F. Odebunmi et al., 2002; Statoil, 2015.				
G. Speight, 2002.				
H. ExxonMobil, 2015; Statoil, 2015.				
I. Stedile et al., 2015a.				
J. Lima et al., 2004; Junming et al., 2009; Wisniewski Jr. et al., 2010; Silva and Souza, 2013; Lu et al., 2014.				
K. Lima et al., 2004; Wisniewski Jr. et al., 2010; Silva and Souza, 2013; Lu et al., 2014.				
L. Silva and Souza, 2013.				
M. Lima et al., 2004; Junming et al., 2009; Wisniewski Jr. et al., 2010.				
N. Wiggers et al., 2009b.				
O. Wisniewski Jr. et al., 2010; Lu et al., 2014.				
P. Biswas et al., 2013; Biswas et al., 2014.				
Q. Boocock et al., 1992; Biswas et al., 2013; Biswas et al., 2014.				
R. Boocock et al., 1992; Idem et al., 1996; Idem et al., 1997.				
S. Idem et al., 1996; Idem et al., 1997.				

iodine index is shown only for bio-oil, as petroleum does not have a significant content of olefins. The water content is higher in bio-oils, although it is still relatively low. While carbon and hydrogen contents are similar to both, bio-oil has lower nitrogen content and higher oxygen content. For the hydrocarbon groups, the aliphatic and aromatic contents are higher in the bio-oil. The amount of oxygenated compounds is higher in bio-oil while the same content in fossil oil is considered insignificant. The bio-oil data available in the literature also considers the presence of unknown compounds, which are not mentioned on the petroleum datasheet.

3. TAG THERMAL CRACKING UNIT

A TAG thermal cracking unit, regardless of the feedstock or the reactor design, can be designed according to the scheme shown in Figure 1. Essentially, the main part of the unit is the reactor, which will produce bio-oil, bio-gas, and coke. According to [Wiggers et al. \(2017\)](#), the thermal cracking of TGA yields an average of 63.2% of bio-oil, 28.7% of bio-gas, and 8.1% of coke.

The main operational variables of the reactor are temperature and residence time. These parameters directly affect the characteristics of the products: the use of higher temperatures and longer residence times enhances the cracking

Figure 1. Scheme for TAG Thermal Cracking Unit.

reactions, producing a light bio-oil and high yields of bio-gas. Schemes for the reactions involved in the thermal cracking of TAGs have been proposed in the studies from [Maher and Bressler \(2007\)](#), [Shirazi et al. \(2016\)](#), [Idem et al. \(1996\)](#), and [Kubátová et al. \(2011\)](#). A stronger reaction process also increases the formation of aromatic compounds and coke, which can be noted in the proposed reactions schemes.

Indeed, the thermal cracking step favors a better co-processing of bio-oil than pure vegetable oil. [Ng et al. \(2015\)](#) reports that the co-processing of canola oil in a fluid catalytic cracking (FCC) unit

can result in a lower liquid yield and higher contents of CO and CO₂ in the gas fraction of the FCC. Alternatively, [Gomes et al. \(2007\)](#) suggests that vegetable oil is fed into the hydrotreatment unit together with diesel oil. This alternative deals with the oxygen content in the vegetable oil, but higher amounts of hydrogen are required in the hydrotreatment unit.

When TAG sources are cracked in a thermal cracking reactor prior to the treatment, most of the oxygen atoms are removed during the formation of CO and CO₂. These compounds comprise part of the bio-gas formed in the reactor and, even though they are not desirable for co-processing, the biogas produced is important to the functioning of the unit. Due to its composition (mainly short hydrocarbons) and high HHV, TAG can be used as a fuel for the burner, providing the main source of thermal energy required for the reaction. Table 2 shows the average composition of bio-gas reported in several publications in the literature. Based on this data it is possible to assume a HHV of around 40 MJ.kg⁻¹, demonstrating the potential of bio-gas as a fuel ([Wiggers et al., 2009b](#); [Idem et al., 1997](#); [Biswas et al., 2014](#); [Idem et al., 1996](#)). In the literature, generally, data on the propane and butane content are obtained from a balance

Table 2. Composition of biogas from TAG Thermal Cracking.

Component	Range (%)
CO	2.5 - 12.9
CO ₂	2.5 - 10.42
H ₂	0.6 - 4.7
CH ₄	9.6 - 29.3
C ₂ H ₄	22.9 - 32.4
C ₂ H ₆	8.4 - 11.5
C ₃ H ₈	1.4 - 8.7
C ₄ H ₁₀	8.7 - 15.2

considering other identified compounds. However, other important compounds, such as propene and butene, are also present in the gas fraction. Ethene is also an important feedstock for petrochemicals and its high content in the biogas fraction should be highlighted.

Besides bio-oil and biogas, coke is also formed as the solid fraction in the reactor. This is associated with clogging and, thus, it must be removed from the reactor (Yang et al., 2013). Controlling the burning process in the heated reactor, using air instead of biomass, allows the combustion and removal of the coke (Wiggers et al., 2017). Another approach is to design the reactor in such a way that the coke fraction can be used to produce thermal energy for the reaction, as in the case of a FCC unit, or apply the heat carrier concept (Barros et al., 2008).

Despite its similarity to crude oil, TAG bio-oil has a higher AI, a high content of olefins, and a presence of oxygenated compounds. In an oil refinery, olefins appear in the FCC and delayed coking (DC) units but, after fractioning, hydrotreating units reduce their levels. Since fuels derived from bio-oil contain olefins, they can be processed in the hydrotreating unit together with fossil fuels. The high content of renewable olefins also can provide an important feedstock for the chemical and petrochemical industry (Sadrameli & Green, 2007).

The oxygen can also be removed in the hydrotreatment process. Here, it is important to highlight that most of the oxygen atoms from the parental triglyceride molecule are removed in the formation of CO and CO₂ in thermal cracking reactions, considering the insignificant amounts of other oxygenated compounds in the gas phase. This suggests that after the oxygen removal, other compounds in the C1-C4 range are formed (Idem et al., 1996). The oxygen removal will reduce significantly the hydrogen consumption in the hydrodeoxygenation reactions that can occur in the hydrotreatment unit.

On the other hand, higher acid values are unacceptable in a refinery because of the potential for infrastructure damage due to corrosion (Quelhas, 2012). Thus, it is also necessary to consider a neutralization unit to upgrade the bio-oil and make it suitable for processing using the equipment in the refinery. The reduction or

neutralization of acidity can be achieved using potassium or sodium hydroxide, or via an esterification reaction using methanol or ethanol (Junming et al., 2009; Wisniewski et al., 2015; Moens et al., 2009), since the acidity is due mainly to the presence of carboxylic acids (Kraiem et al., 2017). In this study, the bio-oil processed in the neutralization unit is referred to as the upgraded bio-oil and the acid index should be suitable for processing in a refinery ($\leq$ of 0.5 mg KOH g⁻¹).

4. BIO-OIL CO-PROCESSING

An oil refinery is a complex site with several units where crude oil is turned into valuable hydrocarbons. It can be designed to deliver three main products: fuel, lube oil, or feedstock for the petrochemical industry (Fahim et al., 2010).

In a modern refinery for fuel production, there are three major processes: physical separation, chemical conversion (thermal and catalytic), and treatment. *Physical separation* fractions crude oil and other streams using properties such as boiling point and solubility, aiming to prepare them for further processing. The main operations of physical separation include the distillation and liquid-liquid extraction (solvent deasphalting and solvent extraction). While physical separation does not involve chemical changes, in *thermal and catalytic* reactions it transforms heavy streams of the refinery into valuable hydrocarbons. Thermal conversion processes (i.e. DC, flexicoking, and visbreaking) are used to upgrade vacuum residues. In catalytic conversion, the catalysts are used to promote the chemical reactions. It offers some advantages over thermal conversion, notably allowing a wider variation in the feed composition. However, both feed and catalyst must be compatible to avoid excessive coke formation and catalyst deactivation (Speight, 2013). Examples of catalytic conversion processes are catalytic reforming, hydrocracking, and FCC. Lastly, *treatment processes* are designed to remove impurities from petroleum fractions. Hydrotreating is one of the major processes used for this purpose. It removes impurities such as sulfur, nitrogen, oxygen compounds, chloro compounds, waxes and metals. The saturation of olefins in the fractions derived from FCC and DC is also performed in the hydrotreatment.

Figure 2. Flow chart of modified and simplified oil refinery.

Regarding the thermal conversion processes, DC plays an important role in this study. It involves the thermal cracking of the vacuum residue, which is usually contaminated with high levels of sulfur. In this process, high temperatures (around 485°C) and short residence times are applied to produce light products (gases, gasoline, and gasoil); coke is produced as a co-product. There are three types of coke: sponge, shot, and needle (Fahim et al., 2010), the latter being a desirable product (Quelhas, 2010).

In relation to the chemical conversion processes, the FCC unit is one of the major and most important components of the refinery. The FCC unit produces mostly gasoline, but also some gasoil and refinery gases. The main active component of the catalyst used is a zeolite, which is responsible for the cracking process. In general, some coke is generated, which remains deposited on the catalyst. A regeneration section is required to burn off the coke and to allow the heated catalysts to be reused (Vogt & Weckhuysen, 2015).

Based on the information above, Figure 2 shows a scheme indicating three possibilities for the insertion of upgraded bio-oil in a standard oil refinery. As mentioned, the bio-oil properties are similar to those of petroleum. Lower sulfur content is clearly an advantage, while the drawbacks are associated with a high acid index and high amounts of olefins and oxygenated compounds. Considering that the neutralization process decreases the acid index, this paper proposes three co-processing routes: (1) insert the upgraded bio-oil with the crude oil before the atmospheric distillation unit; (2) in the fractionator of the FCC unit; and (3) in the fractionator of the DC Unit. The co-fed of upgraded bio-oil in the hydrotreatment unit was not considered due to its wide range boiling point.

Option 1 considers inserting the upgraded bio-oil in the crude oil at the beginning of the oil refining process, in the atmospheric distillation unit. This option would allow a larger amount of upgraded bio-oil to be inserted compared with options 2 and 3; however, the differences in the distillation behavior due to the presence of olefins in the upgraded bio-oil must be evaluated, since this will change product composition.

Option 2 proposes the insertion of the upgraded bio-oil in the FCC unit, specifically in the fractionator column, see Figure 2. Usually, olefins

are present in the FCC products obtained from crude oil processing (Sadeghbeigi, 2012) and, therefore, their presence in the upgraded bio-oil is not a barrier to this option.

Alternatively, option 3 considers the insertion of upgraded bio-oil in the delayed coking unit, and also in the fractionator. As seen in Figure 2, with this option the quench oil can be substituted. Because the DC feedstock is contaminated with sulfur, it can lead to low quality products. The insertion of the upgraded bio-oil at this point could reduce the overall content of sulfur. Nevertheless, all streams derived from the FCC and DC fractionators need to pass through a hydrotreatment to reduce sulfur and olefins content. The oxygenated compounds could also be reduced in this step.

There are still some challenges to overcome before the bio-oil co-processing in the oil refining process can be performed. First, the AI needs to be reduced in a neutralization step to obtain the upgraded bio-oil, with reactive distillation being an option, as performed by Wisniewski et al. (2015), Junming et al. (2008), and Wang et al. (2013), with appropriate levels of AI reduction. In addition, Hu et al. (2017) reviewed some of the bio-oil upgrading methods involving acid-catalyzed reactions. Nevertheless, an in-depth study to identify viable neutralization processes for bio-oil should be the focus of further research.

The reactor design and kinetics are also challenges related to obtaining viable operation procedures for TAG thermal cracking. These are usually related to the scale-up of reactor designs to industrial capacity with the development of reliable kinetic models to aid scale-up techniques. However, thermal cracking involves hundreds of simultaneous reactions, making it hard to propose a realistic kinetic model. Also, although some data are available in the literature (Frainer et al., 2014; Jacomel et al., 2015; Meier et al., 2015; Periyasamy, 2015), a great amount of research still needs to be carried out on thermal cracking kinetics. In addition, considering the high content of unknown compounds, the chemical characterization of bio-oil needs to be improved.

In the case of *Option 1*, the distillation unit does not receive a feedstock with a high olefin content, since, generally, olefin levels in petroleum are low. It is also necessary to consider the presence of

esters from carboxylic acids, produced in the neutralization unit. Thus, one must evaluate the new operational conditions with an upgraded bio-oil blend.

The fractionators of the FCC or the DC unit could deal with this high content of olefins in the bio-oil. However, the upgraded bio-oil must have compatible acidity levels.

The hydrotreatment process applied to bio-oil also requires further investigation. The saturation of the olefins in upgraded bio-oil could increase the exothermic reactions resulting in difficulties related to temperature control. Also, the hydrogen consumption in the hydrodeoxygenation reactions applied to remove oxygen compounds from upgraded bio-oil needs to be evaluated.

5. CONCLUSIONS

The joint processing of thermal cracking bio-oil and petroleum in a standard refinery appears to be one of the best ways to stimulate the use of bio-oil. Considering that most parts of the refinery would operate in a manner similar to that applied in petroleum refining, the need for intensive capital investment to build new industrial plants can be avoided. In addition, bio-oil from thermal cracking of triglycerides has properties, such as low sulfur content, that are of interest in relation to the refining process. On the other hand, the high acid index, the high content of olefins, and the presence of oxygen require special treatment. The challenges associated with this joint processing should be the target of new research studies to explore the potential for implementing this strategy at existing refineries.

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