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BIORREFINERÍA INTEGRADA USANDO COPROCESAMIENTO DE BIOMASA

INTEGRATED BIOREFINERY USING BIOMASS CO-PROCESSING

Eduardo Falabella Sousa-Aguiar [1], *Vitor Loureiro Ximenes* [2]

RESUMEN

Se presentan los conceptos de biorrefinería y biorrefinería integrada. Asimismo, se destaca la importancia de la conversión de residuos en las biorrefinerías integradas. Además, se enfatiza el concepto de coprocesamiento como una manera de introducir carbono verde en el esquema de refinación existente. Distintas posibilidades de insertar biomasa líquida en distintas unidades de una refinería son destacadas. Por otro lado, se discute la posibilidad de utilizar, como materia prima para coprocesamiento, aceites vegetales puros o *bio-oils*, que resultan de la pirólisis catalítica o no catalítica de residuos. También se discuten resultados de unidades de hidrotratamiento en los que se hayan utilizado aceites vegetales puros o aceites de cocina usados. Finalmente, se presentan resultados con respecto al coprocesamiento de *bio-oil* en una unidad de desasfaltación, indicando que esa pareciera ser una excelente oportunidad para insertar carbonos verdes en combustibles.

ABSTRACT

The concepts of biorefinery and integrated biorefinery are presented. The importance of residues conversion in integrated biorefineries is also highlighted. Furthermore, the concept of co-processing as a way to introduce green carbon in the existing refining scheme is also emphasized. Different possibilities of inserting liquid biomass in different refinery units are featured. Pure vegetable oils as well as bio-oils generated via catalytic or non-catalytic pyrolysis of biomass are discussed as potential feedstocks for co-processing. Results regarding hydrotreating units in which pure vegetable oils or even waste cooking oils undergo co-processing are discussed. Finally, results concerning the co-processing of bio-oil in the deasphalting unit are presented, indicating that this seems to be an excellent opportunity to insert green carbons in fuels.

Palabras clave: Biorrefinería integrada, coprocesamiento, pirólisis, *bio-oil*, carbón verde.

Keywords: Integrated biorefinery, co-processing, pyrolysis, bio-oil, green carbon.

1. Introduction

The oil refining industry is a mature segment of the industry. Nevertheless, it has a rather promising future, regardless of the many challenges concerning environmental issues. As a matter of fact, the main challenges of the refining industry in the future are the following [1]:

- increasing stringent environmental regulation;
- growing demand for cleaner fuels;
- globalization;
- increase in the production of derivatives from declining quality oil;
- uncertainty about the consumer's choice;
- growing pressure of several segments of the society aiming at the reduction of GHG (greenhouse gases);
- maintenance of its profitability.

Hence, in order to cope with so many requirements, the refinery must search for intelligent alternative solutions to meet them all. The search for alternative raw materials such as biomass, natural gas, and coal is a must. Also, alternative refining routes such as synthetic fuels are striking back.

Furthermore, the traditional oil refineries will encompass the concept of "biorefineries" [2]. According to the 2008

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Farm Act, the term means a facility (including equipment and processes) that converts renewable biomass into biofuels and biobased products and may produce electricity.

More recently, the term "integrated biorefinery" has been coined [3]. An integrated biorefinery is capable of efficiently converting a broad range of biomass feedstocks into affordable biofuels, biopower, and other bioproducts. Moreover, the integrated biorefinery must cope with the problem of residues. Integrated biorefineries are similar to conventional refineries, generating a variety of products to optimize both the use of the feedstock and production economics. It must be borne in mind that integrated biorefineries imply the use of innovation, or rather, new chemical routes must be developed in order to reduce costs, improve competitiveness, and, above all, explore the potential of residues.

Indeed, there are plenty of possibilities of using different types of biomass aiming at producing various potential commercial products such as fuels and intermediates for the petrochemical industry. Different chemical routes may be deployed in order to achieve the main goal of all processes, which is the generation of bio-based commercial products.

Eventually, the concept of integrated biorefinery brings about another important concept regarding oil refining: co-processing.

2. Co-processing

Co-processing is, by definition, the use of blends in already-existing units. Co-processing usually concerns the simultaneous conversion of bio residues and intermediate petroleum distillates in existing petroleum refineries to produce renewable hydrocarbon fuels. Unlike the current common blending of biofuels into the finished petroleum product, co-processing makes the use of biomass within the processing of petroleum.

In principle, vegetable oils can be rather easily co-processed in the installed facilities of the refineries. Also, different types of bio-oils resulting from both catalytic and non-catalytic pyrolysis of lignocellulosic biomass can undergo processing in different units of the refinery [4], as depicted in **Figure 1.**

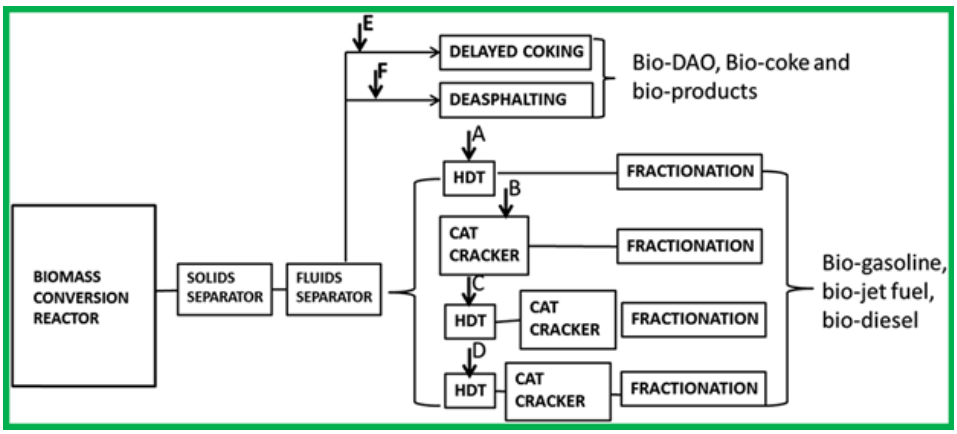

Figure 1. Potential insertion of liquid biomass in different refinery units

2.1 Co-processing Pure Vegetable Oils

Vegetable oils are more easily co-processed in existing refinery facilities than mineral oils or bio-oils resulting from pyrolysis. Coconut, sunflower, maize, olive, peanut, and cottonseed oils are some of the potential oils proposed for studies in co-processing.

The basic scheme of vegetable oils processing in the refineries usually involves two units: the hydroprocessing unit and the FCC (fluid catalytic cracking) unit.

As far as the hydroprocessing unit is concerned, the idea is rather simple: blending certain amounts of vegetable oils with the regular feedstock of the unit and then allowing the operation to proceed as usual. Also, the refinery may have the stand-alone unit, in which pure vegetable oils will be processed. Notwithstanding, one must not forget that operational conditions will have to be adjusted to the new feedstock, since a new reaction scheme will take place.

In natural oil catalytic processing, one may propose that under hydroconversion conditions, hydrogenation of double bonds occurs initially, followed by thermal cracking reactions of the saturated long chains of carbon atoms (acrolein and carboxylic acids are generated). Then, carboxylic acids molecules can react through the decarboxylation mechanism (resulting in CO_2), or via decarbonisation (with the production of CO and H_2O), or by the dehydration mechanism producing *n*-paraffins and H_2O. Finally, acrolein molecules can react in the presence of the catalyst generating C_3, whereas CO can react with hydrogen generating CH_4 and H_2O.

The addition of 10% soya oil to the regular gasoil feed in an adiabatic reactor [5] caused a fast temperature increase at the beginning of the reactor. After 20% height, however, curves showing the temperature rise against reactor height are parallel, indicating that the conversion of vegetable oil occurs at the entrance of the catalyst bed. Therefore, the addition of vegetable oils does not seem to change the traditional hydrotreating (HDT) mechanism.

Recently, Petrobras has developed a new process in which a vegetable oil is co-processed in one of its refineries. The process is called H-Bio [5].

H-BIO is a technology that allows the production of diesel from renewable feedstock, such as vegetable oils, by processing them in the existing refining scheme. In the H-BIO technology, vegetable oils are co-processed with petroleum gasoil in hydro treating units. The converted product contributes to improve the diesel pool quality in the refinery, increasing the cetane number and reducing the sulphur content. **Figure 2** presents the concept of the H-Bio process.

For every 100 liters of soybean oil, 96 liters of diesel are produced along with 2.2 m^3 of propane, with a hydrogen consumption of approximately 35 m^3.

Another interesting and successful process was the hydroconversion of waste cooking oil (WCO) [5]. The catalytic hydrotreating technology is an effective conversion technology of WCO to diesel, offering high yields (~90%) of a new renewable diesel fuel consisting of mainly *n*- and some *iso*-paraffins within C8-C25 range, by using a commercial hydrotreating catalyst NiMo/Al_2O_3. Catalytic hydrocracking of WCO could potentially lead not only to renewable diesel but also to renewable gasoline, depending on the hydrocracking catalyst employed.

Aiming at evaluating the effect of different commercial hydro processing catalysts on WCO conversion to diesel, three different commercial catalysts were compared [5]:

a. A hydrotreating catalyst
b. A mild-hydrocracking catalyst
c. A hydrocracking catalyst

The highest conversion (~83%) and diesel yields (over 94%) were observed in the case of the hydro treating catalyst (a), which was also the most efficient one regarding heteroatom removal.

2.2 Co-processing Bio-oils

Bio-oils (BO) and crude palm oils (CPO) often result from two basic types of biomass treatment: catalytic (CPO) and non-catalytic pyrolysis (BO) [6, 8]. BO and CPO have different compositions. CPO presents much lower oxygen content. However, carbon residue for CPO was much higher (~30%), indicating that CPO is not suitable for fuel production.

The problems of co-processing bio-oils are often related to the instability thereof [7]. Bio-oils produced via fast pyrolysis present a low-viscosity, single-phase liquid. The deployment of such bio-oils requires that these initial properties be retained. Unfortunately, bio-oils may undergo several reactions, which will provoke an increase in viscosity with time of storage.

For that reason, a "stability parameter" [10, 11, 12] has been proposed. It is the slope of a plot of viscosity (cp) against time (h). This plot is frequently a straight line with a positive derivative. It is worth noticing that aging effects are a function of temperature, being accelerated as the temperature increases. Obviously, the stability parameter will affect the performance of different bio-oils whenever co-processing is concerned.

2.2.1 Co-processing Bio-oils: Pre-treatment

The most used approach, and object of several publications, consisted in the improvement of this renewable stream through its conversion via acid catalysis. For instance, one may improve bio-oil properties using a fixed-bed zeolite catalyst reactor. Yields of hydrocarbons depended on the type of zeolite catalyst used. HZSM-5 was the best catalyst, followed by H-Mordenite. The reactions occurring in the presence of the acidic site of zeolites remove oxygen from the bio-oil molecules in the form of water and carbon oxides.

2.2.2 Co-processing Bio-oils: FCC Unit

The first studies were published in 1997 indicating the FCC feed as a potential point of insertion of bio-oil in the refining scheme. Nevertheless, it was pointed out the difficulty of its feasibility due to bio-oil insolubility in fossil streams. Subsequently, several studies have been carried out in fixed bed microactivity reactor system (MAT) (bench scale).

It has been observed that CO production occurs because of the removal of oxygenated functional groups, as well as an increase in the coke yield and a consequent reduction in hydrocarbon conversion due to the blockage of acidic sites.

In the first studies [13], 2.5% of hydrotreated bio-oil with 85% of vacuum gas oil underwent cracking in an FCC pilot unit. It was observed an increase in the yields of coke and naphtha, with a reduction in the gas yield.

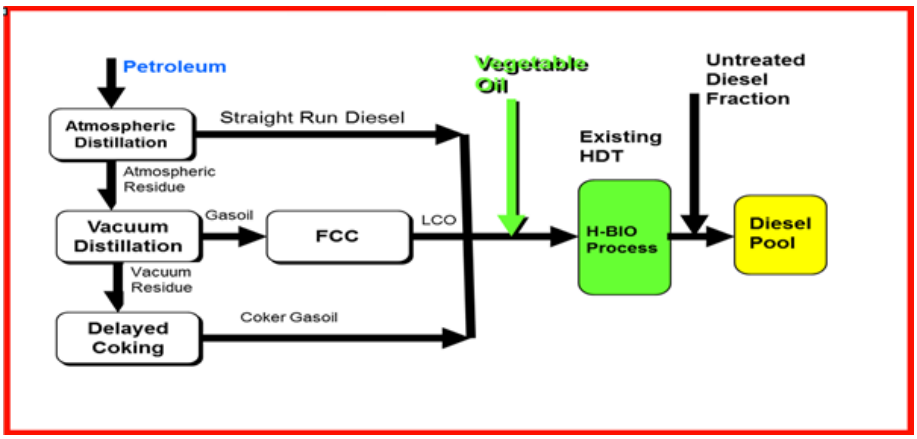

Figure 2. The H-Bio Processing Scheme

Graça *et al.* [14] performed a series of studies with the objective of specifically evaluating the impact of phenolic compounds on catalytic cracking with different types of catalytic systems, observing higher deactivation rates. They also observed the effect of the type of feed: naphthenic feed was less affected than paraffinic feed.

Studies in demonstration plants were carried out by Pinho *et al.* [9]. Two blends were tested, one with 10% and another with 20% bio-oil. Due to the immiscibility of the feeds and the chemical instability of the bio-oil, it was necessary to inject the streams in different axial positions. The 10% bio-oil test did not promote significant changes in the yield profile of the products, including gasoline and coke. On the other hand, at 20%, there was a significant reduction in gasoline, in addition to increased coke production. When 10% bio-oil is co-processed, only 2% of gasoline carbon was from renewable origin, while when 20% bio-oil undergo co-processing, the content was between 3 and 5%.

Pinho's study revealed an important scale effect, mainly related to the segregated injection, which makes the results in demonstration units better than those obtained in bench scale, especially when coke yield is concerned.

One important question, however, is yet to be answered. Is renewable carbon being retained in noble fractions, such as gasoline and diesel, when co-processing is carried out?

In fact, studies performed by Fogassy *et al.* using ^{14}C isotopic analysis indicated that most of the carbon present in the bio-oil is transformed into gases (10.6% bio-carbon) and coke (15.8% bio-carbon), whereas gasoline has approximately only 7% of bio-carbon.

1.2.3 Co-processing Bio-oils: Deasphalting Unit

Deasphalting is a process of liquid/liquid extraction, using a solvent. The solvent promotes solubilisation of molecules located on external layers of the micelles, whereas resins and asphaltenes precipitate. The extract is known as "deasphalted oil", due to its low asphaltene content, having the raffinate a high concentration of asphaltenes.

Usually, the following four classes of molecules may be found in Vacuum Residue (SARA analysis): (a) saturate, (b) aromatic, (c) resin and (d) asphaltene.

The deasphalting process aims at improving properties of Vacuum Residue, mainly regarding carbon residue. The deasphalted oil is destined to the FCC unit.

Falabella and Ximenes [15] studied the possibility of using the unity as a pre-treatment of bio-oils, considering that the deasphalting process improves the quality of the resulting oil. As a matter of fact, dosing bio-oil in the deasphalting unit generated a deasphalted oil with lower carbon residue, improving the quality thereof. Hence, more deasphalted oil may be incorporated in the FCC pool.

3. Conclusions

Co-processing vegetable oils and bio-oils in already existing refinery units might be an interesting alternative since the impact on the CAPEX would be almost negligible compared to the construction of new dedicated units. However, challenges regarding feedstock storage and handling due to instability of bio-oils and vegetable oils must be surpassed. In addition, the presence of impurities may corrode equipment and poison the catalyst.

Although bio-oil is a very promising feedstock, its natural properties require that at least an upgrading step be carried out before co-feeding it with petroleum oil in the refineries. Therefore, one of the main objectives of researchers working with bio-oil co-processing is to set the minimum degree of pre-treatment needed to introduce a bio-oil feed in refineries.

The major hurdle to be surpassed is the tendency of coke formation over the catalyst surface.

Regarding co-processing, the main concern still lies on the presence of oxygen compounds in the feedstock, leading to the formation of by-products and causing catalyst deactivation by poisoning or undesired side-reactions. Moreover, blending strategy is limited due to hydrogen deficiency of the feedstock, which increases coke formation if no fossil feed is added to set the hydrogen carbon ratio.

For that reason, new catalytic systems and process alternatives are still under development for making the technology practicable.

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