



A Review on Coprocessing for Decarbonization: Bio-Oil Deoxygenation Towards FCC

Amanda Lienthier^{1,2*}, Gustavo Brandão de Melo², Ana Luiza Gomes², Luiz Antônio Magalhães Pontes^{2,3}, Ronaldo Costa Santos^{1,3}

¹ Universidade Senai Cimatec, Salvador, Bahia, Brazil

² Universidade Federal da Bahia, Salvador, Bahia, Brazil

³ IBTR, Salvador, Bahia, Brazil

amandalienthier@fieb.org.br

ronaldo.ead@gmail.com

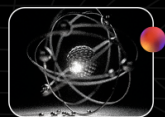
Abstract: The growing demand for sustainable solutions has driven the development of processes for harnessing renewable resources, such as bio-oil derived from the pyrolysis of lignocellulosic biomass. This study presents a review of the literature, categorizing studies published in the last 15 years to evaluate the main pathways of bio-oil deoxygenation. The methodology applied searched indexed databases using keywords such as catalytic pyrolysis, deoxygenation, bio-oil, and zeolites. The results pointed to the main bio-oil deoxygenation pathways—hydrodeoxygenation (HDO), decarboxylation (DCX), and decarbonylation (DCO)—with a focus on the influence of heterogeneous catalyst types and operating parameters, aiming at the technical and environmental feasibility of coprocessing in fluid catalytic cracking (FCC) units. The use of model molecules enabled a deeper understanding of the reaction mechanisms involved and the identification of favorable conditions for producing hydrocarbons compatible with commercial fuels. The analysis of reaction mechanisms and catalyst properties revealed that the selectivity and conversion of deoxygenation reactions are closely related to the nature of active sites, the acidity of the support, and the porous structure of the materials. Metallic catalysts such as Pt, Pd, and Ru demonstrated high catalytic activity but entail high costs, reinforcing the interest in alternatives such as modified zeolites and bifunctional catalysts. Tuning acidity and introducing mesopores proved to be effective strategies for facilitating the diffusion of bulky intermediates, reducing secondary cracking, and minimizing coke formation. However, excessive desilication may compromise the structure and selectivity of the catalysts, requiring tighter control during material preparation. The results indicate that an in-depth investigation of catalysts, combined with precise control of reaction conditions, can optimize the performance of these materials in overcoming structural and operational limitations, thereby enabling the efficient integration of biofuels into conventional refining processes.

Keywords: decarbonization. Deoxygenation. Zeolites. FCC.

1. Introduction

The pressing need to mitigate the effects of climate change has driven decarbonization to become a strategic vector in the transition towards a low-carbon economy, demanding our immediate attention and action [1]. This process, which involves reducing the carbon intensity associated with economic activities—particularly within the energy matrix—stands as one of the key pillars for sustainable development on a global scale, uniting us in a common goal [2]. The pursuit of alternative pathways to those based on fossil feedstocks, with an emphasis on

the use of renewable sources, has become increasingly established to produce high-value-added chemical and energy inputs [3]. Lignocellulosic biomass, in particular, stands out for its abundance, low cost, and conversion versatility, offering a strategic option for restructuring production chains to be more resilient and environmentally responsible. Among the emerging technologies for biomass utilization, pyrolysis has garnered significant attention due to its ability to produce bio-oil—a liquid rich in oxygenated compounds—as well as char and combustible gases [4].



Although bio-oil holds potential for electricity generation and fuel production, its high content of oxygenated compounds—derived mainly from lignin and hemicellulose—undermines its thermal stability, viscosity, and calorific value, thereby hindering its direct application as a fuel [5].

Deoxygenation - the process of reducing the content of oxygenated compounds - is a critical step in adapting bio-oil to the requirements of conventional industrial processes. Among the most relevant chemical pathways are hydrodeoxygenation (HDO), decarboxylation (DCX), and decarbonylation (DCO), which promote the removal of water, carbon dioxide, and carbon monoxide, respectively [6].

Following deoxygenation, the coprocessing of bio-oil in fluid catalytic cracking (FCC) units represents an attractive strategy for its integration into existing refineries [7]. However, significant gaps remain in our understanding of deoxygenation mechanisms under different reaction conditions, as well as in the rational selection of heterogeneous catalysts. Our novel approach is capable of promoting efficient and selective conversions, a unique contribution to the field.

This article aims to address these gaps by evaluating deoxygenation pathways for bio-oil, with a focus on the influence of catalyst types and operational parameters. Our research has the potential to significantly impact the technical and economic feasibility of coprocessing in FCC units, and to advance knowledge on the

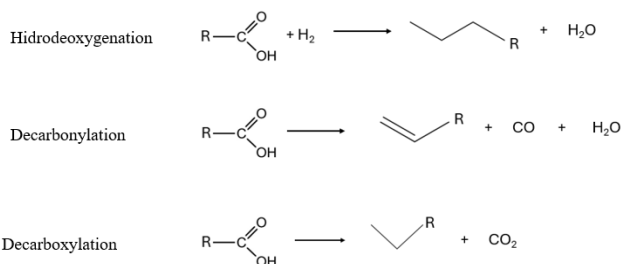
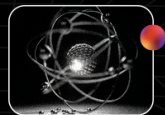
integration of biofuels into conventional infrastructures, promoting sustainable solutions for the refining industry.

2. Deoxygenation Reactions

The chemical composition of bio-oil, although variable depending on the biomass source and processing conditions, is predominantly composed of fatty acids, alcohols, aldehydes, and ketones [8]. According to Hermida and colleagues (2014), the chemical deoxygenation of bio-oil proceeds via primary reaction pathways such as decarboxylation, decarbonylation, and hydrodeoxygenation, whose prevalence is strongly influenced by the reaction atmosphere and the type of catalyst employed [9].

As illustrated in Figure 1, the decarboxylation (DCX) process involves the selective removal of oxygen from oxygenated biomass compounds, releasing it predominantly in the form of carbon dioxide (CO_2). Decarbonylation (DCO) eliminates oxygen as carbon monoxide (CO) and water, requiring higher energy input and potentially accelerating catalyst deactivation. Hydrodeoxygenation (HDO), in turn, removes oxygen as water (H_2O) through hydrogen consumption and is effective in converting unsaturated fatty acids and triglycerides into more stable saturated hydrocarbons [10].

Figure 1. Chemical Deoxygenation Pathways



Under inert atmospheres, the DCX and DCO pathways are predominant, resulting in n-alkanes, isoalkanes, cyclic hydrocarbons, and aromatics. However, the introduction of hydrogen shifts the dominant pathway to HDO, favoring the formation of n-alkanes and the saturation of double bonds. These pathways are often accompanied by parallel reactions such as thermal and catalytic cracking, as well as gas-phase reactions that break carbon chains and generate lower molecular weight hydrocarbons. [11].

3. Reaction Parameters

According to the reaction mechanism proposed by Nguyen et al. (2024), DCX occurs through the formation of a carboxylate intermediate on the catalyst surface, which is thermally decomposed with the release of CO_2 and a saturated hydrocarbon, as shown in Figure 2 [12].

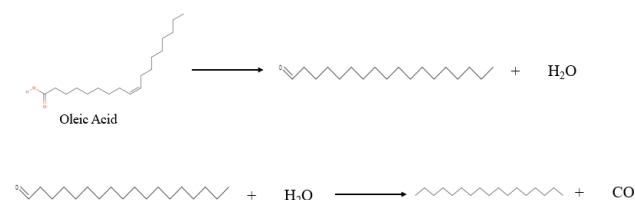
Figure 2. Reaction Mechanism of Oleic Acid DCX



In DCO, the process begins with the hydrogenation of the carbonyl group of the free fatty acid (FFA), forming water and an aldehyde molecule. The aldehyde then decomposes,

producing CO and a saturated hydrocarbon, as illustrated in Figure 3 [13].

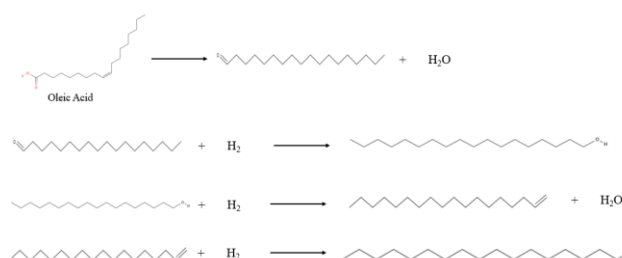
Figure 3. Reaction Mechanism of Oleic Acid DCO



Both DCO and DCX are endothermic processes and yield hydrocarbons with one carbon less than the original FFA.

In contrast, HDO is an exothermic process involving three consecutive reactions that produce a hydrocarbon with the same number of carbons as the original FFA, as shown in Figure 4 [14].

Figure 4. Reaction Mechanism of Oleic Acid HDO



The HDO mechanism of oleic acid (OA) holds great promise for the future of biofuel technology. It begins with the hydrogenation of the carbonyl group, initially forming a fatty aldehyde and water. This aldehyde then undergoes further hydrogenation to produce a primary alcohol, which subsequently undergoes sequential dehydration and additional hydrogenation steps, ultimately yielding the



corresponding saturated hydrocarbon and additional water. In parallel, the generated saturated hydrocarbons may undergo isomerization, resulting in branched compounds with enhanced properties for biofuel applications. [15].

Deoxygenation, cracking, and isomerization reactions are catalyzed in the presence of specific functional groups and acidic sites on the catalyst, with the carboxyl ($-\text{COOH}$) group of OA being particularly susceptible to decarboxylation, releasing CO_2 [16]. Thus, effective catalysts for HDO must exhibit a high capacity to adsorb and activate C–O and C–C bonds, in addition to promoting selective hydrogenation [17]. Although noble metals such as Pt, Pd, and Ru exhibit superior performance in these steps, their high cost and limited availability have driven research into alternative catalysts, such as supported transition metals (Ni, Co, Mo), which can combine catalytic activity, selectivity, and economic feasibility for industrial-scale applications.

4. Desired Catalyst Properties

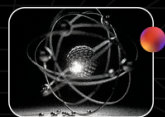
The efficiency of deoxygenation reactions is closely linked to the physicochemical properties of the catalysts employed, particularly the nature of the active sites present on their surface. Activation of the carboxylic group ($-\text{COOH}$) at acidic sites and the subsequent cleavage of the C–C bond are critical steps for CO_2 release via decarboxylation. In specific catalytic systems, competitive CO_2 adsorption may indicate a

stronger preference for this pathway, potentially limiting the occurrence of other desired reactions. This limitation underscores the need for further research and development in this area [18].

Ferreira et al. (2024) investigated the reaction conditions for palmitic acid deoxygenation in a 100 mL Parr reactor, employing carbon nanotube (CNT) materials as catalysts, achieving 90% C16 conversion at 350 °C and 30 bar hydrogen (H_2). Reactions using higher amounts of Co–Mo/oxidized CNT catalysts produced greater quantities of C15, indicating that DCX reactions were favored due to increased acidity [19].

Strapasson et al. (2025) explored the role of catalyst support acidity and metal–support interactions in the selectivity and stability of acetone hydrodeoxygenation reactions, with a specific focus on bifunctional catalysts based on Platinum (Pt) and Platinum-iron (Pt/Fe). The study found that catalysts with predominantly Brønsted acidity favor the selective cleavage of C–O bonds, while those with predominant Lewis acidity promote the formation of C–C coupling products and cascade cleavage. The authors also highlighted the crucial role of metallic sites in hydrogenation and dehydrogenation, shedding light on this aspect of the process and making the reader feel enlightened about the intricacies of HDO reactions [20].

The use of zeolites as catalysts not only holds promise for reducing operational costs but also signifies a potential shift in the landscape of fuel production. Some of these materials are already commercially employed in conventional fuel



production processes, paving the way for a more cost-effective and sustainable future.

In their study, B Valle et al. (2021) delved into the role of zeolite properties in bio-oil deoxygenation and hydrocarbon production via catalytic cracking. They highlighted the pivotal role of zeolite Y in hydrogen transfer reactions, attributing this to its shape selectivity, which leads to the production of more aliphatic than aromatic hydrocarbons [21].

Li et al. (2018) explored the potential of La₂O₃-modified ZSM-5 zeolite in the production of light olefins from three bio-oil model compounds, including oleic acid, through catalytic deoxygenation. Their study concluded that the introduction of La³⁺ into the zeolite channels significantly increased the pore radius and

enhanced the acidity of weak and medium acid sites. This promising result led to the production of approximately 90% of the liquid product being composed of aromatic hydrocarbons such as naphthalene and BTX [22].

Pacheco et al. (2025) evaluated hydrogen-free deoxygenation using ZSM-5 and Y zeolites as catalysts in a micro-pyrolyzer, finding that zeolite Y produced more branched alkanes, and that incorporating sodium (Na) increased the yield of gasoline-range hydrocarbons and light olefins [23].

Based on data reported in the literature, Table 1 was compiled with the reaction conditions for bio-oil deoxygenation, presenting the results corresponding to the highest conversion obtained.

Table 01. Reaction Conditions for Bio-Oil Deoxygenation

Nº	Reaction Conditions	Reactor	Main Products	Reference
1	1,75g AO, 6La/ZSM5, 600 °C	Fixed bed	Light olefins	(Li et al., 2018)
2	Bio oil, ZSM-5, 450 °C	Fluid bed	C2-C4, C5+	(Valle et al., 2022)
3	5% AO, Ni/Z, 380 °C	Fixed bed	C8-C16	(Liu et al., 2025)
4	Bio oil, ZnO, 300 °C	Parr	Hydrocarbons	(Cheng et al., 2017)
5	OAME, Na/Y/ZSM5, 650 °C	Micropyroliser	Hydrocarbons	(Padilha et al., 2022)
6	Palmitic acid, Co-Mo/Al ₂ O ₃	Parr	C16	(Ferreira et al, 2024)
7	Tetralin, Ecat-DI, 500 °C	Fixed bed	C5-C11	(Pujro et al., 2019)
8	Glycerol, TS1/ZSM5, 320 °C	Fixed bed	Gasoline, LCO, HCO	(Rafiani et al., 2025)
9	Bio oil, NaZSM5, PtZSM5, 300 °C	Parr	C9-C20	(Pacheco et al., 2025)
10	Biomass, ZSM5, 450 °C	Fixed bed	Aromatic	(Pagano et al., 2025)

Data analysis reveals that the reaction conditions employed in deoxygenation processes show a certain degree of convergence, with temperatures ranging between 300 °C and 400 °C, depending

on reactor configuration and the nature of the catalyst used. Catalyst selection is directly related to the desired product profile, influencing both selectivity and conversion efficiency. Acidic,



metallic, or bifunctional catalysts are employed according to the predominant pathway (DCX, DCO, or HDO) and the type of model substrate. Product characterization is typically performed using gas chromatography (GC), often coupled with mass spectrometry (GC–MS), enabling precise identification of the hydrocarbons formed and monitoring of compound distribution in the C₁–C₂₀ range. This analytical approach is essential for correlating operating conditions with the underlying reaction mechanisms, providing valuable insights for optimizing coprocessing processes in industrial units.

Recent studies indicate that catalysts with basic sites, such as modified zeolites, favor deoxygenation via decarbonylation, initially reacting with fatty acids to form metal salts that subsequently decompose into hydrocarbons. Conversely, aluminosilicates and oxides with Lewis acidity have proven effective in decarboxylation reactions, whereas oxides such as ZnO and acidic zeolites favor decarbonylation [24].

To enable the coprocessing of bio-oil in FCC units, the aromatic content must be minimized, as aromatics in these units lead to high coke formation. Therefore, secondary reactions such as oligomerization, cyclization, and aromatization should be avoided. In this regard, zeolites with high acidity and/or restricted microporosity may not deliver good yields [25]. The high acidity and shape selectivity of unmodified HZSM-5 make it highly selective in the cracking of vegetable oils, resulting in the

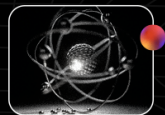
production of light hydrocarbons and aromatics [26].

Analyzing the effects of zeolite Y on fatty acid deoxygenation, Li et al. (2018) reported low yields in the production of light olefins and gasoline-range hydrocarbons [22]. Although such limitations exist for lighter fractions, studies such as that by Sun et al. (2025) suggest that zeolite Y may be effective for producing heavier hydrocarbons. These zeolites have larger pore sizes, which facilitate the ingress and egress of bulky intermediates derived from fatty acids, favoring the formation of heavier hydrocarbons—ideal for coprocessing in FCC units [27].

Modifying acidity and introducing mesopores can improve the diffusion of bulky intermediates and reduce secondary cracking. However, excessive desilication may compromise catalyst structure and selectivity, requiring greater care in preparation [15].

5. Final Considerations

The catalytic deoxygenation of bio-oil is an essential step for its coprocessing in conventional petroleum refining processes, such as fluid catalytic cracking (FCC), directly contributing to decarbonization strategies and the energy transition. The use of suitable catalysts capable of promoting selective pathways—such as decarboxylation, decarbonylation, and hydrodeoxygenation—is crucial for obtaining hydrocarbons compatible with commercial fuels.



In this context, the use of model molecules, such as oleic acid, has proven effective for understanding reaction mechanisms and evaluating the influence of operating parameters on conversion and selectivity. The literature shows that metallic catalysts, although highly active, present economic limitations, reinforcing the interest in alternatives such as modified zeolites, which offer advantages in terms of cost, availability, and compatibility with well-established processes.

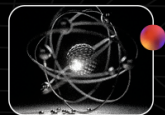
The preparation of these catalysts involves tuning acidity, creating mesopores, and optimizing metal-support interactions. These approaches represent a promising strategy to overcome challenges associated with coke formation and the production of undesirable fractions. The selection of catalytic materials, combined with careful control of reaction conditions, can enable the efficient coprocessing of bio-oil in FCC units, fostering the production of renewable fuels with lower environmental impact and greater economic viability.

Moreover, the application of zeolites in catalytic deoxygenation processes can reduce the need for high hydrogen pressures, favoring oxygen removal in the form of CO and CO₂ through decarboxylation and decarbonylation reactions.

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