

CHAPTER 1

Catalysts for Co-processing Biomass in Oil Refining Industry

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1.1 Introduction

The refining industry has been confronted by challenges whose solution is actually non-trivial. A growing demand for cleaner fuels is generating more stringent environmental regulations all over the world. Additionally, it must be borne in mind that the quality of current crude oil is inferior to that of the crude oil produced several years ago. Indeed, the crude oil nowadays may be rather heavy, acidic and more impure; hence, it will require new steps in the refining process, such as, for instance, desulphurisation units. Such new units, however, are very energy consuming and will certainly reduce the

overall thermal efficiency of the refinery, not to mention the profitability thereof. Moreover, conventional desulphurisation processes often require hydrogen, whose production *via* Shift reaction will also produce CO₂, a well-known greenhouse gas. Thus, society's demand to improve the air quality by using cleaner fuels may come at the expense of higher greenhouse-gas emissions during the production of such fuels. Globalisation and oscillating customer choice, as well as the growing pressure to reduce emissions, are parameters that ought to be taken into account when the overall profitability of the refinery is discussed. Undoubtedly, the aforementioned requirements are changing the traditional goals of petroleum refineries, frequently imposing a riddle whose answer is quite intricate. Clearly, alternative intelligent solutions are not straightforward and must be developed, requiring much effort and research. Nevertheless, the reduction of greenhouse-gas emissions by fostering the deployment of alternative raw materials such as biomass is an option that must not be disregarded. In fact, biomass utilisation is playing an important role in the concept entitled "the refinery of the future". At any rate, regardless of the new chemical route chosen, the role of catalysis is sovereign, since it is easier to change the catalyst, rather than changing the entire production systems to generate a new drop-in product. New catalysts must be developed, thereby avoiding rather expensive investment in the hardware of the refinery.

As already stated, the refining of the future will deal with the presence of biomass as an alternative feedstock to the traditional oil feedstock. Therefore, it will comprise the concept of Biorefineries, which, according to the 2008 Farm Act,¹⁻⁵ may be defined as "a facility (including equipment and processes) that converts renewable biomass into biofuels and bio-based products, and may produce electricity". More recently, another important concept described by the term *Integrated Biorefinery*⁶ has been coined. An integrated biorefinery is capable of efficiently converting a broad range of biomass feedstocks into affordable biofuels, biopower, and other bioproducts. By definition, the integrated biorefinery must cope with the problem of residues. Hence, integrated biorefineries are similar to conventional refineries; however, integrated biorefineries still require much research. In other words, new processes must be developed in order to reduce production costs and improve competitiveness. Essentially, the potential of residues must be explored and innovative chemical routes have to be proposed.

The concept of an integrated biorefinery may be applied to several types of traditional refineries, using different raw materials.^{7,8} Furthermore, aiming at the better utilisation of existing facilities, co-processing is often indicated. Co-processing is, by definition, the utilisation of blends in already existing units. In principle, vegetable oils can be rather easily co-processed in the installed facilities of refineries. In addition, different types of bio-oils, resulting from both catalytic and non-catalytic pyrolysis of lignocellulosic biomass, can also undergo processing in different units of the refinery.

Vegetable oils are more easily co-processed in existing refinery facilities. Indeed, co-processing of vegetable oils can be incorporated into a refiner's

operating strategy with minimal detriment to catalyst stability or yields; however, the importance of the base feedstock and operational conditions must not be overlooked.

Coconut, sunflower, maize, olive, peanut and cottonseed oils are some of the potential oils proposed for studies in co-processing. Nevertheless, soybean, palm and rapeseed oils, which are readily available, are the most studied vegetable oils.⁹

The basic scheme of vegetable oil processing in refineries encompasses two units: the hydroprocessing unit and the fluid catalytic cracking (FCC) unit. As far as the hydroprocessing unit is concerned, the idea is rather simple. Blend certain amounts of vegetable oils with the regular feedstock of the unit and then allow the operation to proceed as usual. Of course, operational conditions will have to be adjusted to the new feedstock, since a new reaction scheme will take place. As a matter of fact, the following reactions will be carried out:

- (a) In the first step of the reaction pathway, the unsaturated fatty acid chains will be rapidly converted into fully saturated *n*-paraffins;
- (b) In the second step, the bonds between fatty acids and glycerol must be broken (cleavage of a carbon–oxygen bond), thereby ensuring that the products will have appropriate size for the diesel pool.

It is obvious that a convenient catalyst should be developed to promote both reactions.

Regarding FCC units, the same philosophy is used, that is to say, the policy of blending. However, unlike hydrotreating units where the catalyst cannot be changed without the unit being shutdown to reload the reactor, continuous replacement of catalyst in the FCC unit permits the refiner to change the inventory and use tailor-made catalyst formulations to optimize yields.

The problems of co-processing bio-oils are often related to the instability thereof. 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. In fact, bio-oils resulting from fast pyrolysis are not a product of thermodynamic equilibrium, being produced *via* short contact times and rapid cooling or quenching.

The main reactions that may take place upon storage of bio-oils are the following:⁹

- Organic acids with alcohols to form esters and water;
- Organic acids with olefins to form esters;
- Aldehydes and water to form hydrates;
- Aldehydes and alcohols to form hemiacetals, or acetals and water;
- Aldehydes to form oligomers and resins;
- Aldehydes and phenolics to form resins and water;

- Aldehydes and proteins to form oligomers;
- Organic sulphur to form oligomers;
- Unsaturated compounds to form polyolefins;
- Air oxidation to form more acids and reactive peroxides that catalyze the polymerization of unsaturated compounds.

All those reactions will generate a product slate that will bring about an increase in the viscosity of bio-oils with time of storage. For that reason, a “stability parameter” has been proposed.¹⁰ This parameter represents the slope of a plot of viscosity (cp) against time (h). This plot is frequently a straight line with a positive derivative, which represents the stability parameter. It is worth noticing that aging effects are a function of temperature, being accelerated as the temperature increases. An Arrhenius plot of the stability parameter gives straight lines, which is a clear indication that the increase in viscosity is a result of chemical reactions.¹¹

It is clear that aging is a result of several reactions, most of them undesirable. Such reactions will increase the average molecular weight of the bio-oil. Hence, chemical properties of bio-oils will certainly change upon aging. For that reason, it is likely that the stability parameter will affect the performance of different bio-oils whenever co-processing is concerned.

Ramirez and co-workers^{10,12,13} have issued several interesting patents in which bio-oils from different sources may undergo upgrading in order to be processed in the refineries. Indeed, different types of treatments may improve the upgrading of bio-oils. Such possibilities are depicted in Figure 1.1. It must be borne in mind, however, that the required upgrading process will depend on the type of bio-oil produced and the stability thereof. Most of the existing biomass conversion processes produce low-quality bio-oils, since they are highly unstable and present high oxygen contents. These bio-oils will often require extensive secondary upgrading and a special refining scheme, which may even include more than one upgrading step.

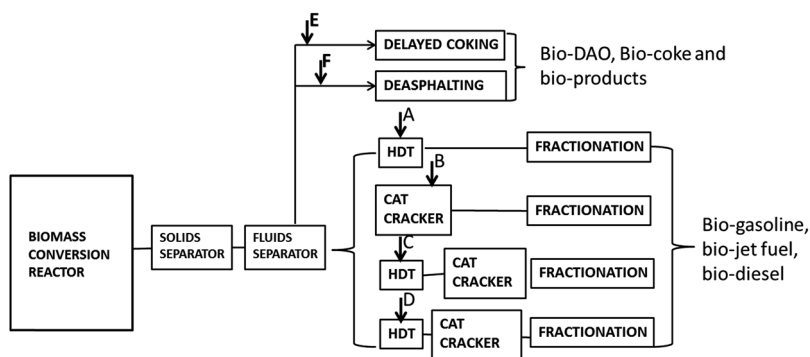


Figure 1.1 Potential use of bio-oil in a refinery. (Adapted from ref. 13).

Other traditional processes carried out in the refineries such as delayed coking and deasphalting may employ alternative feedstocks in which vegetable oils or bio-oils are blended with the regular feedstock. Hereinafter, such possibilities will be discussed along with hydroprocessing and FCC.

1.2 Bio-oil in FCC

Fluidized catalytic cracking (FCC) is a conversion process in petroleum refining schemes, which aims to reduce the molecular mass of molecules from the streams produced by petroleum fractionation. Usually, the FCC feed contains fractions of molecules produced in the atmospheric and vacuum distillation of petroleum, which are known as gasoils. It is also possible to complete the FCC feed with streams produced by other types of fractionation, such as the deasphalted oil obtained in the solvent deasphalting process. The reactions that occur in the FCC process convert these heavy fractions into more noble products, maximizing the yields in the distillation range of LPG, diesel and, mainly, gasoline. Among the processes found in refineries, FCC is the one that has been most studied to allow the insertion of bio-oil in the refining scheme through co-processing strategies. The acidic character of the FCC cracking catalyst allows the occurrence of reactions that promote the removal of oxygen from the bio-oil molecules, eliminating it in the form of CO, CO₂ and H₂O.

For a long time, the deoxygenation processes of molecules originating from biomass conversion in the presence of zeolitic catalysts have been studied. In 1986, Chen *et al.* evaluated the conversion of sugars catalyzed by ZSM-5 zeolite, reporting the production of hydrocarbons, coke, water and carbon oxides.¹⁴ With bio-oil, initially, the most used approach, and the object of several publications, consisted of the improvement of this renewable stream through its conversion *via* acid catalysis. Adjaye *et al.* in 1995^{15,16} were pioneers in the attempt to upgrade a bio-oil produced by Ensyn (a leader Company involved in the production of biocrudes from forest and agriculture residues) using a fixed bed zeolite catalyst. Production of coke, gases, water, and an organic phase containing several hydrocarbons was observed. It was shown that the yields of hydrocarbons were dependent on the type of catalyst, with HZSM-5 generating the highest selectivity to these products. In addition, it was found that the aromaticity of the organic phase was also higher with the use of HZSM-5, followed by H-mordenite, revealing a possibility to alter the product profile only by changing the type of catalyst.

At that time, the incentive to develop advanced biofuels was not so intense. Yet, several studies on the same theme were followed and the effectiveness of zeolitic catalysts in the conversion of bio-oil to hydrocarbons was already scientifically known. 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. Therefore, the mechanisms require the simultaneous rejection of carbon and/or hydrogen in order to reduce

the oxygen content. With this knowledge, Chen *et al.*¹⁴ proposed the use of a modified hydrogen-carbon ratio to evaluate the most suitable conditions of treatment of the bio-oil through catalytic cracking – the effective C:H ratio. This parameter differentiates the oxygen-bound hydrogen from the carbon-bound hydrogen, since they have different characteristics for the catalytic cracking process.

Another pioneering group in bio-oil catalytic cracking studies was Samolada *et al.*, and they evaluated the non-catalytic hydrogenation of bio-oils and their subsequent processing in a bench scale FCC unit (50–300 g h⁻¹) with commercial catalysts. An increase in coke yield was observed; nevertheless, it was shown that its co-processing with LCO in the proportion 15/85 was able to reduce this tendency. Besides, it was possible to produce a specified gasoline with high octane number, despite the reduction in the yield of this fraction.¹⁷

In the last decade, with the incentive to increase biofuel participation in energy matrices, especially biofuels from lignocellulosic material, the intensification of studies contemplating bio-oil improvement and its use as an automotive fuel was observed. In this context, and due to the well-known ability of zeolite catalysts to convert bio-oil-derived molecules to hydrocarbons under FCC conditions, research groups around the world have begun to study the co-processing of bio-oil with fossil streams in FCC. In 1997, a study was published in the report AIR2-CT93-1086, indicating the FCC feed as a potential point of insertion of bio-oil in the refining scheme.¹⁸ Nevertheless, the lack of its feasibility due to bio-oil insolubility in fossil streams was noted.

In 2007, Corma *et al.* published the first scientific results of renewable feed cracking along with the fossil stream. The scenario was promising for advanced biofuels, with incentives through public policies, international cooperation agreements and high petroleum prices. It was the beginning of the dissemination studies on the development of a process that would serve as a basis for a gradual transition between the fossil and the renewable matrix. This new approach was also taking advantage of the existing units in the refining schemes and the knowledge acquired over time from catalytic cracking processes. They studied the co-processing of gasoils and oxygenated molecules in FCC bench units, publishing the results of the performance evaluation of several catalysts in the conversion of glycerol, sorbitol and mixtures of these two compounds with vacuum gasoil.¹⁹ In 2008, Domine *et al.* published a co-processing study using model bio-oil and diesel molecules, finding higher deactivation rates in the presence of oxygenated compounds. They also observed CO production due to 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.²⁰

The first study beyond the bench scale was published by Lappas *et al.* in 2009, which co-processed 2.5% of hydrotreated bio-oil with 85% of vacuum gas oil in a FCC pilot unit, diluting it with 12.5% of light cycle oil (LCO) to

facilitate the feed injection and dispersion. Despite the small differences, they observed an increase in the yields of coke and naphtha, with a reduction in the gas yield.²¹

Graça *et al.* concentrated their efforts on the understanding of the catalytic mechanisms and the proposal of more efficient catalysts for the cracking of feeds containing oxygenated compounds. In 2009, they published a study in which three model molecules of bio-oil (phenol, acetic acid and hydroxy-acetone) were mixed to a gasoil in order to evaluate the co-processing in a bench scale FCC unit.²² In this study, two different commercial catalytic systems were used, one being 100% e-CAT and the other one containing 10% ZSM-5. Increased conversion was observed when the oxygenated molecules were co-processed with e-CAT. With the additive, it was observed that the presence of oxygenates reduced the fossil molecule conversion, which was attributed to the greater interaction between these molecules and the ZSM-5 sites.

Subsequently, Graça *et al.* published a series of studies with the objective of specifically evaluating the impact of phenolic compounds in catalytic cracking with different types of catalytic systems.^{23–26} The tests used phenol and guaiacol as model molecules of bio-oil and *n*-heptane and methyl-cyclohexane as gasoil model molecules. It was found that in the co-processing of phenolic compounds with paraffinic feeds, the deleterious effects of oxygenated compounds on catalyst deactivation were not as significant as with naphthenic feeds. The size effect of the oxygenated molecule on the deactivation of the systems was also evaluated, concluding that guaiacol, due to its higher kinetic diameter, was preferentially adsorbed at the intersections of the channels near or at the entrance of the catalyst pores, facilitating their desorption when subjected to FCC temperatures. It was concluded, therefore, that phenol causes more damage than guaiacol in relation to FCC catalytic system deactivation when operating in co-processing mode.

Graça *et al.* published a new study evaluating the effect of co-processing guaiacol with *n*-heptane, but now also with actual gasoil, using several zeolitic catalysts.²⁷ The systems tested were HZSM-5, HY, commercial e-CAT and e-CAT with ZSM-5. Again, a negative effect of the presence of guaiacol in relation to the catalyst deactivation rate was observed, especially with HZSM-5 and with e-CAT and in the presence of the actual feed. With the other systems, the deactivation intensification in the presence of oxygenates was reduced. Regarding product quality, the presence of phenolic compounds in the gasoline range was observed, indicating that there are molecules of this chemical class that are inert to cracking and boil in the temperature range of naphtha.

FCC co-processing was one of the routes contemplated for the transformation of bio-oil into biofuels. However, other routes have also been evaluated and developed, such as, for example, the hydrogenation of bio-oil. In this process, discussed in more detail hereinafter, oxygen rejection occurs through hydrodeoxygenation reactions, and may even generate a

hydrocarbon product without heteroatoms. However, the severity of the process, the need for catalysts with noble metals and the high demand for hydrogen indicate that the cost associated with the production of hydrocarbons by this route may hardly reach economic viability. Nonetheless, less severe hydrogenation processes could be used as a pre-treatment of bio-oil for FCC co-processing.

Mercarder *et al.* decided to evaluate the complementarity of the hydrogenation and cracking processes for the transformation of bio-oil into bio-fuel. They understood that this strategy could significantly reduce the cost of hydrogenation by reducing the desired degree of hydrodeoxygenation, as well as facilitating cracking by raising the bio-oil effective C/H ratio. They published two studies evaluating the effects of hydrodeoxygenation conditions of a bio-oil produced by VTT, with the aim of co-processing the hydrogenated product with atmospheric residue in the FCC.^{28,29} It was shown that the higher severity of the hydrogenation was responsible for the increase of carbon recovery in the organic product, but it did not significantly affect the feasibility of bio-oil co-processing in a bench scale FCC unit. It was also observed that the conversion of the most reactive oxygenated functional groups, which would be responsible for the increase of the repolymerization reactions, already occurs under milder hydrogenation conditions. In the experiments without atmospheric residue, a significant increase in coke and gas yields was observed, revealing the importance of the presence of a non-hydrogen deficient fossil stream during catalytic co-cracking.

Using the same strategy, in 2011, Fogassy *et al.* evaluated the co-processing of 20% hydrotreated bio-oil with gasoil in a MAT unit using HZSM-5, HY and FCC equilibrium catalysts.³⁰ Steric hindrances and catalyst acidity effects were observed in the feed conversion, which resulted in a scheme of cracking mechanisms during co-processing. It was also shown that the higher pore size and the higher acidity of zeolite HY favoured the overcracking of molecules in the naphtha and LCO ranges, increasing the yield of gases, LPG and coke. Furthermore, HY zeolite allowed the occurrence of bimolecular reactions, increasing the concentration of paraffinic and aromatic compounds in the liquid fractions. It was also verified that the lignin oligomers did not enter into the pores of the catalytic systems, being cracked on the catalyst surface, with consequent coke generation and blocked access to the acid sites.

Since the hydrogenation of the bio-oil could allow its subsequent processing in FCC, other processes that had the capacity to reduce its oxygen content could act in the same way. In 2012, Agblevor *et al.* used a product of the catalytic pyrolysis of biomass, denominated in this study as bio-crude, as a renewable feed for FCC co-processing.³¹ This bio-crude is more stable than bio-oil due to the more efficient removal of reactive functional groups by deoxygenation reactions promoted during pyrolysis in the presence of a catalyst. The experiment feeds consisted of mixtures of 15% m m⁻¹ bio-crude and 85% m m⁻¹ gasoil, and were evaluated in an ACE unit (Advanced Cracking Evaluation) using an equilibrium catalyst. Evaluating the results under isoconversion, the yields of naphtha, light cycle oil (LCO), heavy cycle oil

(HCO) and gas liquid processing (GLP) did not change when the bio-crude was introduced, but the liquid fractions showed an increased presence of aromatic carbon.

One of the relevant issues in bio-oil improvement studies is the ability of the process to retain renewable carbon in noble fractions, such as gasoline and diesel. Fogassy *et al.*, in 2012, presented a discussion on the distribution of renewable carbon during bio-oil co-processing experiments in FCC.³² To do this, they conducted a series of experiments by co-processing 10% hydrogenated bio-oil with 90% vacuum gas oil in a bench scale FCC unit. In relation to the analytical technique used to determine the bio-carbon distribution, ¹⁴C isotopic analysis was used as an indication of the renewable carbon content. It has been observed that most of the carbon present in bio-oil is transformed into gases (10.6% bio-carbon) and coke (15.8% bio-carbon), whereas gasoline has approximately only 7% bio-carbon. In this study, the increase in coke yield was explained by two mechanisms: repolymerization of oxygenated molecules, especially phenolic compounds; and hydrogen deficiency, due to the occurrence of deoxygenation reactions *via* dehydration.

Schuurman *et al.* discussed in a review published in 2013 the impacts of bio-oil co-processing on FCC units.³³ They noticed that most studies show that the co-processing of HDO with gasoil does not imply a loss in gasoline yield, but results in a reduction in the production of bottoms and GLP, as well as an increase of coke yield. In addition, the gasoline produced by the co-processing strategy has higher levels of aromatic and olefinic compounds, which in general lead to an increase in octane numbers. This characteristic – higher levels of unsaturation – is attributed to the increase in the consumption of hydrogen, which is produced through hydrogen transfer, by the deoxygenation of the molecules from the bio-oil. The decrease of the reduction character of the reaction media leads to lower rates of hydrogenation of unsaturated compounds. This phenomenon can also explain the increase in coke production. Another relevant fact is the inertia of the phenolic compounds to the FCC catalysts, so that they always appear in the products obtained by co-processing of bio-oil. In the review, the mechanisms involved in the co-processing are also discussed, indicating the preferential adsorption of the oxygenated compounds in the strongest external acid sites, mainly Lewis acid sites (EFAL), reducing their availability for the cracking of hydrocarbons, especially those of greater molecular mass, which do not access the pores. Because of this preferential adsorption, there is an increase in the yield of coke, which in turn ends up blocking the pores and reducing the conversion rates, as shown in several studies with model molecules.

A study comparing the effectiveness of processes to improve the quality of bio-oil before FCC co-processing was published in 2014. Thegarid *et al.* conducted a study comparing the co-processing of 10% hydrotreated bio-oil and catalytic bio-oil (CPO) with vacuum gas oil in a bench scale FCC unit.³⁴ With both bio-oils, an increase in gas production was observed, with CO₂ appearing in their compositions and hydrogen content decreasing. No significant changes were observed in the gasoline yield, although the aromatic content

increased in the co-processing experiments, especially at high catalyst-to-oil (CTO) ratios. Phenol molecules were found in the co-processing products, being even more significant in cases with CPO. LCO was more converted in the presence of bio-oils and a great increase in coke yield was observed. Lastly, they concluded from the results that the bio-oil produced by catalytic pyrolysis is more appropriate to be co-processed in FCC, especially due to the greater retention of renewable carbon in liquid products.

Gueudré *et al.* published a study using the same data as Thegarid *et al.* (2014),³⁴ but now focusing on the effects related to coke.³⁵ It was verified that the coke yield increased in both co-processing cases, being higher in the presence of the hydrogenated bio-oil. In addition, it was found that only 40% of the coke generated during co-processing has a renewable origin, which can be explained by the occurrence of higher rates of hydrogen transfer from the fossil molecules and their consequent aromatization and transformation into coke, when the bio-oil is present. They also verified that the co-processing is responsible for the production of a coke with distinct chemical characteristics, making it more easily manageable due to the presence of oxygen and less graphitic structure. However, this coke generated by the bio-oil is responsible for accelerating the catalyst deactivation, changing its acidity and crystallinity more quickly.

Lindfors *et al.*, in 2015, compared some possible steps upstream of FCC co-processing.³⁶ They carried out a study contemplating the producing and co-cracking of bio-oil with low humidity, catalytic bio-oil or hydrotreated bio-oil with 80% vacuum gas oil in a FCC bench unit. An increase in gasoline yield was observed in the co-processing experiments, with catalytic bio-oil being the best case in this respect. It was explained that possibly some aromatic compounds present in the catalytic bio-oil are already in the gasoline range and they are not cracked during the process, explaining the higher naphtha yield. Regarding coke yield, all co-processing experiments generated a higher amount of solid fraction. However, it is possible to distinguish the result of the HDO sample, whose value was the closest to pure gasoil. Thus, it was concluded that the oxygen content could not be considered as the only criterion to predict the tendency to produce coke during co-cracking of bio-oil. It was also suggested that a better correlation can be obtained by using the micro carbon residue and the effective H/C ratio to estimate coke yield.

In 2015, Pinho *et al.* published the first results of bio-oil co-processing with gasoil on a demonstration scale unit, with a feed rate of 150 kg h⁻¹.³⁷ The bio-oil used was produced by BTG in a rotary cone unit using pine sawdust. Two blends were tested, one with 10% and the other 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, thus avoiding heating the bio-oil at a temperature above 50 °C. It was observed that 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. In order to quantify the renewable carbon in the gasoline range, the products were sent for isotopic analysis of ^{14}C . The results showed that when 10% bio-oil is co-processed, only 2% of the gasoline carbon was from renewable origin, while when 20% bio-oil underwent co-processing, the content was between 3 and 5%. Through the mass balance, it was possible to determine that this value corresponds to 30% of the carbon present in the biomass, and this value is higher than that estimated by Fogassy *et al.* (2012).³² This study also revealed a scale effect, mainly related to the segregated injection, which makes the results from demonstration units better than those obtained on bench scale, especially in relation to the coke yield. Due the early bio-oil injection and its small proportion, temperature and CTO tend to be much higher when the bed meets the renewable charge. The higher temperature promotes a thermal cracking of the renewable current, which facilitates its secondary conversion into the pores of the catalyst.

By 2015, Graça *et al.* were continuing their studies on catalyst synthesis and evaluation, focusing on the co-processing of oxygenated molecules in FCC. They published the results of a study evaluating the effect of FCC catalysts containing ZSM-5 zeolites with different textural properties in the co-processing of model diesel and bio-oil molecules.³⁸ The aim was to minimize the deactivation caused by the presence of phenolic compounds, as reported in previous publications. Several ZSM-5 catalysts were prepared by alkaline post-treatment of the original sample, with the main objective of altering their pore distribution. It was found that mesopore formation, keeping the existence of microporosity, reduces the rate of deactivation of the catalyst in the presence of phenol, without any loss of shape selectivity.

Wang *et al.*, in 2016, produced catalytic bio-oil and co-processed it with 90% gasoil in a FCC pilot unit.³⁹ No operational problems were observed up to 10% bio-oil, and the co-processing led to higher conversions than that with only the fossil feed in the same CTO. In addition, there was no change in the yield profile of most of the products. The only exception was the gaseous fraction, especially hydrogen, which presented lower yields due to its transfer between fossil and renewable molecules. Finally, it was possible to estimate through isotopic analysis of carbon 14 that 7% of the carbon present in the gasoline range had a renewable origin when 10% bio-oil was co-processed, which is significantly higher than that found during the thermal bio-oil co-processing.

In 2016, Ibarra *et al.* conducted experiments co-processing 20% bio-oil with gasoil in order to better understand the mechanisms of coke generation and its characteristics.⁴⁰ The conversions were greater when bio-oil was cracked, either pure or mixed with gasoil. In the latter case, a synergistic effect was also observed, which made the conversion of the mixture higher than those determined for the pure feeds. Although the presence of bio-oil is responsible for higher coke yields, it was noticed that the deposit generated during co-processing is less deleterious than with gasoil alone. The solid deposit originating from bio-oil has a larger fraction soluble in

dichloromethane, which is lighter than the insoluble coke. It was observed that, during co-processing, there was an attenuation of the coke deposit, especially that from insoluble coke, explained here by the higher amount of steam when the bio-oil is also fed, which comes from the own renewable feed. Steam is responsible for the rectification of insoluble coke precursors from catalyst pores, and it competes with hydrocarbons for the acid sites, reducing the condensation reaction rates. It was also observed that the insoluble coke is usually deposited in the catalyst meso and macropores, while the coke generated during the bio-oil cracking is deposited in the micropores of the catalyst. Still, hydrogen transfer reactions between gasoil and bio-oil also act to reduce coke formation from oxygenates and the high temperatures help in the cracking of the coke from the bio-oil, contributing to reducing the deactivation route *via* oxygenates.

A new study on demonstration scale was published in 2017. Pinho *et al.* tested the co-processing of 5% m m^{-1} and 10% m m^{-1} bio-oil, confirming the positive effect of the axially segregated injection.⁴¹ In the presence of bio-oil, a reduction in gas and LPG production was observed, with an increase in the olefinicity of the C3 and C4 molecules. In one of the series of experiments, gasoline overcracking was observed for all the feeds, maximizing yields between 68% and 69% conversion. At these points, gasoline yields were similar in the tests with and without bio-oil. LCO yield increased only in the 10% test and the yield of bottom products increased slightly for the two cases with bio-oil. Regarding the presence of oxygenated compounds in the cracked effluent, only phenolic compounds were detected, which, depending on the amount, may be a benefit to fuel stability. Finally, it was determined by carbon 14 isotopic analysis that, for the tests with 5% bio-oil, there is 1% renewable carbon in gasoline.

More recently, Gueudré *et al.* published a new study evaluating the effect of the bio-oil hydrogenation severity in subsequent co-processing in a FCC bench scale unit.⁴² They observed that all tests with bio-oil showed increased naphtha yields, but no influence of the hydrogenation step on this variable was observed. On the other hand, the gasoline quality experienced an optimum hydrodeoxygenation severity point, determined by the MON and RON maximum values found in gasoline, with a H_2 consumption of 202 NL per kg of pyrolysis liquid, equivalent to an intermediate hydrogenation.

The intensification of studies and the significant number of publications and forums on co-processing of bio-oil in FCC have been improving the maturity of this route. Some difficulties, such as the increase in the deactivation rate of the catalytic systems, have already been addressed and have technological solutions. The increase in the number of studies has also provided intense analytical developments in the characterization of oxygen-containing matrices, and these techniques have improved the understanding of the phenomena involved in co-processing. Tests in a demonstration unit, conducted by Pinho *et al.*, demonstrated the advantages of scaling up and indicated the technical feasibility of the route for bio-oil insertion into the

refining scheme, bringing the possibility of producing second-generation biofuels by co-processing closer.

1.3 Co-processing in Hydrotreating Units

Hydrotreating (HDT) processes have been employed for decades in the petroleum refining industries with different purposes, such as fuel contaminant removal or upgrading of heavier streams.⁷ In the past 5 years, the demand for renewable jet fuel and green diesel, both commonly produced by hydrotreatment of vegetable oil, has spiked. This has occurred mostly because of new regulations regarding CO₂ emissions. These green fuels are usually blended with fossil fuels before reaching the final consumer. This represents a great disadvantage from the logistics point of view, if there is one plant dedicated to producing biofuels and the fossil fuels are produced in refineries. This logistic operation devoted to blending fossil fuels and green fuels comes at a cost not only from the economic point of view, but also from the environmental one. On the other hand, when vegetable oil is co-processed in hydro-treatment units in refineries with fossil streams to produce fuels, there is no need for blending. Moreover, the capital expenditure (CAPEX) needed for co-processing vegetable oil in HDT units is almost negligible if compared to the capital invested for the construction of a new plant devoted to hydroprocessed esters and fatty acids (HEFA process), especially if the HDT unit has been working in subcapacity mode.

The traditional catalysts employed in the HDT process are tungsten/molybdenum sulphide catalysts supported on alumina and promoted with Ni and Co. The reactor is a trickle-bed type and the process is carried out at high temperature and pressure. The most relevant reactions in HDT are hydrodesulphurisation (I, HDS), hydrodenitrogenation (II, HDN), hydrodemetallization (III, HDM) and hydrodeoxygenation (IV, HDO). In the case of co-processing vegetable oil, HDO and HDN are undoubtedly especially pertinent. These reactions involve the hydrogenolysis of the carbon-heteroatom bond. Depending on the source of the vegetable oil, other reactions such as the hydrogenation of olefins (HO) can be very relevant as well.^{7,43,44}

In the traditional HDT process, generally, a hydrocarbon base or a mixture of hydrocarbons and vegetable oil containing no more than 20% renewable oil is mixed with a hydrogen stream, resulting in the feed for the reactor. This feed is pre-heated and injected into the first catalytic bed at temperatures between 220–350 °C. Most of the reactions are exothermic, as are most hydrogenations. To achieve a better temperature control inside the reactor, the amount of hydrogen mixed with the feed stream is not sufficient for full conversion. Because of that, another stream of hydrogen must be injected between the first and second bed of the reactor.

From the process engineering perspective, one of the challenges when co-processing vegetable oil in HDT units is the high exothermicity of the triglyceride conversion associated with the generation of water, CO and CO₂

gases. That is the reason why no more than 20% of renewable oil can be co-processed in traditional HDT units without major modifications in the process hardware. From the catalysis point of view, much work has been devoted to understanding the effect of co-processing vegetable oil on the activity and stability of the traditional HDT catalysts.

In this context, a lot of work has been done investigating the effect of additional water, CO and CO₂ on conventional HDT catalytic systems.^{45–48} The CO₂ produced due to decarboxylation greatly affects the activity of the HDT catalysts. One reason for that is the competition for hydrogen between the desired reactions HDS/HDN/HDO and the undesired reaction triggered by CO₂ addition to the systems.⁴⁶ Among these undesired reactions, the more relevant is the RWGS reaction, consuming H₂ for the formation of CO. It is also interesting to observe that depending on the operational conditions, the effect of CO₂ can be more relevant. For the case of HDN, more severe conditions lead to greater activity loss. On the other hand, for HDS, higher temperatures result in less activity loss. Another important reaction taking place in the HDT reactor when co-processing renewable oil is decarbonylation, leading to CO and water formation. The effect of CO has also been extensively investigated in the literature,^{45,49,50} and it has been very well established that the presence of CO in the reaction causes a loss of activity in HDN, HDO and especially HDS. This loss of activity can be attributed mainly to competitive adsorption of CO on the catalyst active sites. Finally, the water formed due to deoxygenation and decarbonylation also affects the activity of traditional HDT catalysts. This subject is a matter of controversy, with some studies attributing a slight decrease of activity to the presence of water,⁵¹ while others argue that water does not significantly affect the catalytic activity during HDT.^{52,53} There are even results which indicate an increase of activity as a result of low concentrations of H₂O in HDT streams.⁵² More recently, Berzegianni, Dagonikou and Sklari⁴⁵ published a paper as an attempt to clarify that question. The results of this work support the idea that H₂O addition has no significant effect on catalytic activity. Moreover, their results demonstrate that even the loss of surface area of HDT catalysts during long times on streams cannot be attributed to the presence of water.

1.4 Co-processing Bio-oil in HDT Units

A simplified but representative composition of a regular bio-oil would be around 50 wt% carbon, 7 wt% hydrogen and 43 wt% oxygen.⁵⁴ Thus, the high oxygen content of bio-oils, which translates also into high water content, implies a much lower energy density (15–19 MJ kg⁻¹) when compared to petroleum oil (40 MJ kg⁻¹).⁵⁵ Moreover, due to the high instability of bio-oil, associated with problems of phase separation and immiscibility with regular fossil fuels, high natural acidity and viscosity, the use of bio-oil directly as a liquid fuel is problematic.^{56,57} Therefore, proper bio-oil upgrading is essential to overcome bio-oil natural deficiencies and to use it efficiently as a

liquid fuel. Hydrotreatment (HDT) is a promising method for bio-oil upgrading, in which oxygen levels can be significantly reduced, by means of water formation upon reaction with hydrogen. Traditionally, HDT of bio-oil is performed under high H_2 pressures (>70 bar) and multiple temperature stages are employed.^{58,59}

One of the major problems related to bio-oil upgrading *via* hydrotreatment is the severe catalyst deactivation observed during reaction.^{59,60} Phenolic compounds present in bio-oil are believed to strongly adsorb on the surface of the catalyst, forming species that are precursors of coking.⁵⁵ Accordingly, carbon deposits, or coke formation, are the main reason for catalyst deactivation during hydrotreatment of bio-oil and intense efforts have been devoted in order to design new catalysts less propitious to coke deposits. In more severe cases, even reactor plugging may occur due to intense carbon deposit formation.⁶¹ The most studied catalysts for bio-oil HDT are noble metals, which are rather expensive, or transition metal sulphides, which are already employed as catalysts for petroleum oil HDT. Oxygen content in bio-oil can be reduced to levels as low as 0.2 wt% by means of hydrodeoxygenation.⁶²

The main idea behind co-processing bio-oil with petroleum oil is to benefit from the vast and consolidated infrastructure of oil refineries. In this sense, not only capital, but also operational costs could be drastically reduced and become essential for the economic feasibility of bio-oil upgrading. In addition, by blending bio-oil and petroleum oil feeds or by just performing, essentially, the same unit operations with bio-oil that are already done with petroleum oil, a very similar product slate could be obtained.⁵⁸ Hence, drop-in fuels and chemicals could be produced with no need for drastic changes in the already consolidated supply chain.

Nevertheless, as already mentioned before, raw bio-oil has some unique properties that make the direct blending of bio-oil with petroleum oil, for instance, in a hydrotreatment unit, not trivial at all. Several authors have proposed that the direct blending of these two streams would be unfeasible and at least a mild pre-HDT of bio-oil, in order to lower its oxygen content and acidity, would be necessary.^{58,62–65} A reduction in oxygen levels to at least 7 wt% is recommended before blending bio-oil with other refinery streams.⁶⁵ Differently from petroleum oil, bio-oil has low nitrogen and sulphur contents, so where bio-oil HDT is concerned, the main reaction occurring is hydrodeoxygenation (HDO), rather than hydrodenitrogenation (HDN) or hydrodesulphurisation (HDS). Moreover, the number of heteroatoms, mainly oxygen, present in bio-oils is an order of magnitude higher when compared to petroleum oil.^{62,63} Obviously, there are several other reactions that may also occur such as decarbonylation, decarboxylation, cracking/hydrocracking, isomerisation, among others. The type of catalyst support used may have a strong influence on the extent of these reactions. Although removing oxygen *via* HDO has some drawbacks, such as high hydrogen consumption, removing oxygen *via* decarbonylation/decarboxylation, yielding CO and CO_2 , reduces the overall carbon efficiency of the process.⁶² In a nutshell, removing

oxygen as water while avoiding saturation of the remaining hydrocarbons would be the best outcome.^{58,66} In that way, not only would hydrogen consumption and carbon loss be minimized, but also unsaturated hydrocarbons, such as alkenes and aromatics, that have higher value, would be produced. However, it is known that removing oxygen *via* HDT is easier if the hydrocarbon is already saturated.⁵⁸ Therefore, this offers another difficulty to overcome where proper catalyst design is concerned. Ideally, the catalytic system should be very active to HDO, but not so much for the saturation of hydrocarbons, robust, in the sense of low coke formation and stability properties, and cheap. These characteristics introduce a barrier that should be surpassed in order to design appropriate catalysts for bio-oil HDT.

During the first studies regarding bio-oil HDT, it was found that efficiently performing HDT in a single stage, with high temperatures (>300 °C), was challenging due to severe coke and heavy tar formation that, eventually, resulted in reactor clogging and catalyst deactivation.^{58,65,66} Therefore, a two-step approach was developed by Elliot *et al.*,⁶⁷ in which the first stage involved a mild HDT step at lower temperatures (<300 °C) in order to stabilize the bio-oil and reduce coke like material formation.^{66,68} After a second stage, at temperatures of ~350 °C, a significant reduction in the bio-oil oxygen content could be achieved. However, coke formation can still be an issue even with this strategy. The yield of upgraded product, in this case, was 30–50 wt% of the original bio-oil, the rest being gaseous products, water and coke.⁶⁵

As Co-MoS₂/γ-Al₂O₃ and Ni-MoS₂/γ-Al₂O₃ are traditional HDT catalysts employed in the refinery, they were a natural starting choice for bio-oil HDO. When this type of catalyst is employed, Co and Ni actually play the role of promoters, donating electrons to the molybdenum atoms. As a result, the bond between molybdenum and sulphur is weakened, generating a sulphur vacancy site, which is, indeed, the active site for HDS and HDO reactions.⁶⁹ With the progress of the reaction, the catalyst may oxidize, which translates into a decrease in activity. Therefore, co-feeding H₂S, in order to regenerate the sulphide sites, might be necessary to keep the catalyst activity.⁶⁹ Transitional and noble metal based catalysts have also been applied to bio-oil HDO with a certain degree of success. However, the use of noble metals as catalysts is rather dependent on the content of sulphur in the bio-oil, as they are sensitive to high S levels and could be readily poisoned, not to mention their high prices.⁶³

Where HDT catalysts are concerned, γ-Al₂O₃ is the most common support utilised. However, in the case of bio-oil HDO, the presence of water allied with high temperatures can promote the conversion of alumina into boehmite (AlO(OH)), which in turn can oxidize the Ni particles present in the catalyst. Moreover, the relatively high acidity of alumina is responsible for a great affinity with phenolic compounds that, ultimately, are responsible for coke formation.^{62,63,69} Therefore, several other supports have been studied as HDO catalysts. Carbon and SiO₂ appear to be promising alternatives due to their neutral nature, able to avoid coke formation. However, the use of carbon as

support introduced a new problem regarding catalyst regeneration, since the catalysts could not be regenerated through a simple calcination procedure.^{64,65} Titania (TiO_2), ceria (CeO_2) and zirconia (ZrO_2), are also some interesting alternatives, because even though they present some intrinsic acidity, they have the ability to activate oxy-compounds, resulting in an increase in the activity.⁶⁹

Another possible strategy to overcome the problems associated with carbon deposition during bio-oil HDT is to add a hydrogen donor, such as methanol, tetralin or decalin, to the bio-oil feed. The added hydrogen donors play several roles in this case. First of all, they improve the extent of cracking and hydrogenation reactions but also, by diluting the bio-oil feed, they decrease the probability of polymerization at high temperatures.⁶¹

Table 1.1 sum ups some relevant studies concerning bio-oil HDT from recent years. Baldauf *et al.*⁷⁰ reported high deoxygenation rates of 88–99.9% for bio-oil upgrading in a continuous bench scale unit. The authors employed commercial CoMo and NiMo HDT catalysts and oil yields of 32–36% were obtained at temperatures ranging from 350 to 370 °C. However, rapid catalyst deactivation, coking and plugging were observed. Elliot *et al.*⁷¹ studied different approaches for bio-oil HDT. First, a Pd/C catalyst was employed to perform the HDT of different types of bio-oils at temperatures ranging from 310–360 °C. In this case, solid coke encrusted catalyst particles along with some degree of corrosion in the reactor wall were observed. In a next step, the authors used the previously hydrotreated bio-oil and performed a hydrocracking reaction with a commercial sulphided catalyst provided by UOP. The use of pre-stabilized oil allowed operation at higher temperatures (405 °C) and lower hydrogen pressures without coke formation in the catalyst bed. The last alternative studied was the use of a non-isothermal process where both Pd/C and the commercial catalyst were employed in the same reactor without a uniform temperature profile. The temperatures ranged from 250–410 °C. The results are shown in Table 1.1.

Wildschut *et al.*⁷² studied several heterogeneous noble metal catalysts (Ru/C, Ru/ TiO_2 , Ru/ Al_2O_3 , Pt/C and Pd/C) and typical hydrotreatment catalysts (NiMo-S/ Al_2O_3 and CoMo-S/ Al_2O_3) for bio-oil deep and mild HDO. The authors concluded that the Pd/C catalyst was the most suitable for mild HDO (250 °C, 100 bar H_2). However, for deep HDO (350 °C, 200 bar H_2), Ru/C appears to be the best choice, even though Pd/C also performed well. The authors observed that in a general manner, TiO_2 and C supported catalysts performed much better than alumina supported ones. Venderbosch *et al.*⁷³ evaluated a configuration of four reactors in series working at different temperatures and employing a Ru/C catalyst. Even though the strategy was successful, the use of four different reactors may have a great impact on the costs of the process.

Ardiyanti *et al.*⁷⁴ evaluated a series of bimetallic NiCu catalysts supported on CeO_2 - ZrO_2 , ZrO_2 , SiO_2 , TiO_2 , Sibunite and C for the hydrotreatment of fast pyrolysis oil in a batch reactor at 200 bar H_2 pressure. The reactions

Table 1.1 Relevant studies in bio-oil HDT.

Author	Catalyst	T (°C)	Pressure (bar)	Deoxygenation level (wt%)	Oil yield (wt%)	Time (h) ^a
Baldauf <i>et al.</i> ⁷⁰	CoMo/Al ₂ O ₃	370	–	99.9	32.8	4
	CoMo/Al ₂ O ₃	350	–	95.1	32.7	4
	NiMo/Al ₂ O ₃	370	–	97.2	33.6	6.67
Elliott <i>et al.</i> ⁷¹	Pd/C	340	138	71	62	4
	Pd/C + Commercial C	250–410	138	98.4	50	6.67
Wildschut <i>et al.</i> ⁷²	Commercial	405	103	98.8	61	5
	CoMo/Al ₂ O ₃	250	100	41	27	4
	NiMo/Al ₂ O ₃	250	100	36	30	4
	Ru/Al ₂ O ₃	250	100	37	23	4
	Ru/TiO ₂	250	100	50	37	4
	Ru/C	250	100	45	35	4
	Pd/C	250	100	56	43	4
	Pt/C	250	100	36	58	4
	CoMo/Al ₂ O ₃	350	200	82	25	4
	NiMo/Al ₂ O ₃	350	200	75	27	4
	Ru/Al ₂ O ₃	350	200	79	35	4
	Ru/TiO ₂	350	200	77	66	4
	Ru/C	350	200	86	53	4
	Pd/C	350	200	85	65	4
	Pt/C	350	200	76	27	4
Venderbosch <i>et al.</i> ⁷³	Ru/C	175	200	17	95	0.1
	Ru/C	225	200	35	50	0.1
	Ru/C	175/225/375/400	241	45	54	0.18
	Ru/C	350/375/400/400	230	64	52	0.45
Elliott <i>et al.</i> ⁷⁷	Ru–S/C + NiMo–S	170/390	138	99	45	5.26
	Ru–S/C + CoMo–S/C	170/390	138	95	43	5.26

Ardiyanti <i>et al.</i> ⁷⁴	NiCu/CeO ₂ -ZrO ₂	150/350	200	67.1	40.6	1/3
	NiCu/ZrO ₂	150/350	200	59.9	38.9	1/3
	NiCu/TiO ₂	150/350	200	62.3	45.5	1/3
	NiCu/CRH	150/350	200	55.9	44.9	1/3
	NiCu/Sibunit	150/350	200	86.5	35.9	1/3
	NiCu/ δ -Al ₂ O ₃	150/350	200	57.4	42.2	1/3
Xu <i>et al.</i> ⁷⁸	Ru/C	250	20	36	52	3
	Ru/C	300	20	48	42.3	3
	Ru/C ^b	250	20	46	84.6	3
	Ru/C ^b	280	20	53	76.5	3
	Ru/C ^b	300	20	68	69.4	3
Ardiyanti <i>et al.</i> ⁷⁹	NiPd/SiO ₂	150/350	120 ^c	58.6	39.9	1/3
	NiCu/SiO ₂	150/350	120 ^c	58.1	44.3	1/3
	NiCu/SiO ₂ -ZrO ₂ -La ₂ O ₃	150/350	120 ^c	67.8	37.4	1/3

^aBold values are the inverse of LHSV. Italic values are the inverse of WHSV.

^b1-butanol was used as solvent.

^cPressure at room temperature.

were performed at two temperatures stages, the first at 150 °C for a period of 1 h, and the second at 350 °C for 3 h, in order to avoid polymerization of the bio-oil and resulting coke formation. The authors observed that the highest HDO activity was from the NiCu/TiO₂ catalyst, however a moderate leaching of both Ni and Cu was observed. NiCu/ δ -Al₂O₃ presented the lowest leaching levels. Moreover, the NiCu/TiO₂ catalyst was responsible for the production of an oil product with the highest quality among all catalysts.

Moreover, several other authors, instead of working directly with bio-oil, decided to work with model compounds such as guaiacol. For instance, Gutierrez *et al.*⁷⁵ evaluated the performance of mono and bimetallic noble metal catalysts supported on zirconia, such as, Rh/ZrO₂, Pt/ZrO₂, Pd/ZrO₂, RhPd/ZrO₂, RhPt/ZrO₂ and PdPt/ZrO₂ on guaiacol HDO at 300 °C. The authors also compared the performance of the noble metal catalysts with a traditional CoMo-S/Al₂O₃ catalyst and discovered that the Rh-containing catalysts were more active and less susceptible to coke formation than the conventional catalyst.

In conclusion, although bio-oil is a very promising feedstock, its natural properties require that at least one upgrading step is carried out before co-feeding it with petroleum oil in 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 without having a major impact on them. In addition, there are several studies being carried out aiming at developing new catalysts more suitable to bio-oil hydrotreatment particularities. The major hurdle to be surpassed is the tendency of coke formation over the catalyst surface. Therefore, the area of co-processing bio-oil in HDT units still needs to be studied and new catalytic and process alternatives must be presented in order to make the idea practicable.

1.5 Conclusions

The traditional refining industry has been challenged to comply with environmental pressure and market requirements. In this context, biomass utilisation is playing an important role and catalysis is the main tool for developing “the refinery of the future”. Many studies have been carried out on new technologies with potential to produce hydrocarbon fuels from sustainably sourced feedstocks. It has been shown that 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. Indeed, co-processing utilises the original refinery infrastructure by blending bio-derived oils with the regular feedstock, lowering the costs of fuel production from renewables. However, challenges regarding feedstock storage and handling due to the instability of bio-oils and vegetable oils have to be

surpassed. In addition, the presence of impurities may corrode equipment and poison the catalyst.

Generally speaking, one should consider some important key aspects⁷⁶ related to the perspective of co-processing renewable oils in existing refinery units:

- Guarantee of safety in operation and handling materials. Hazards and generation of new by-products must be taken into account.
- Reliability concerning product quality for complying with clients' property specifications.
- Predictability of the amount of products meeting the market demand and how feedstock oscillations will affect quality and productivity.
- Assured profitability, considering feedstock price and eventual additional costs related to maintenance, catalyst deactivation and inputs.

Regarding the latest research works on co-processing, the main concern still lies in the presence of oxygen compounds in the feedstock, leading to the formation of by-products, with possible catalyst deactivation by poisoning or undesired side-reactions. Moreover, the blending strategy is limited due to the 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 in development for making the technology practicable.

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