

## Review

# Biomass Conversion to Value-Added Chemicals and Fuels Using Natural Minerals as Catalysts or Catalytic Supports

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## Abstract

Biofuels and value-added chemicals can be produced using biomass. These products can substitute the corresponding petroleum-based ones, reducing the carbon footprint, ensuring domestic production, and minimizing/exploiting organic wastes in a circular economy philosophy. Natural mineral-based catalysts seem to be a promising, eco-friendly, and low-cost approach for biomass valorization. This article attempts to highlight the potential of natural mineral-based catalysts for various processes targeting the above valorization. Natural zeolites and clays can be used as catalysts/CO<sub>2</sub> adsorbents and catalytic supports in various biorefinery processes (pyrolysis, gasification, hydrothermal liquefaction, esterification/transesterification, hydrotreatment, cracking, isomerization, oxidation, condensation, etc.). Acid/base, redox, and textural properties of these materials are key factors for their catalytic performance and can be easily regulated by suitable treatments, like calcination, acid/base-washing, metal impregnation, doping, etc., which are discussed in this article. The application of natural minerals in biorefinery processes makes them greener, cost-effective, and easily scalable.

**Keywords:** biomass; natural catalyst; montmorillonite; dolomite; mordenite; palygorskite; bentonite; biofuel; biochemical



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## 1. Introduction

Biomass and especially residual biomass valorization to produce value-added chemicals and biofuels is of crucial importance to cover the ever-growing global demands. Traditional fossil fuels and chemicals coming from the petroleum industry are limited and with negative environmental footprints. The current state of global oil reserves is estimated to be about 1.65 trillion barrels, which means that, with today's consumption rate, they are predicted to be finished by 2070 [1]. Additionally, the natural gas reserves are estimated to be 1.15 trillion barrels of oil equivalent, which corresponds to 52 years of natural gas left at current consumption levels [2]. Friedlingstein et al. [3] describe the global carbon budgets and the environmental consequences of fossil fuel consumption, proving the urgent need for their replacement.

In this frame, biomass and organic residues appear to be valuable alternatives to mineral crude oil. The research on such source valorization has made significant progress in recent years, a fact that is also evident from the very valuable review articles that have been published [4–15]. The exploitation of these raw materials not only advances sustainability objectives but also aligns with the growing consumer demand for eco-friendly and biodegradable products.

The complex, unstable, and variable composition of the biomass, which depends on its source, makes its upgrading challenging [16]. Therefore, catalytic biomass upgrading is vital in converting renewable biomass into a variety of fine chemicals, fuels, or materials. Heterogeneous catalysts play a crucial role in biomass conversion, as they offer significant advantages over homogeneous catalysts, including low toxicity, easier recovery and reuse, and reduced waste generation, in total agreement with green chemistry principles.

Despite commercial heterogeneous catalysts achieving high yields for the conversion of biomass to biofuels and biochemicals, difficulties have been found due to catalyst deactivation [17]. To reduce the cost of relevant processes, natural mineral catalysts have been investigated. For example, lignocellulose conversion methods based on such catalysts have already been applied in several pilot and demonstration plants for the production of platform chemicals globally [18]. Innovative catalysts and catalytic support materials based on natural minerals seem to be of high significance for the continually growing new chemical processes concerning biofuels and biochemicals production. These catalysts should have tailored properties, and they must also be suitable for large-scale production through environmentally friendly and cost-effective processes. Minerals, like natural clays and zeolites, are now emerging as potential catalysts for industrial applications [19].

Taking into account the above-described concept, in this study, we present a comprehensive review of the most recent studies on the use of minerals either as catalysts or as catalytic supports for biomass conversion to biofuels, value-added chemicals, and eco-friendly material products. Acid/base, redox, CO<sub>2</sub> absorbance ability, and textural properties of minerals are crucial for their performance in biomass valorization processes. These properties can be easily tuned by simple treatments, like calcination, acid/base-washing, metal impregnation, doping, etc., as we will discuss in the following sections of this review. Acid/base-treatment of natural minerals and/or calcination results in catalysts and CO<sub>2</sub>-adsorbents constituted by bare natural minerals. On the other hand, synthetic catalysts can be obtained using natural minerals as support, adding metals or metal oxides for preparing bifunctional catalysts with acid/base and redox functionalities.

## 2. The Use of Minerals as Catalysts for Lignocellulosic Biomass Valorization

Biomass conversion to value-added products (mainly food/feed, biofuels, biochemicals, composites and fibers, pulp and paper, etc.) is the main objective of biorefineries. Such installations are continuously growing nowadays. Waste and non-food biomass (forestry, waste, grass, and short rotation coppice, agriculture, marine, aquatic, and others) are the major raw materials-feedstock of new biorefineries. These installations incorporate advanced processes to create a diverse portfolio of products. Over 3450 biorefineries have been established in the EU [20]. They exploit biomass of plant and animal origin, which is categorized into: lignocellulosic, sugar/starch, triglyceride (vegetable oils and animal fats), manure, etc. The treatment of lignocellulosic biomass is the most complicated, demanding a series of pretreatment steps before its full exploitation. The solid nature of this kind of biomass makes its catalytic processing difficult, especially when solid catalysts are used, because of insufficient contact. Thus, non-catalytic processes, like pyrolysis and gasification, are chosen traditionally for the conversion of lignocellulosic biomass to gases, bio-oil, and char, which could be further upgraded to value-added products. Catalytic pyrolysis, hydrodeoxygenation, gasification, and enzymatic processing of lignocellulosic biomass are emerging processes that need advances in catalyst development [21].

Pyrolysis is a thermochemical process in which biomass is heated at moderate temperatures (300 °C to 800 °C) in a totally inert atmosphere to produce bio-oil, biochar, and syngas [22]. Gasification is also a thermochemical process aiming for biomass conversion

to syngas ( $H_2$ , CO,  $CH_4$ , and other volatile compounds). This process takes place at high temperatures (700 °C to 1200 °C) under an almost inert atmosphere containing a controlled amount of oxygen and/or steam [23]. In general, pyrolysis produces more bio-oil and char, while gasification produces mainly syngas and some methane and tar. Bio-oil composition depends on the raw biomass and pyrolysis conditions. Generally, it contains water, organic acids, aldehydes, ketones, furans, phenols, and sugars, while pyrolytic lignin constitutes its heavy fraction. Thus, it has a low Higher Heating Value (HHV), high acidity, and low stability. These characteristics exclude its application as a drop-in fuel and make its upgrading inevitable. Bio-oil upgrading involves its deoxygenation in the presence (hydrotreatment) or not of  $H_2$ . Gasification products are less dependent on the kind of feedstock, in contrast to the pyrolysis ones [24].

### 2.1. Biomass Pyrolysis

As already mentioned, pyrolysis enables the decomposition of a wide range of waste biomass into bio-oil (a raw material for obtaining valuable chemicals and fuels), syngas, and char, simultaneously reducing the waste biomass volume. The relevant processes are easily scaled up and coupled with existing facilities. In catalytic pyrolysis, biomass is decomposed with the assistance of a catalyst [25]. Catalysts can be used inside a pyrolysis reactor (in situ) or in a next reactor downstream (ex situ). Wang et al. [26] have compared these two approaches using microreactors. Various types of catalysts (such as acidic, basic, metallic, mixed metal oxides, natural minerals, inorganic salts, metal–organic frameworks, etc.) have been examined for catalytic pyrolysis [25]. Natural mineral catalysts, being eco-friendly and low-cost ones, are very important for catalytic pyrolysis processes.

A comprehensive review article, published recently by Zulkafli et al. [27], concluded that the co-pyrolysis of biomass with plastic results in enhanced yield and quality of bio-oil, reducing the concentration of undesired oxygenated compounds and coke formed. Solid catalysts (zeolite- and mineral-based catalysts) used in such processes play a critical role in the increase in the yield and the quality of liquid fuel obtained. Fifteen years ago, Kumar et al. [28] published a work examining the influence of solid catalysts on lignocellulosic biomass (eucalyptus wood) in situ pyrolysis carried out in a semi-batch reactor. They found that the fast heating rate of the reactor at a pyrolysis temperature of 450 °C, and using a feedstock particle size of 2–5 mm, are the favorable parameters for increased yield of bio-oil. However, the bio-oil production was found to be independent of the presence of various catalysts tested (mordenite, kaolin clay, fly ash, and silica–alumina). In contrast, Kosivtsov et al. [29] found that the pyrolysis of peat was strongly accelerated in the presence of natural aluminosilicates (kaolin, bentonite, Cambrian clays, and clay mergel) and synthetic zeolites. Natural minerals affect catalytic activity, accelerating hydrocarbons (methane, ethane, and propane) formation by two times compared to the non-catalytic process. Bentonite clay was found to be the most effective catalyst when it was introduced at 2% (wt.) and a temperature of 460–480 °C. Salan et al. [30] studied catalytic pyrolysis of pulper rejects using activated clinoptilolite and sepiolite as catalysts, in a fixed-bed reactor working at 500 °C under  $N_2$  (50 mL/min). The non-catalytic pyrolysis resulted in a relatively high gas yield (21.44%), while in the presence of clinoptilolite and sepiolite, the highest liquid (61.4%) and char (32.19%) yields were achieved. The catalytic pyrolysis not only enhanced bio-oil yield but also improved fuel characteristics, especially in the presence of clinoptilolite catalyst. Gandidi et al. [31] investigated the catalytic performance of natural materials (zeolite, dolomite, kaolin, and activated carbon) on the in situ pyrolysis of *Spirulina platensis* microalgae using a batch-like reactor working at 500 °C for 60 min and two configurations concerning biomass and catalyst placements (layered and mixed). Activated carbon and zeolite proved to be very promising for bio-oil

production, independently of the configuration used. Kaolin in a layered and zeolite in a uniform mixture configuration were more suitable to produce light bio-oil.

Merdun et al. [32] studied catalytic co-pyrolysis of greenhouse vegetable wastes and coal (450–550 °C) in a tube reactor, using natural catalysts (calcite, dolomite, and zeolite) placed downstream for treatment of fast pyrolysis products. The results obtained reveal no significant influence of the catalysts' presence on the product yields (biochar, bio-oil, and gases). This is in agreement with the results obtained by Kumar et al. [28]. However, Vo et al. [33] studying the co-pyrolysis of bamboo and polystyrene in a fluidized bed reactor (in situ catalytic pyrolysis) found that the catalyst used plays a key role in the quality of the produced bio-oil. In this sense, dolomite proved to be a more effective catalyst than HZSM-5, red mud, and  $\text{Fe}_2\text{O}_3$ . The same group [34] using the above reactor system also studied fast pyrolysis of cashew nut shells (a waste biomass with high carbon content and low oxygen content) using dolomite as a catalyst and  $\text{CO}_2$  absorbent. They investigated the operation conditions of the process and found that, concerning the dolomite catalytic performance, it has a substantial effect on the pyrolysis of biomass. More precisely, dolomite enhances dehydration, decarboxylation, and aromatization reactions and increases syngas production.

Charusiri [35] has studied fast pyrolysis of residues from the paper mill industry to bio-oil and value-added chemicals using dolomite as a catalyst (1–5 wt.%) in a continuous pyrolyzer. The bio-oil obtained under the best conditions contains complex organic compounds with aromatic, acid, and hydrocarbon groups. As was expected for the pyrolysis bio-oil, it appears to have low heating value and high acidity, which implies the necessity of further upgrading in order to meet the transportation fuel standards. Veses et al. [36], using a similar type of pyrolyzer (auger reactor), compared sepiolite, bentonite, attapulgite, and red mud as catalysts for the pyrolysis of wood biomass. The optimum bio-oil production was achieved at a temperature of 450 °C and a catalyst to biomass ratio (1:6, in weight). An increase in the latter results in a reduction in bio-oil production and an increase in char yield. All the catalysts studied improved the properties (viscosity, acidity, oxygen content, and calorific value) of the obtained bio-oil.

Mohamed et al. [37] performed thermogravimetric analysis and microwave-assisted pyrolysis experiments using switchgrass alone and in the presence of bentonite or clinoptilolite, trying to study non- and catalytic pyrolysis of the above feedstock. It was found that the mineral catalysts significantly decrease the decomposition temperature of pseudo-lignin (the most stable fraction of switchgrass biomass); meanwhile, they also increase the pyrolysis rate and conversion percentage, reducing the activation energy of pseudo-lignin decomposition. Clinoptilolite used as a catalyst in microwave-assisted pyrolysis increased the phenolic fraction of bio-oil by 49% in comparison with the non-catalytic experiment. In an effort to valorize lignocellulosic household waste, Rijo et al. [38] studied the pyrolysis of such materials using inorganic waste materials (marble, limestone, dolomite, bauxite, and spent fluid catalytic cracking catalyst) as catalysts. Pyrolysis tests were performed in a fixed-bed reactor at 400 °C and showed that all the catalysts studied promote gasification and decrease the concentration of carboxylic acids in the bio-oil produced. Sandoval-Rangel et al. [39] studied the slow pyrolysis of pecan nut shells, mixing them with various natural minerals (dolomite, clinoptilolite, and limestone) in their calcined and non-calcined form, with the target to improve the quality of pyrolysis products. They prefer to use the term “additive” instead of “catalyst” for the above materials because they want to stress that the CaO-containing materials act not only as catalysts but also capture  $\text{CO}_2$  produced upon biomass pyrolysis. The addition of both non-calcined and calcined minerals enhanced the decomposition of biomass and facilitated deoxygenation reactions. Calcined materials enhanced gas yields at the expense of bio-oil production. Calcined clinoptilolite proved to

be the most effective material, resulting in valuable syngas and fuel-range molecules acting both as a pyrolysis catalyst and CO<sub>2</sub>-trap.

Song et al. [40] tried to exploit municipal solid waste by in situ and ex situ catalytic pyrolysis using iron-based materials (iron oxide and iron ore) as catalysts. Their TGA experiments using a mixture of waste and catalyst proved that iron-based materials facilitate in situ pyrolysis, promoting the production of aliphatic and monocyclic aromatic hydrocarbons. This was confirmed by catalytic tests in a tubular reactor where the biomass and catalyst were placed in two separate and consecutive beds (ex situ pyrolysis). In a similar context, Syazaidah et al. [41] studied the ex situ catalytic pyrolysis of chicken litter to produce bio-oil. Biomass was pyrolyzed at 500 °C, while the catalytic treatment took place in a subsequent fixed-bed reactor at 600 °C, with biomass to catalyst mass ratios of 20:3 and 20:1.5. Two catalysts have been examined (ZSM-5 and dolomite). The authors do not clarify whether dolomite is a chemically synthesized material or a natural one. However, it proved to be more efficient than ZSM-5, increasing 19% the bio-oil production instead of 8% increase obtained with ZSM-5. Stefanidis et al. [42] showed that MgO materials derived via grinding and calcination of natural magnesite mineral are promising catalysts for the upgrading of fast pyrolysis bio-oil of beech wood sawdust, exhibiting similar or even better performance in comparison with that of an industrial ZSM-5 catalyst. The basic sites of the MgO catalysts favored oxygen removal reactions (acid reduction, ketonization, and aldol condensation), resulting in CO<sub>2</sub> formation instead of CO, and water was favored over ZSM-5 zeolite. Although the coke formed over the MgO catalysts was slightly increased, it was softer (burned out at lower temperatures) than that formed on ZSM-5 zeolite, facilitating the regeneration of MgO catalysts.

Karod et al. [43] investigated the in situ catalytic pyrolysis of cherry pits using natural clays—montmorillonite, attapulgite, and illite—as low-cost catalysts. The study demonstrated that clay addition modified product distribution, generally lowering gas yields and enhancing liquid and char fractions. Montmorillonite favored alkene and fatty acid formation, increasing calorific value but also oxygenates, while attapulgite and illite reduced oxygenated compounds, producing lighter hydrocarbons more suitable as “drop-in” fuels. The resulting clay–biochar composites exhibited higher surface areas, though reduced adsorption capacity due to loss of functional groups. This dual valorization—improving bio-oil quality and generating functional biochar—highlights the potential of clays as sustainable, non-precious catalysts.

A welcome progression is the shift from layered clays to carbonate minerals, with dolomite standing out as the most extensively studied low-cost catalyst due to its strong basicity and abundance. Bisen et al. [44] investigated the catalytic co-pyrolysis of rice husk and high-density polyethylene using calcined dolomite as a low-cost catalyst. The study focused on improving bio-oil yield and fuel quality examined through thermogravimetric, GC–MS, and NMR analyses. Results showed that dolomite significantly enhanced hydrocarbon selectivity, reducing oxygenated compounds by 17% and increasing carbon and hydrogen contents by 72.4% and 12.26%, respectively. The produced bio-oil exhibited improved properties, including higher calorific value (43.41 MJ/kg), lower viscosity, and a cetane index of 51.3, closely matching diesel standards. These findings highlight dolomite’s effectiveness for sustainable biofuel production.

Ly et al. [45] investigated the catalytic fast pyrolysis of tulip tree (*Liriodendron*) biomass in a bubbling fluidized-bed reactor, comparing silica sand and calcined dolomite as bed materials. Dolomite, after activation at 900 °C, significantly altered product distribution: while the maximum bio-oil yield decreased slightly (44.8 wt.% vs. 49 wt.% with sand), its quality improved with higher heating values (23.1–28.0 MJ/kg) and reduced oxygen content (29–41 wt.%). Importantly, dolomite promoted deoxygenation mainly via dehydra-

tion, leading to lower CO and CO<sub>2</sub> emissions, higher H<sub>2</sub>/CO ratios, and greater selectivity toward light aromatics (C<sub>5</sub>–C<sub>11</sub>). These changes indicate improved fuel properties and potential syngas utility. The study highlights dolomite's low cost and efficiency in enhancing bio-oil upgrading, though issues of coke formation and char yield increase remain challenges for long-term catalyst stability.

Ly et al. [46] investigated the catalytic fast pyrolysis of mixed food waste in a bubbling fluidized-bed reactor using HZSM-5, dolomite, and red mud as catalysts. Among these, HZSM-5 (Si/Al = 3:1) exhibited strong deoxygenation capacity, favoring the production of polycyclic aromatic hydrocarbons and pyridine derivatives, while dolomite promoted H<sub>2</sub> release and aliphatic hydrocarbons through dehydrogenation. Red mud enhances decarboxylation, yielding lighter cyclic ketones. A catalytic run reduced oxygenates and raised the higher heating values of bio-oils from 27.7–31.6 MJ/kg (non-catalytic) to 30.5–35.7 MJ/kg. The study demonstrated that inexpensive natural and industrial catalysts can upgrade low-quality pyrolysis oils into biofuels with higher carbon content and improved stability.

Mysore Prabhakara et al. [47] explored the dual role of dolomite as both a CO<sub>2</sub> sorbent and a deoxygenation catalyst during the fast pyrolysis of beech wood in a bench-scale fluidized bed reactor. Operating at 500 °C, they found that dolomite not only moderated the oxygen content of the resulting bio-oil (from 47.3 wt.% to 21.5 wt.%) but also produced CO<sub>2</sub>-free, H<sub>2</sub>-rich gas. The pH of the bio-oil increased significantly (from 3.2 to 6.0) while acids and anhydrosugars were completely eliminated. Importantly, intermediate compounds like cresols and cyclopentanones were enhanced, making the oil more suitable for downstream upgrading. This dual functionality suggests dolomite as a low-cost, naturally derived catalyst that can both improve bio-oil quality and internally generate hydrogen, potentially reducing reliance on external H<sub>2</sub> sources.

Duanguppama et al. [48] studied pyrolysis of *Leucaena leucocephala* using an experimental set-up involving two reactors in series, a fluidized bed reactor for in situ catalytic pyrolysis, and a subsequent fixed-bed reactor for ex situ treatment. Both reactors were loaded with natural zeolite (NZ) and dolomite (DM) catalysts in various combinations (NZ/NZ, DM/DM, NZ/DM, and DM/NZ) at 500 °C. The use of catalysts enhanced the gas yield by 10%, accelerating mainly the deoxygenation reactions. Dolomite catalyzed mainly the cracking reactions, thus increasing the light bio-oil yield. Zeolite catalyst facilitated mainly deoxygenation reactions, resulting in bio-oil with high hydrocarbon content. However, the catalysts' configurations did not influence the yield of the whole process. Aljeradat et al. [49] used various Jordanian minerals as catalysts for the treatment of date kernel pyrolysis products in a tubular reactor (at 500 °C) where the catalyst's bed was placed next to that of biomass. Although the yields of bio-oil, char, and syngas were not affected considerably by the catalyst studied, the zeolitic tuff improved the quality (less acidity and high stability) of the bio-oil produced.

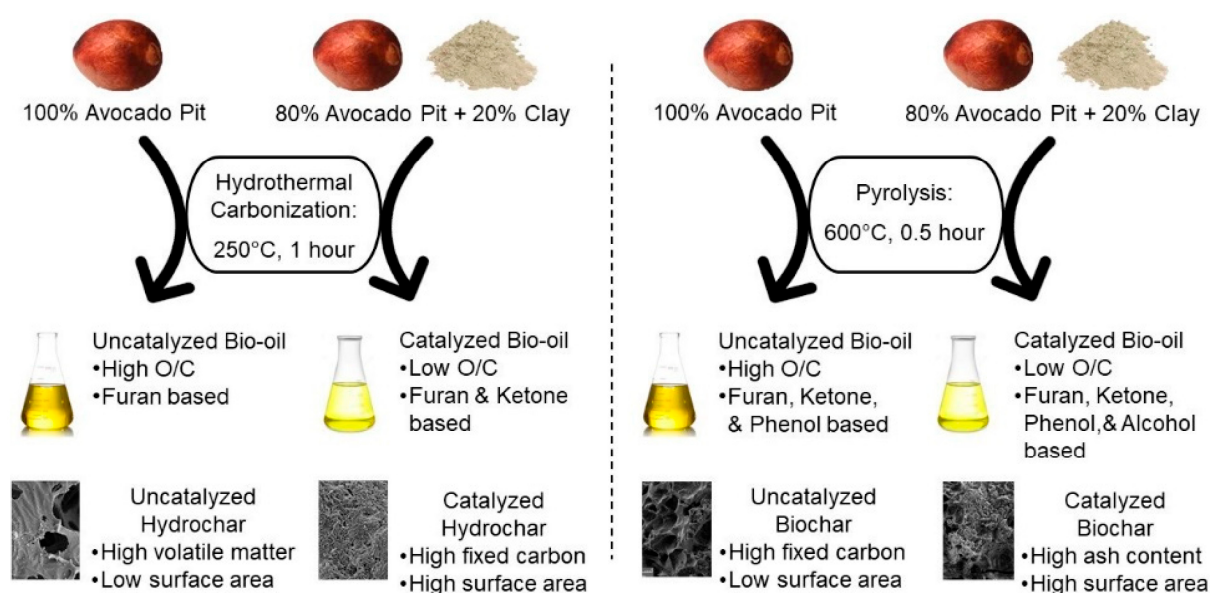
Venegas-Vásquez et al. [50] investigated the catalytic fast pyrolysis of *Pinus radiata* and *Eucalyptus globulus* using Chilean natural zeolite composed of clinoptilolite and mordenite, modified by ammonium ion exchange and impregnated with Cu and Ni for upgrading pyrolysis vapors (ex situ treatment). The Ni-modified zeolite exhibited the highest deoxygenation efficiency, reducing acids, ketones, and esters, while enhancing aromatic yields, especially benzene, toluene, and xylene (up to 30.5 wt.%). Structural analyses (XRD, SEM-EDS) confirmed successful metal incorporation, while NH<sub>3</sub>-TPD showed increased acidity. The study demonstrates that cost-effective natural zeolite catalysts can substitute synthetic ZSM-5 in producing valuable aromatics from biomass pyrolysis.

Nazari et al. [51] tried to understand the role of catalysts in hydrothermal liquefaction (HTL) of woody biomass (biomass to water ratio equal to 0.12, temperature 300 °C, autoge-

nous pressure 90 bar, reaction time 30 min) comparing products distribution and yields, oil compositions and molecular weights, functional groups, boiling points, and thermal stability using birch wood sawdust as biomass feedstock and several homogeneous and/or heterogeneous catalysts (5 wt.% KOH,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{K}_2\text{CO}_3$ , MgO, synthetic hydrotalcite, and ground colemanite ( $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ). Colemanite catalyst, because of its high alkalinity, proved to be among the most promising catalytic materials studied as to the yields of bio-oil and biochar. A similar conclusion was reported by Ma et al. [52], using commercial clay minerals (montmorillonite, dolomite, kaolinite, and sand) for HTL of potato starch. Wu et al. [53] used montmorillonite coming from natural bentonite under mild conditions (montmorillonite:water:cellulose = 0.6:10:1, 200 °C, 2–24 h) and succeeded in the hydrothermal carbonization of cellulose, resulting in a high yield of montmorillonite–hydrochar nanocomposite. Montmorillonite acted as a catalyst for hydrothermal liquefaction, an adsorbent of derived liquid compounds, and an inorganic template for the formation of final hydrochar. Sudibyo et al. [54] evaluated various natural clay minerals (kaolinite, montmorillonite, talc, vermiculite, phlogopite, meixnerite, attapulgite, and alumina) as in situ catalysts for HTL of anaerobically digested cattle manure at 350 °C for 1 h. Montmorillonite proved the most suitable HTL catalyst, conserving its crystalline structure intact after the HTL process.

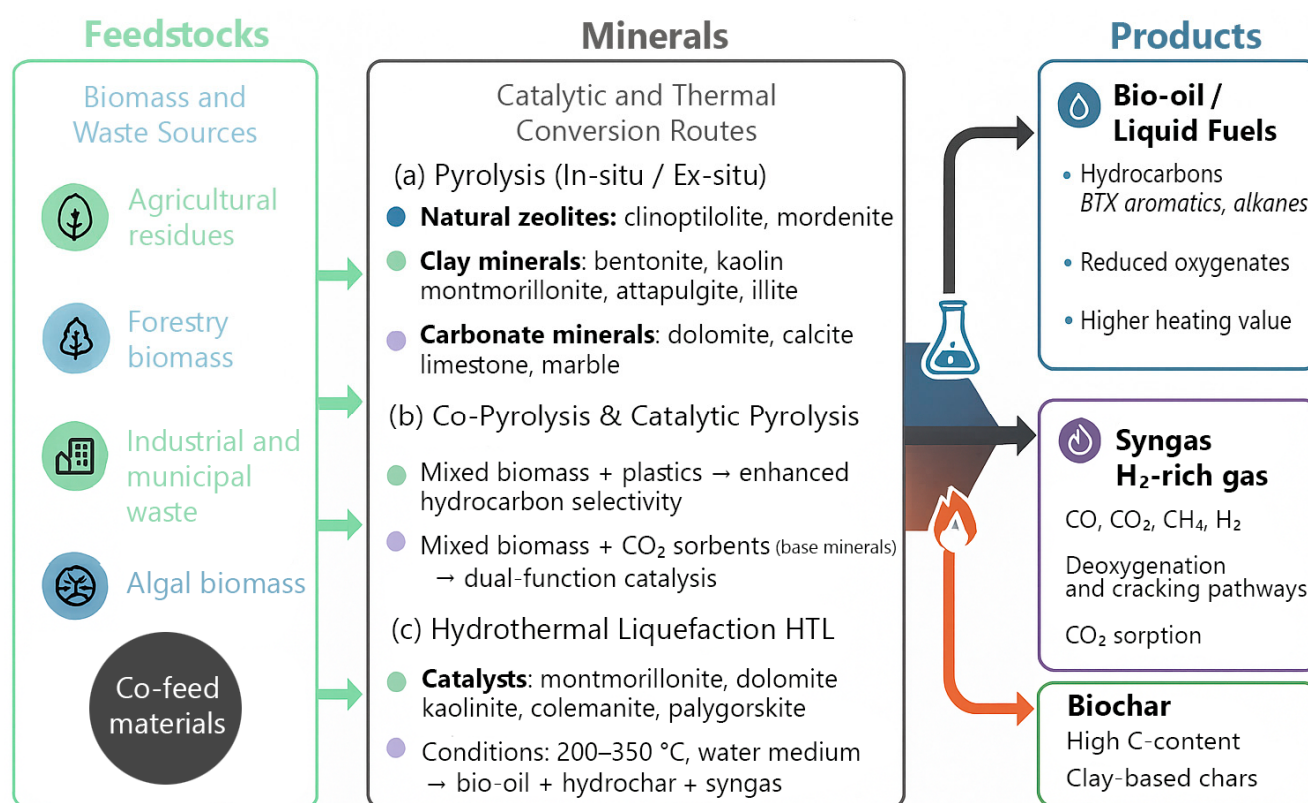
Clay minerals supported catalysts have also been studied for the hydrothermal liquefaction of biomass. Zhu et al. [55] prepared Mo, Co, and CoMo catalysts supported on palygorskite and alumina. The catalysts in their oxide form were evaluated for hydrothermal liquefaction of sewage sludge (batch reactor, 5 g biomass, 30 mL water, 10 wt.% catalyst on dry biomass basis, 320 °C, 15 min). The bimetallic catalyst supported on palygorskite proved to be the most effective one, although it exhibited half the specific surface area of that of  $\text{CoMo}/\text{Al}_2\text{O}_3$ . Chen et al. [56] also studied Co catalysts supported on acid (1M HCl, for 12 h) modified palygorskite for lignin depolymerization. Using a catalyst containing 15 wt.% Co, 1,4-dioxane as a solvent, and ethanol as an in situ hydrogen donor, at 220 °C for 8 h, they obtained low char yield (6.6 wt.%) and enhanced bio-oil yield (63.1 wt.%).

An interesting comparison of in situ pyrolysis with hydrothermal carbonization of avocado pit biomass was performed by Karod et al. [57] using bentonite clay as a catalyst (Figure 1). The use of bentonite improved the bio-oil and biochar quality in both processes.



**Figure 1.** Schematic representation of hydrothermal carbonization and pyrolysis of avocado pit with and without bentonite clay catalyst (conditions and properties of the products) [57].

A summary of the role of minerals as catalysts, catalytic supports, and CO<sub>2</sub>-adsorbents is graphically illustrated in Figure 2. As can be seen, various biomass feedstocks (agricultural residues, forestry biomass, industrial and municipal organic wastes, and algal biomass) can undergo in situ or ex situ pyrolysis/hydrothermal liquefaction using mineral-based catalysts. Mineral catalysts alone can enhance bio-oil yield and reduce the O/C ratio. The latter effect is intensified by metals' addition, which enhances the redox properties of the final catalyst. Base minerals, mainly dolomite, also act as CO<sub>2</sub>-adsorbents, minimizing the carbon footprint.



**Figure 2.** Graphical representation of feedstocks, minerals used as catalysts, and products obtained via pyrolysis.

It is well known that basic catalytic sites promote decarboxylation/decarbonylation reactions upon biomass pyrolysis. For example, calcined dolomite strongly favors decarboxylation of volatile compounds produced upon lignocellulosic biomass (e.g., cashew nut shells) fast pyrolysis and captures the released CO<sub>2</sub> [34]. Acid catalytic sites found mainly in natural zeolites and clays (bare or metal modified) facilitate cracking and aromatization reactions [50].

## 2.2. Biomass Gasification

The conversion of biomass to syngas is an attractive biomass valorization process because of its universal character (independence of the product on biomass type). The major problem in the gasification process is tar formation. Coping with this problem can be achieved using suitable catalysts. Recently, Ciuffi et al. [58] have published a critical review article concerning the gasification of plastics. In this article co-gasification of plastics with biomass has also been reviewed. They concluded that synergistic effects are observed between the raw materials, resulting in higher gas yields and syngas with a high energy content. Among them, natural dolomite and olivine have been mentioned as low-cost and active catalysts [59]. De Andrés et al. [60] compared the behavior of the two minerals

(dolomite, olivine) with that of alumina as catalysts in the gasification of sewage sludge. They have found the following activity for tar elimination: dolomite > alumina > olivine.

The natural minerals, dolomite, olivine, and limonite (pre-calcined at 850 °C for 2 h) were used as catalysts for gasification of sewage sludge in a fixed-bed reactor by Alper et al. [61]. Catalytic minerals provoked a reduction in CH<sub>4</sub> and light organic molecules ( $\leq C_5$ ) in the product gas, increasing hydrogen production. This is evidence that they are very active in tar reforming. Limonite proved to be the optimal natural mineral for H<sub>2</sub> production among the minerals studied. In a very interesting article, Zhou et al. [62] studied the composition and yields of gases produced upon biomass gasification in a pressurized fluidized bed gasifier (8 bar), using different natural minerals (magnesite, dolomite, olivine, and silica sand) as catalysts. They found that dolomite is very active in increasing conversion, H<sub>2</sub> concentration, and syngas yield in the products. The high H<sub>2</sub> yield is attributed to tar cracking taking place on the dolomite surface. On the other hand, the lower coke formation on the used dolomite surface in comparison with that on the used olivine confirms the ability of dolomite particles in tar catalytic cracking. Dolomite is also easily regenerated inside the pressurized fluidized bed gasifier. They also investigated the mechanisms followed by catalytic tar-cracking and reforming over selected natural minerals (dolomite and magnesite), revealing their effective roles in the selective conversion of biomass primary products. Chang et al. [63] used waste from the aluminum industry, the red mud (RM), as a catalyst for the gasification of palm kernel shell wastes (PKS) at 800 °C. The increasing addition of RM promoted the conversion mainly of biochar and slightly that of bio-oil to non-condensable gases.

Nickel catalysts are also suitable for tar elimination during biomass gasification. Liu et al. [64] studied palygorskite-supported nickel catalysts modified by Fe, Mg, Mn, and Ce for cracking of tar produced by rice husk gasification. They found that the kind and content of the additives affected the catalyst activity and selectivity. Fe was the best additive for both tar elimination and H<sub>2</sub> production. The same group [65] has also compared the catalytic performance for the above reaction of quartz, palygorskite, goethite, and hydrothermally synthesized goethite, as well as, of Ni and Ni-Fe catalysts supported on these materials. They found that palygorskite is the most active mineral, reaching tar conversion higher than 55%. However, higher yields of gases are obtained in the presence of natural goethite because Fe<sub>x</sub>O<sub>y</sub> existed in its structure after calcination. Nickel addition improves the activity of the minerals studied. The Ni catalyst supported on goethite (Ni<sub>6</sub>/G) exhibits the highest activity and yield of gases, followed by the corresponding bimetallic catalyst supported on palygorskite (Fe<sub>6</sub>Ni<sub>6</sub>/P).

Chiodo et al. [66] compared dolomite, MgO, and a commercial Ni/Al<sub>2</sub>O<sub>3</sub>–CaO catalyst for the gasification of citrus peel residues to obtain hydrogen-rich syngas. Dolomite proved the best catalyst, while the Ni catalyst seems to be affected by coke formation and sintering upon reaction. Puig-Gamero et al. [67] also studied dolomite as a catalyst for steam co-gasification of olive pomace, coal, and petroleum coke. The presence of dolomite resulted in enhanced H<sub>2</sub>/CO ratio, reactivity, and low H<sub>2</sub>S, NO, and SO<sub>2</sub> emissions. Dolomite was proved by Tian et al. [68] to be a very promising catalyst for air–steam gasification of biomass (*Enteromorpha intestinalis*), as they found that it is more effective for gas production and tar destruction than limestone and olivine. Latifi et al. [69] studied natural olivine ((Mg,Fe)<sub>2</sub>SiO<sub>4</sub>) as a catalyst for bio-oil gasification. They found that metallic iron contained in this material is its active component. A reduction in natural material with H<sub>2</sub> enhances the metallic iron fraction and thus the activity.

Municipal solid waste (MSW) disposal is usually treated mechanically and biologically, resulting in about 40% refuse-derived fuel. This can be gasified to produce syngas. Except for the high hydrogen content, H<sub>2</sub>/CO ratio, and pollutant concentration, the tar content

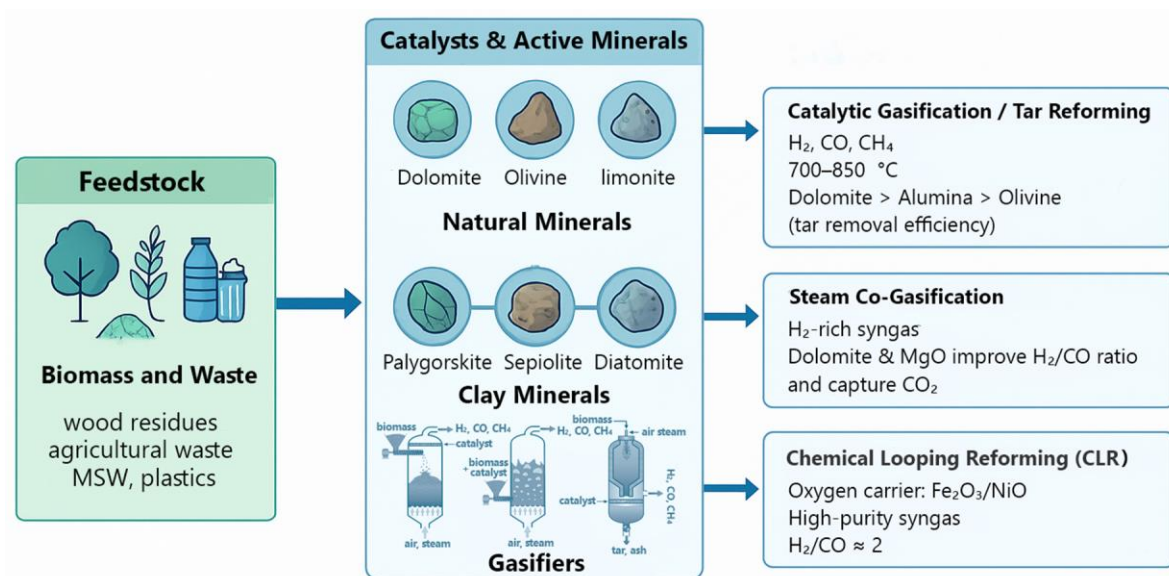
determines the quality of syngas concerning its application in both energy production and chemical synthesis. Clay minerals constitute a wide class of natural materials that can be applied as low-cost catalysts or catalytic support for the above process. Šuhaj et al. [70] studied a Ni-based catalyst supported on natural clay composed of corrensite, palygorskite, sepiolite, quartz, dolomite, and saponite. Their catalyst was prepared by impregnation in the calcined clay and contained 3 wt.% NiO. The presence of the catalyst resulted in tar reduction and an increase in H<sub>2</sub> content. The increase in reaction temperature (700 → 850 °C) and catalyst amount (0 → 40g) had a positive influence on the above.

Chemical-Looping Reforming (CLR) is a process in which oxygen from air is transferred to fuel through a solid oxygen-carrier, avoiding direct contact between fuel and air [71]. CLR of biofuels is considered a promising method to produce syngas. Xu et al. [72] compared M<sub>x</sub>O<sub>y</sub> (M=Cu, Fe, and Ni) catalysts supported on dolomite for the CLR process of toluene used as a biomass representative molecule. Iron and nickel oxide catalysts proved more effective than copper for syngas production. However, the iron oxide catalyst suffers from rapid deactivation and low syngas purity. In contrast, in the presence of the nickel oxide catalyst lower syngas yield is obtained, but its purity is too high (90.59%) with attractive H<sub>2</sub>/CO ratios (~2.0) under different reaction conditions.

Veses et al. [73] studied the catalytic cracking of MSW pyrolysis products for syngas production over calcined (900 °C) dolomite (58% CaO, 36% MgO) and calcite (90% CaO). They found that the combination of pyrolysis with catalytic cracking using the inexpensive and widely available dolomite as cracking catalyst results in the production of a valuable syngas fraction. This research group also studied the catalytic cracking of waste mattress foam pyrolysis products, combining primary pyrolysis with subsequent thermal or catalytic pyrolysis under inert conditions. Natural catalysts such as dolomite and olivine, along with a commercial Ni catalyst, have been tested. The catalytic route significantly reduced tar formation (<10 wt.%) and increased gas yields (up to 79 wt.%), rich in H<sub>2</sub>, CO, and CH<sub>4</sub>, with a heating value of ~18–20 MJ/Nm<sup>3</sup>. Dolomite emerged as the most efficient and low-cost catalyst [74]. Similar results have been obtained by the same group using the aforementioned processes and spent green tea waste as feedstock [75]. These studies highlight the potential of natural mineral catalysts for producing clean fuels and chemicals while providing a sustainable solution for managing challenging waste streams.

Yang et al. [76] prepared catalysts for reforming the pine pyrolysis gas using mineral diatomite as a precursor to prepare foam ceramic and then loaded it with Fe<sub>2</sub>O<sub>3</sub> or CeCl<sub>3</sub>. The diatomite-based foam ceramic increased the pyrolysis gas (CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub>) yield at the expense of liquid yield. The catalyst containing Fe<sub>2</sub>O<sub>3</sub> proved to be the best one.

As already mentioned, gasification is a feedstock-independent process taking place at high temperatures (700 °C to 1200 °C), resulting in high syngas yield. Figure 3 summarizes the contribution of natural mineral-based catalysts used in this process, showing simplified gasifier configurations, the conditions, and the products obtained. Natural mineral catalysts and their derivatives produced by modification with Ni and/or Fe proved to be quite promising for biomass gasification. Their catalytic action increases the syngas yield and quality, reducing tar formation. Dolomite seems to be the best choice due to its CO<sub>2</sub> absorbance efficiency.



**Figure 3.** Graphical representation of feedstocks, minerals used as catalysts, simplified gasifier configurations, and products obtained via gasification.

### 2.3. Other Treatments of Biomass

Closing this chapter, let us discuss some interesting works concerning natural minerals used as catalysts or catalytic supports for accelerating steam or dry reforming of biomass-derived compounds. Valle et al. [77] studied the upgrading of raw bio-oil produced by flash pyrolysis of pine sawdust using calcined natural dolomite (850 °C for 5 h) as a catalyst in a U-shaped continuous working reactor co-fed with bio-oil and steam (Steam:C  $\approx$  6). In the downstream part of the reactor, non-catalytic pyrolysis took place, resulting in pyrolytic lignin, while in the upstream part, where a fixed-bed of dolomite was placed, upgrading of volatile pyrolysis products was achieved. Dolomite provoked a significant reduction in the O/C ratio in the bio-oil obtained, removing the carboxylic acids and sugars and acting as a  $CO_2$  sorbent. The same group in a more recent work [78] using less steam-to-carbon mass ratio (Steam:C  $\approx$  3), revealed that, at short time on stream, the upgraded bio-oil was free of acids and heavy phenols and rich in light ketones ( $\leq C_5$ ). However, carbonation of dolomite and coke formation on its surface alter the composition of the upgraded bio-oil and deactivate the catalyst.

Glycerol is a by-product derived from biodiesel production. Its price has decreased dramatically because of the increase in fuel production worldwide. Thus, the exploitation of this bio-based by-product is urgent. Cruz et al. [79] studied crude glycerol and animal fat mixtures steam reforming over activated alumina and dolomite (fixed bed reactor, 700 and 750 °C). Dolomite produced  $\sim 10$  vol% more  $H_2$ , favoring the water-gas shift reaction. Villegas-Bolaños et al. [80] used Colombian olivine as a catalyst for glycerol steam reforming. Calcined and reduced olivine resulted in high glycerol conversion (96% at 600 °C), producing mainly liquid products. At higher reaction temperatures (700 °C and 800 °C), syngas, with low  $CH_4$  content, was the main product.

Wang et al. [81] used natural palygorskite (attapulgitite) as support of Ni catalysts (Ni load: 5–40 wt.%) for steam reforming of bioethanol. A catalyst containing 20 wt.% Ni proved to be the best one among the catalysts studied concerning both the  $H_2$  yield and catalyst stability. Chen et al. [82] also prepared Ni/palygorskite catalysts modified by Al and used them for dry reforming of  $CH_4$ . All catalysts studied contained 8 wt.% Ni and various loadings of Al (0–20 wt.%). A catalyst containing 8% Al exhibited the best activity and stability, due to its high Ni dispersion and reduced coke formation.

From the above discussion, it is obvious that natural minerals with high acidity and/or alkalinity are quite promising for biomass valorization through thermocatalytic processes (pyrolysis, gasification, and reforming). Dolomite is a popular natural mineral used in biomass valorization experimental and modeling studies [83]. Indeed, more than 50% of the research articles reviewed in this chapter concern the use of dolomite either as a catalyst/CO<sub>2</sub> absorbent [31–35,38,39,41,44–48,52,59–62,66–68,73–75,77–79,83] or catalyst support [70,72].

### 3. The Use of Minerals as Catalysts for Fatty Biomass Valorization

#### 3.1. Biodiesel Production

Biodiesel has emerged as a leading renewable alternative to fossil-derived diesel due to its compatibility with current engines, biodegradability, and capacity to reduce greenhouse gases. The growing demand for sustainable fuels has shifted research toward low-cost feedstocks, such as non-edible oils, microalgae, and waste cooking oils, as well as heterogeneous catalysts that are environmentally benign and recyclable. Natural minerals, including dolomite, montmorillonite, mordenite, halloysite, and palygorskite, are attractive catalytic supports due to their abundance, tunable acidity/basicity, and the possibility of being produced by valorization of industrial waste streams. Modification strategies such as ion exchange, sulfonation, rare-earth doping, and nanoparticle impregnation have enabled these materials to function as highly active bifunctional catalysts capable of simultaneously esterifying free fatty acids (FFAs) and transesterifying triglycerides in high-FFA feedstocks.

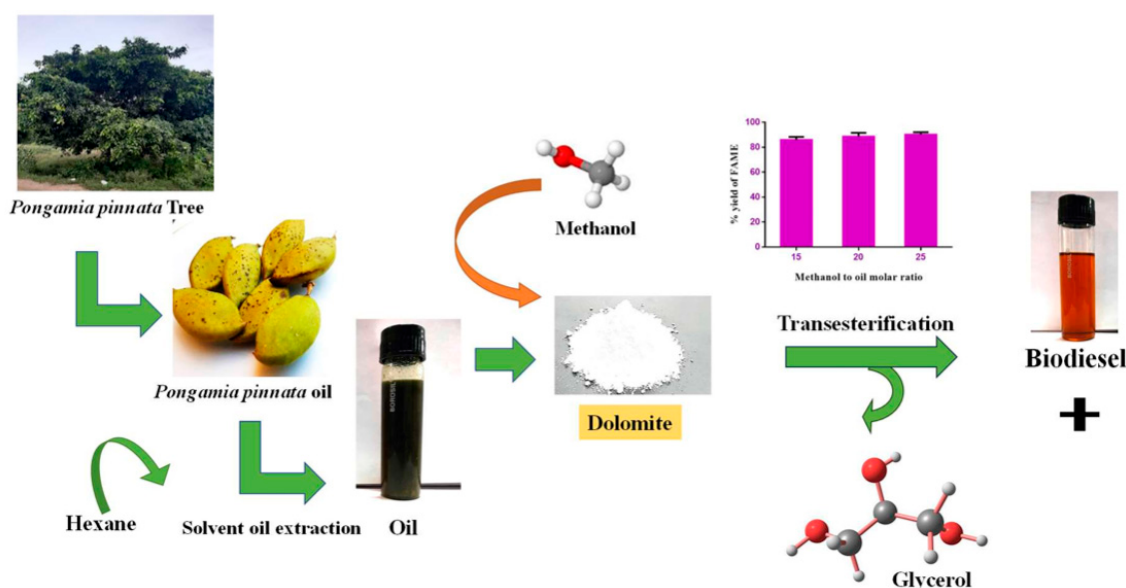
Parallel advances in process intensification, including microwave and ultrasound-assisted transesterification, combined with statistical optimization methods (Response Surface Methodology, Box–Behnken, D-optimal design), have shortened reaction times, minimized catalyst dosages, and enabled industrial scalability. Pilot-scale studies, machine learning modeling, and Aspen Plus simulations confirm the techno-economic viability of mineral-based systems. In this context, Dong et al. [84] optimized FAME production from waste cooking oil using a montmorillonite clay as a catalyst. The optimization results revealed that 96.79% FAME could be achieved at 152 °C for 8.62 h, using 4.88 wt.%, catalyst and methanol to oil molar ratio equal to 11.2.

One of the main minerals used as a catalytic support is montmorillonite. Chen et al. [85] developed a bifunctional 30%Sn-MMT-SO<sub>3</sub>H catalyst from natural montmorillonite for efficient biodiesel production from *Jatropha curcas* oil. The catalyst prepared via Sn<sup>4+</sup> ion exchange and sulfonation retained a layered nanosheet structure (145 m<sup>2</sup>/g surface area, 5.8 nm pore diameter) and exhibited high acidity (1.801 mmol/g) and stability. Optimized conditions (150 °C, 7.5 h, methanol/oil 20.2:1, 7 wt.% catalyst) resulted in 93.1% biodiesel yield with minimal activity loss after five cycles. Kinetic studies indicated a pseudo-first-order reaction with 56.98 kJ/Mol activation energy, while thermodynamics confirmed an endothermic, non-spontaneous process. The synergy of Brønsted and Lewis acid sites enabled simultaneous esterification and transesterification, demonstrating montmorillonite's potential as a low-cost, sustainable support for scalable, high-performance biodiesel catalysts. Taking advantage of the catalytic potential of montmorillonite, Tiwari et al. [86] extended its application by designing a Sn<sub>1</sub>-TPA/K-10 catalyst, further enhancing both Brønsted and Lewis acidity. The study developed a highly active 20% Sn<sub>1</sub>-TPA/K-10 catalyst by partially exchanging protons of tungstophosphoric acid (TPA) with Sn<sup>2+</sup> and supporting it on montmorillonite K-10. This design enhanced both Brønsted and Lewis acidity (2.21 mmol/g) and maintained the Keggin ion structure with strong dispersion confirmed by XRD, FT-IR, UV-Vis, and SEM. A 98.4% butyl levulinate yield was achieved via furfuryl alcohol alcoholysis under mild conditions (110 °C, FAL:BuOH 1:20, 1.2 mol% catalyst) and showed stable performance over five cycles. Compared to other solid acids,

Sn<sub>1</sub>-TPA/K-10 outperformed due to superior acidity, optimized Sn loading, and efficient regeneration. This study demonstrates the potential of montmorillonite supports for stabilizing heteropoly acids, enabling the development of highly selective, recyclable catalysts for biofuel additive synthesis.

A study by Sumari et al. [87] focuses on activated natural mordenite (ANM) used as support for dual basic metal oxides (Na<sub>2</sub>O–K<sub>2</sub>O and MgO–CaO). The catalysts produced were used for kapok seed oil transesterification under ultrasonic irradiation. Zeolite activation improved crystallinity, Si/Al ratio, and acidity, while impregnation tuned catalytic properties. Optimal catalysts resulted in biodiesel yield 72.29% (Na<sub>2</sub>O–K<sub>2</sub>O/ANM, 50%, 1:1) and 84.54% (MgO–CaO/ANM, 40%, 2:1). Biodiesel met SNI 7182:2015 standards and GC-MS analysis showed high methyl linoleate and oleate content. The study highlights that alkalinity rather than surface area determines catalytic activity; MgO–CaO/ANM outperformed Na<sub>2</sub>O–K<sub>2</sub>O/ANM due to stronger basicity, exhibiting better selectivity. This work demonstrates the natural mordenite's versatility as a cost-effective support for designing multifunctional base catalysts for biodiesel production from high-FFA oils. In addition to alkaline-modified mordenite systems, Sathya Selvabala et al. [88] explored an acid-functionalized variant demonstrating that phosphoric acid modification can effectively reduce FFAs in neem oil. They developed phosphoric acid-modified mordenite (PMOR) to esterify FFAs in neem oil, reducing the acid value from 24.4 mg to 1.8 mg KOH/g under optimized conditions (methanol/oil, 6:1, 1 wt.% catalyst, 60 °C). Phosphoric acid enhances surface hydrophobicity and weak acid sites, improving FFA conversion (>92%) and catalytic stability compared to H-mordenite. Kinetic modeling confirmed pseudo-first-order behavior, and Arrhenius analysis revealed a high forward reaction frequency factor, validating PMOR's role as a cost-effective, reusable solid acid catalyst. This catalyst enables pre-treatment of high-FFA oils, facilitating efficient biodiesel production from non-edible and waste feedstocks.

Following the zeolitic-based systems, attention shifts to dolomite, the most extensively studied mineral catalyst in biodiesel research, owing to its abundance and strong basic properties. Çakırca et al. [89] investigated CaO-modified dolomite as a heterogeneous basic catalyst for the transesterification of *Chlorella protothecoides* microalgae oil with methanol. Dolomite was impregnated with calcium acetate and calcined at 850 °C to produce active CaO-MgO phases; the 30% CaO/dolomite catalyst achieved a 90% FAME yield under optimized conditions (6:1 methanol/oil molar ratio, 3 wt.% catalyst, 65 °C, 3 h). Catalyst reusability tests showed high stability for three cycles, with regeneration restoring activity after the fourth. Characterization confirmed increased CaO crystallinity, though surface area decreased slightly. The study demonstrates dolomite's potential as a low-cost, abundant, and eco-friendly catalyst for third-generation biodiesel, leveraging microalgae oil's sustainability advantages. This approach provides a scalable alternative to homogeneous catalysis, minimizing wastewater generation while maintaining high efficiency under mild conditions. The next study from Sudalai et al. [90] evaluated dolomite sourced from healthcare industrial waste as a low-cost, recyclable heterogeneous catalyst for biodiesel production from *Pongamia pinnata* (Karanja) oil, a sustainable non-edible feedstock. Using response surface methodology, they optimized transesterification parameters, achieving a 92.3% biodiesel yield at a 20:1 methanol-to-oil ratio, 75 °C, and 5 wt.% catalyst. The Process is illustrated in Figure 4.



**Figure 4.** Schematic representation of biodiesel production from *Pongamia pinnata* oil using dolomite as a transesterification catalyst [90].

GC-MS analysis confirmed high-quality fatty acid methyl ester (FAME) composition, including methyl oleate and stearate, comparable to diesel standards. Catalyst reusability studies showed only a 7.79% yield reduction after five cycles, demonstrating dolomite's stability and economic potential. This study is notable for introducing waste-derived dolomite in a circular economy framework, simultaneously addressing waste disposal and sustainable biodiesel synthesis. By leveraging tree-based oil crops grown on marginal lands, the approach aligns with REDD+ goals and offers environmental and socioeconomic benefits, including rural livelihood development and emission reduction. Niu et al. [91] designed a cerium-incorporated dolomite catalyst to address the leaching of CaO active sites during biodiesel production. Among three synthesis routes (direct wet impregnation (DWI), solid mixing (SM), and wet impregnation after calcination (WI)), the WI-Ce/dolomite-0.6 catalyst showed superior performance, resulting in 97.21% biodiesel yield from palm oil at 65 °C, methanol/oil ratio 15:1, in 2 h. Characterization (XRD, XPS, BET, SEM) revealed high dispersion of CeO<sub>2</sub>, increased basicity (2.21 mmol/g), and a mesoporous structure (19.34 m<sup>2</sup>/g) while Ce<sup>3+</sup> species improved oxygen vacancy concentration. The catalyst retained 88.63% yield after five cycles, halving calcium leaching versus pure dolomite. Physical properties of biodiesel met ASTM D6751 and EN14214 standards. This study highlights the rare-earth modification as a strategy to stabilize natural mineral catalysts, offering cost-effective, durable options for industrial transesterification. While Niu et al. [91] demonstrated how rare-earth doping enhances dolomite's stability, Subramani et al. [92] advanced its application to both laboratory and pilot scales, proving industrial viability. Specifically, Subramani et al. [92] evaluated dolomite as a green, low-cost heterogeneous catalyst for biodiesel production from *Madhuca indica* (mahua) seed oil at both laboratory and pilot scale. Optimal lab-scale transesterification (20:1 methanol/oil, 5 wt.% catalyst, 60 °C) achieved 93% biodiesel yield in 10 h, comparable to KOH (96%) and HCl (94%) homogeneous catalysis but with easier separation and reusability. Pilot-plant trials (12:1 methanol/oil, 4 wt.% catalyst, 70 °C, 4 h) confirmed scalability, producing 5 L of high-purity FAME. Techno-economic analysis using Aspen Plus showed dolomite had the shortest payback period (2.96 years) and lowest capital cost (\$4.87M) versus alkali and acid systems, making it an industrially viable solution. Comprehensive characterization (GC-MS, FT-

IR, and NMR) validated biodiesel quality, while the study highlights dolomite's role in reducing waste and enabling sustainable biodiesel commercialization.

Korkut and Bayramoglu [93] optimized ultrasound-assisted biodiesel production from canola oil using three heterogeneous catalysts: CaO, calcined dolomite, and calcium diglyceroxide (CaDG). Through a D-optimal design and ANOVA modeling, they determined that ultrasound significantly enhances biodiesel yield by improving mass transfer and catalyst surface activity. Maximum yields were 99.4% for CaO, 96.6% for calcined dolomite, and 87.1% for CaDG at optimal conditions (5.35% catalyst, methanol/oil ratio ~7.5, 40 W ultrasound, 60 °C). The catalysts' basicity strongly correlated with their performance, with dolomite offering a cost-effective, scalable option. This work demonstrates ultrasound's potential for process improvement in biodiesel synthesis and highlights statistical modeling as a tool for optimizing heterogeneous catalysis.

Vargas et al. [94] developed bifunctional solid catalysts from industrial and household wastes, including fly ash, dolomite, eggshells, and sulfonated PET-char to synthesize biodiesel from mixtures of refined palm oil and waste cooking oil. Among the eight catalysts tested, fly ash exhibited superior bifunctionality, achieving >95% FAME yield and FFA conversion with blends containing 25% waste cooking oil while maintaining performance across variable feedstock acidity. Dolomite catalysts favored transesterification with sulfonation, improving esterification ability but lowering the basic site strength. PET-derived char materials displayed high acidity and surface area, while eggshell-derived CaO-SiO<sub>2</sub> materials showed moderate activity. This study demonstrates the viability of waste valorization in catalyst production, promoting circular economy principles and reducing biodiesel costs.

An interesting work focusing on dolomite comes from Sudalai et al. [95]. This paper demonstrated a copper-impregnated industrial waste dolomite catalyst (Cu@dolomite) for biodiesel production from *Madhuca indica* oil, emphasizing scalability and sustainability. Catalyst characterization (XRD, BET, SEM-EDX) confirmed high CaCO<sub>3</sub>/CaO content, mesoporosity (~20 nm), and strong copper dispersion. Using a Box–Behnken RSM design, optimal conditions (15:1 methanol/oil ratio, 3 wt.% catalyst, 75 °C, 6 h) yielded 96.1% FAME with 92.6% yield after five reuse cycles. GC–MS, NMR, and FTIR analyses verified biodiesel quality with all properties meeting ASTM/EN standards.

A detailed techno-economic analysis via Aspen Plus (1000 kg/h plant capacity) showed profitability with a 3.5-year payback period. Engine testing of B10–B30 blends revealed lower CO and smoke emissions but slightly higher NO<sub>x</sub>, confirming biodiesel's suitability as a diesel substitute. This study is worth noting for its integration of catalyst valorization, process optimization, emissions evaluation, and scale-up feasibility, presenting a complete industrialization pathway.

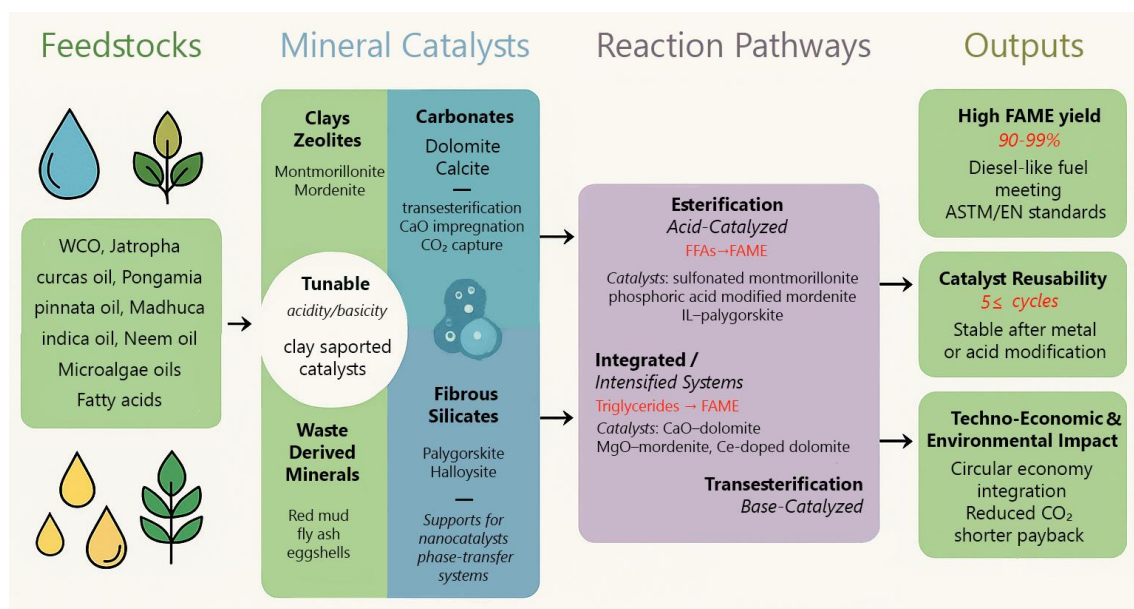
Beyond dolomite, other minerals such as palygorskite and halloysite have also been employed as catalyst supports. For instance, Zhang et al. [96] functionalized palygorskite with ionic liquids, achieving efficient esterification performance. They developed a novel heterogeneous polyionic liquid catalyst by graft-polymerizing acidic ionic liquid monomers onto nanofiber-like palygorskite supports pretreated with silane coupling agents. The optimized catalyst with 41% ionic liquid loading achieved a 69% methyl oleate yield from oleic acid esterification under mild conditions (75 °C, 12:1 methanol/oleic acid ratio, 5 h) while using less than half the ionic liquid required in homogeneous systems. Despite some deactivation, the catalyst retained 22% yield after six cycles, demonstrating reusability. Characterization (FT-IR, XPS, SEM, NH<sub>3</sub>-TPD) confirmed preserved crystalline structure, high Brønsted acidity, and strong chemical grafting, thus reducing ionic liquid leaching. This study highlights palygorskite's low cost, high surface area, and nanofiber morphol-

ogy as an effective scaffold for ionic liquid catalysts, offering a scalable route for solid acid design.

An interesting study comes from Casiello et al. [97]. They developed multifunctional nanocatalysts using halloysite (Hal) and hectorite (Ht) clays functionalized with tetrabutylammonium iodide (TBAI) and ZnO nanoparticles for biodiesel production from waste lipids. The Hal-TBAI@ZnO catalyst, optimized via Design of Experiments (DOE), achieved 99% FAME yield under mild conditions (116 °C, 21 h, 35 mg catalyst) and maintained 77% yield after five cycles, demonstrating excellent recyclability and no Zn leaching. The Ht-TBAI@ZnO variant also showed significantly improved activity over pristine Ht. Systematic testing of multiple clay minerals (Hal, Sep, Pal, Bent, Ht) linked catalytic performance to acidity, morphology, and alkali content. This work highlights the synergy of phase-transfer functionality and ZnO acidity in designing cost-effective, eco-friendly clay-supported nanocatalysts for sustainable biodiesel synthesis from high-FFA waste streams.

The last work in this section also focuses on dolomite. Sudalai et al. [98] optimized solvent-based oil extraction from *Madhuca indica* seeds and converted the oil to biodiesel using a copper-coated dolomite catalyst. Using Response Surface Methodology with a Central Composite Design, they achieved 50.9% oil yield under optimal conditions (70 °C, 6 wt./wt. solvent-to-seed ratio, 4 h). Transesterification with a 20:1 methanol-to-oil ratio and 5 wt.% Cu@dolomite at 75 °C yielded 94.31% FAME, confirmed by GC-MS analysis. The modified dolomite demonstrated high catalytic activity, reusability, and economic viability while FAME composition met EN 14103:2011 standards. This integrated study highlights process improvement and the waste-derived catalyst design, demonstrating that *Madhuca indica* is a promising non-edible feedstock for sustainable biodiesel production.

Heterogeneous catalysts based on natural minerals are indeed significant progress for biodiesel production, ensuring the financial viability of the process, the eco-friendly character, and circular economy principles adaptation. Figure 5 summarizes the most promising minerals studied as catalysts for biodiesel production via esterification (acid-minerals) and transesterification (base-minerals) routes.



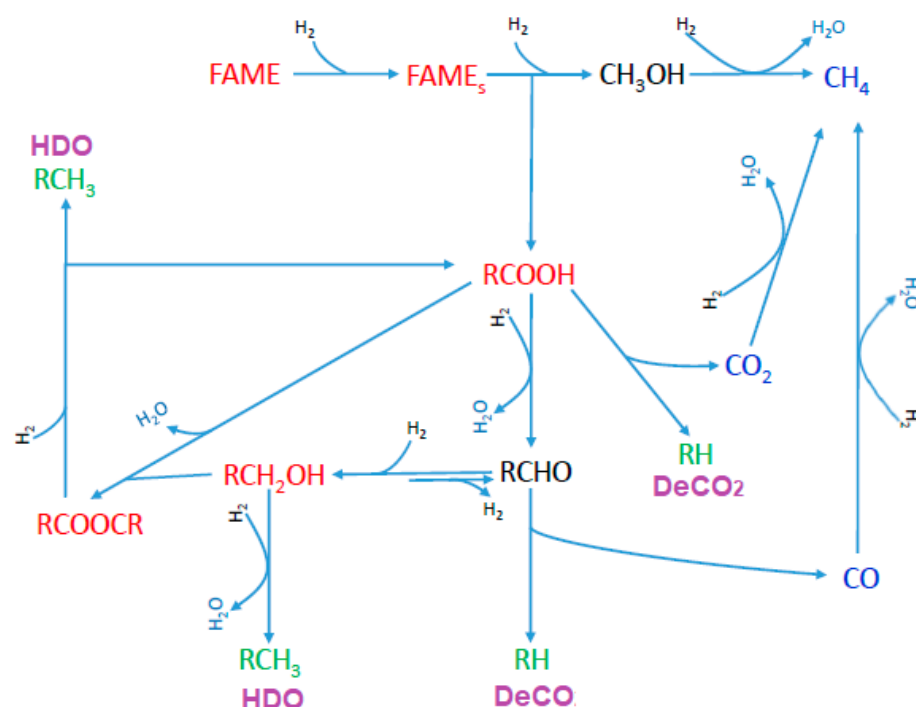
**Figure 5.** Graphical representation of feedstocks, minerals used as catalysts, reaction pathways, and outputs of biodiesel production.

### 3.2. Hydrotreated Vegetable Oil Production

Hydrotreated vegetable oil (HVO) or green (renewable) diesel is a second- and third-generation biofuel produced via hydrodeoxygenation (HDO) or selective deoxygenation (SDO) of renewable lipid-based feedstocks. Unlike conventional FAME, HVO is a pure hydrocarbon fuel fully compatible with existing engines and infrastructure, with superior stability and cetane numbers. Current research focuses on using natural minerals, including mordenite, clinoptilolite, palygorskite, montmorillonite, and dolomite as affordable, abundant catalyst supports that can replace expensive commercial carriers. Strategies such as acid/base activation, dealumination, rare-earth or transition metal doping, and nanostructuring enable high dispersion of active phases (Ni, Mo, Fe), improving selectivity and reducing coke formation. These studies highlight the development of cost-effective, scalable catalysts from locally sourced minerals, enabling circular economy approaches and supporting the decarbonization of diesel production.

Fani et al. [99] investigated biodiesel upgrading to green diesel via hydroprocessing using nickel (Ni) supported on mineral mordenite. Greek-origin mordenite was acid-treated with HCl, which significantly increased its surface area ( $156 \text{ m}^2/\text{g}$ ). Four preparation methods for supporting nickel were compared: Deposition–Precipitation (DP), Incipient Wetness Impregnation (IWI), Wet Impregnation (WI), and Infiltration (INF). The DP method resulted in the best results: high Ni dispersion, small nickel crystallite size ( $\sim 6.8 \text{ nm}$ ), and improved external surface area. The 30 wt.% Ni catalyst achieved near-complete biodiesel conversion and up to 25 wt.% HVO in liquid products while minimizing coke formation and maintaining balanced acidity. This work demonstrated that mordenite, an abundant and low-cost zeolitic material, is an effective support for selective deoxygenation catalysts concerning upgrading of the biodiesel to green diesel.

Taking into account the above encouraging results, Fani et al. [100] studied acid- and acid-base-activated mineral mordenite ( $\text{MO}_A$ ,  $\text{MO}_{AB}$ ) as supports for 30 wt.% Ni catalysts in biodiesel selective deoxygenation to HVO. Double activation improved mesoporosity (14 nm), Ni dispersion ( $\sim 7 \text{ nm}$  particles), and balanced acidity, resulting in 94 wt.% diesel-range hydrocarbons after 9 h at  $350^\circ\text{C}$  and 40 bar  $\text{H}_2$ . Kinetic analysis confirmed pseudo-first-order behavior with an activation energy of  $64.4 \text{ kJ/mol}$ .  $\text{MO}_{AB}$ -based catalysts showed lower coke formation and sintering, demonstrating the importance of zeolite textural engineering for coke-resistant SDO catalysts. Figure 6 illustrates the reaction pathways followed upon biodiesel transformation to HVO over Ni supported on double-activated mordenite catalysts, proposed by the authors [100]. The main routes involve: (i) decarboxylation ( $\text{DeCO}_2$ ) of FFAs produced by FAME hydrogenolysis; (ii) decarbonylation ( $\text{DeCO}$ ) of the aldehydes produced by FFAs reduction; and (iii) hydrodeoxygenation (HDO) of the alcohols produced by the aldehydes' reduction.



**Figure 6.** Proposed reaction network for biodiesel upgrading to HVO over Ni supported on activated (acid or acid-base) natural mordenite [100].

The work of Putra et al. [101] deals with mixed-phase mineral zeolites (mordenite and clinoptilolite) impregnated with Fe. They developed a Fe-impregnated natural zeolite (Fe/NZ) catalyst for hydrodeoxygenation of palm oil to HVO. The mixed-zeolite maintained crystallinity post Fe loading. At 375 °C, 12 bar H<sub>2</sub>, and 2 h, Fe/NZ achieved 89% conversion and 76% diesel-range hydrocarbons selectivity (C<sub>15</sub>–C<sub>18</sub>) outperforming unmodified NZ (58%). Characterization (XRD, BET, SEM-EDX, and FTIR) confirmed Fe dispersion without framework collapse. This low-cost catalyst demonstrated strong deoxygenation selectivity and minimal cracking, promising scalable green diesel production.

Putra et al. [102] continued their studies on zeolites, investigating dealuminated and NH<sub>4</sub><sup>+</sup>-exchanged Indonesian natural zeolite as a low-cost catalyst for the hydrodeoxygenation of refined palm oil. The catalyst, rich in the mordenite phase, displayed improved Si/Al ratio (7.42), mesoporosity, and balanced acidity. Under the optimized conditions (375 °C, 12 bar H<sub>2</sub> and 2 h), it achieved 52% conversion and 70% selectivity to C<sub>15</sub> alkanes via decarbonylation, resulting in diesel-range fuel with cetane numbers of 71–77. This work highlights NH<sub>4</sub><sup>+</sup>-form zeolites as selective, mild-acidity catalysts for a sustainable, non-metal-based pathway to green diesel production.

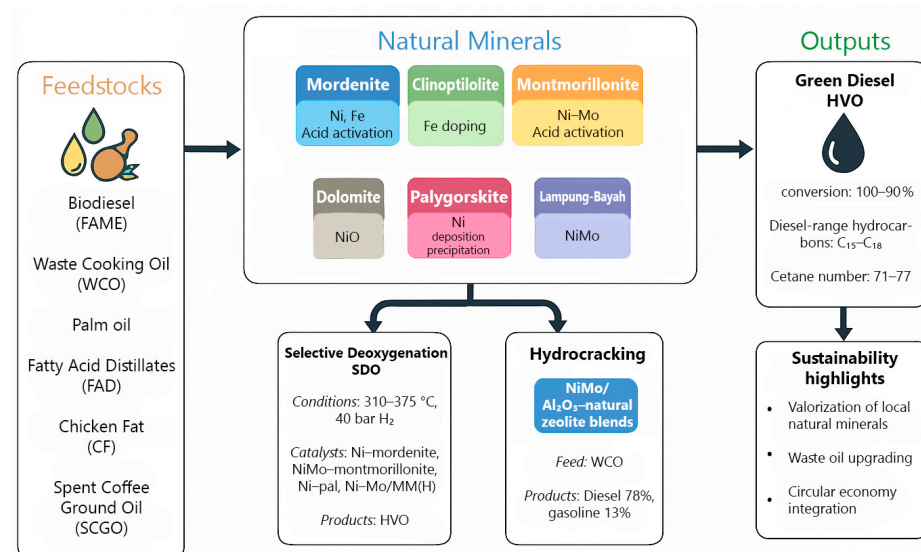
Aside from mordenite-rich zeolites, clinoptilolite phases have also been valorized. Kurniawan et al. [103] evaluated Indonesian Lampung, Bayah, and Tasikmalaya zeolites (clinoptilolite, mordenite phases) as supports for NiMo/Al<sub>2</sub>O<sub>3</sub>-zeolite catalysts for hydrocracking waste cooking oil (WCO). Acid dealumination raised Si/Al ratios (up to 13.6) and surface areas (Bayah: 191 m<sup>2</sup>/g). On the NiMo/Al<sub>2</sub>O<sub>3</sub> (75%)–Bayah Zeolite (25%) catalyst was achieved 93% conversion at 370 °C, producing 78% diesel and 13% gasoline-range hydrocarbons. Characterization (XRF, XRD, FTIR, BET) linked zeolite acidity and metal dispersion to relatively high hydrocracking efficiency. This study demonstrated the suitability of the domestic zeolites for high-performance sustainable hydrocracking catalysts, thus reducing the reliance on imported supports and valorizing WCO.

Besides zeolitic systems, montmorillonite clays have also attracted attention due to their tunable acidity and high surface reactivity. Lycourghiotis et al. [104] valorized

acid-activated natural montmorillonite as a support for Ni and Mo–Ni catalysts used in the selective deoxygenation (SDO) of waste cooking oil (WCO) to HVO. The optimized 20Ni2Mo/MM(H) catalyst achieved 100% WCO conversion and 96 wt.% in HVO (C15–C18) surpassing monometallic Ni catalysts. Mo promotion enhanced nickel dispersion, acidity, and oxygen vacancy density, shifting the reaction network toward alcohol dehydration, thus improving carbon efficiency). Detailed characterization (XRD, TEM, XPS, H<sub>2</sub>-TPR, NH<sub>3</sub>-TPD) revealed strong Ni–Mo synergy at the nanoscale. This study demonstrates montmorillonite’s industrial viability as a low-cost catalyst support for third-generation green diesel production.

In addition to mineral mordenite and montmorillonite, mineral palygorskite has also emerged as a very promising low-cost support for the development of very efficient solid catalysts for third-generation green diesel production. In fact, Lycourghiotis et al. [105] developed nickel catalysts supported on palygorskite via deposition–precipitation for the selective deoxygenation of waste cooking oil under solvent-free conditions (310 °C, 40 bar H<sub>2</sub>, 9 h). A 30 wt.% Ni catalyst achieved ~100% conversion and 81.9 wt.% n-alkanes (C15–C18), outperforming higher Ni loadings in other catalysts due to optimal dispersion and acidity balance. Characterization (XRD, TEM, XPS, NH<sub>3</sub>-TPD) revealed Ni nanoparticles (6–12 nm), nickel silicates, and moderate acidity, critical for decarbonylation pathways. This work highlights palygorskite as a low-cost natural support enabling efficient, scalable green diesel production from residual feedstocks. Continuing their research, Lycourghiotis et al. [106] evaluated a 30 wt.% Ni catalyst supported on mineral palygorskite for the selective deoxygenation of FAME and residual fatty raw materials: waste cooking oil (WCO), fatty acid distillate (FAD), spent coffee ground oil (SCG), and chicken fat (CF). At 310 °C, 40 bar H<sub>2</sub>, the yield achieved using CF was 98% diesel-range n-alkanes, outperforming WCO (83%), FAD (68%), and SCGO (10%), revealing strong feedstock effects. FAME was more reactive, rapidly converted to hydrocarbons without intermediates. Characterization (XPS, TEM, XRD) showed minimal Ni loss, stable support structure, and coke/carbon deposition related to feedstock impurities. This study highlights Ni supported on palygorskite as a robust, low-cost catalyst for diverse feedstocks.

Acid natural minerals proved to be suitable supports for metallic catalysts (mainly Ni) used for the production of HVO through hydroprocessing of fatty biomass. Figure 7 summarizes graphically the findings of relevant studies.



**Figure 7.** Graphical representation of feedstocks, minerals used as catalysts, hydroprocessing routes, and outputs of HVO production.

### 3.3. Biofuels Produced by Deoxygenation

Catalytic cracking has emerged as one of the most versatile thermochemical routes for the deoxygenation of renewable feedstocks into liquid biofuels. Unlike esterification or hydroprocessing, catalytic cracking does not require methanol or hydrogen addition and can operate under relatively flexible conditions, making it particularly attractive for its large-scale integration in existing refinery infrastructures. Zeolite-based catalysts are central to this approach due to their tunable acidity, shape-selective micropores, and thermal stability, which enable effective cracking of triglycerides, fatty acids, and lignocellulosic intermediates. The incorporation of natural zeolites such as mordenite and clinoptilolite, as well as earth-abundant minerals like montmorillonite, palygorskite, dolomite, and marble waste, has gained momentum, offering low-cost and sustainable alternatives to conventional catalysts.

Recent research has demonstrated that the acidity–basicity balance, pore architecture, and metal promotion (Ni, Mo, Fe, Zn) significantly affect product selectivity, coke resistance, and catalyst reusability. Studies have shown enhanced production of diesel-range hydrocarbons, light aromatics, and alkanes, while suppressing oxygenated compounds such as carboxylic acids and phenols. Innovative approaches, including catalyst functionalization, hierarchical structuring, machine learning-based optimization, and integration with CO<sub>2</sub> sorption, further enhance the potential of these systems for high-quality biofuel production.

In this section, representative works are reviewed, encompassing experimental studies and process intensification strategies, as well as review articles to illustrate the progress and remaining challenges in catalytic cracking for deoxygenation. These studies demonstrate the suitability of zeolites and mineral-based catalysts in advancing scalable, cost-effective, and environmentally friendly routes for renewable biofuels.

Zamri et al. [107] reviewed the recent advances in triglyceride catalytic pyrolysis using heterogeneous dolomite catalysts for biofuel production. Dolomite, composed mainly of CaO and MgO after calcination, offers strong basicity, low cost, and environmental friendliness. The review emphasizes how raw, calcined, and metal-doped dolomites enhance deoxygenation, reduce acidity, and improve stability compared to conventional catalysts. Notably, Ni-activated dolomite achieved superior selectivity and resistance to coke formation, while MgO-enriched dolomites improved yields of light biofuels. This work highlights dolomite's versatility and scalability as a sustainable catalyst for catalytic cracking pyrolysis of triglycerides.

Several researchers have explored metal-modified mineral zeolites, which combine acidity and textural diversity with earth-abundant availability for the bio-jet fuel synthesis. Specifically, Abdullah et al. [108] optimized the catalytic cracking of palmitic acid using Fe<sup>3+</sup>-modified mineral mordenite from Indonesia to produce aviation fuel components. The Fe<sup>3+</sup> exchange enhanced Brønsted and Lewis acidity (81.66 and 26.77 mmol/g), increased the surface area (198 m<sup>2</sup>/g) and reduced pore size (7.36 nm) compared to parent mordenite, while preserving the crystalline structure. Under cracking at 310 °C, the catalyst achieved 61.94% conversion with 62.9% selectivity toward C8–C16 hydrocarbons - alkanes, alkenes, cycloalkanes, and aromatics - relevant to aviation fuel. Pentadecane was identified as a key intermediate, undergoing further cracking, isomerization, and dimerization. Compared to H<sup>+</sup>-unmodified mordenite, Fe<sup>3+</sup>-mordenite produced a broader spectrum of aviation-fuel-like compounds, confirming the importance of metal ion modification for zeolite-based catalysts in bio-jet fuel synthesis.

Buyang et al. [109] investigated the catalytic pyrolysis of Reutealis trisperma oil (RTO) using raw dolomite as a natural catalyst. Without prior calcination, dolomite significantly enhanced liquid bio-oil yields, reaching 77.39% at 450 °C, while reducing char formation to just 0.11%. GC–MS analysis revealed a higher proportion of hydrocarbons and improved

fuel properties, such as lower viscosity (3.12 cSt), higher calorific value (41.61 MJ/kg), and increased density compared to non-catalytic pyrolysis. Importantly, subsequent esterification reduced carboxylic acid content from 55.47% to 3.32%, further upgrading fuel quality. This study highlights raw dolomite as a cost-effective, eco-friendly catalyst for producing stable bio-oils, offering a sustainable route for renewable energy applications.

Hafriz et al. [110] investigated catalytic pyrolysis of WCO using Malaysian dolomite as a deoxygenation catalyst. Upon calcination at 900 °C under N<sub>2</sub>, dolomite was transformed into active MgO–CaO phases, significantly enhancing basicity, porosity, and CO<sub>2</sub> adsorption. The catalyst achieved 76.5% liquid hydrocarbon yield (C<sub>8</sub>–C<sub>24</sub>), predominantly alkanes and alkenes with minimal oxygenates (23.5%) and low acid value (33 mg KOH/g), outperforming commercial zeolites (ZSM-5, HY) in product quality. SEM and XRD confirmed structural activation while GC-MS analysis revealed a favorable hydrocarbon distribution in the gasoline–diesel range. In a next study, Hafriz et al. [111] investigated the effect of different synthesis techniques of Ni catalysts supported on Malaysian dolomite in the deoxygenation of WCO for renewable green fuel production. The study compared precipitation, impregnation, and co-precipitation methods in order to determine how preparation techniques influence physicochemical and catalytic properties. Among them, the precipitation-derived catalyst exhibited superior performance, achieving the highest WCO conversion (68%), pyrolysis oil yield (36.4%), and lower coke formation (32%). Characterization (XRD, BET, CO<sub>2</sub>-TPD, SEM, TEM, and XRF) revealed that precipitation enhanced surface area, mesoporosity, and bifunctional acid–base sites, all of which favored deoxygenation reactions. Although the co-precipitated catalyst showed higher basicity, it was more prone to coke formation, while the impregnated catalyst achieved the highest hydrocarbon yield but with higher oxygenated by-products. Overall, precipitation proved the most effective synthesis technique for producing high-quality green diesel fractions (C<sub>13</sub>–C<sub>20</sub> hydrocarbons) from WCO. Ali et al. [112] investigated NiO supported on Malaysian dolomite as a bifunctional acid–base catalyst for converting sludge palm oil into diesel-range hydrocarbons via catalytic pyrolysis. Conversion 83.9% in hydrocarbons was achieved with 68.1% diesel selectivity after 45 min at 400 °C. This outperforms higher temperature runs due to reduced soap and oxygenates formation. NiO enhances acidity, mesoporosity, and coke resistance, promoting decarboxylation/decarbonylation pathways. A second fractional distillation step slightly increased saturation and reduced oxygenates. Continuing in the same subject, Hafriz et al. [113] investigated the catalytic deoxygenation of WCO using NiO-modified Malaysian dolomite to produce green fuels within the gasoline, kerosene, and diesel range. By applying response surface methodology and central composite design, the authors optimized temperature, time, catalyst loading, and N<sub>2</sub> flow. Optimum conditions (410 °C, 60 min, 5.5 wt.% catalyst, 175 cm<sup>3</sup>/min N<sub>2</sub>) yielded >98% WCO conversion, high hydrocarbon selectivity (C<sub>8</sub>–C<sub>24</sub>), and reduced coke formation. Their catalyst exhibited synergistic acid–base properties, enhanced porosity, and strong resistance to sintering, enabling efficient cracking–deoxygenation pathways. Biofuel products met international quality standards, demonstrating dolomite's potential as a low-cost, abundant support for scalable green diesel production.

Kanchanatip et al. [114] explored the catalytic performance of Thai dolomite modified with varying MgCO<sub>3</sub> loadings (0–30 wt.%) for pyrolytic-catalytic cracking of waste cooking oil into light biofuels. Characterization (XRD, SEM-EDX) confirmed successful Mg incorporation, while the cracking experiments at 450–550 °C revealed optimal conditions at 500 °C with 20 wt.% Mg/dolomite, yielding 84.5% pyrolytic oil with 65% light biofuels (gasoline and kerosene). Most products met viscosity standards, though acidity levels remained high, suggesting blending with petroleum fuels for practical applications.

Complementing dolomite, marble waste (MW) has recently gained attention as another calcium-rich mineral source offering both catalytic activity and opportunities for industrial waste valorization. Tamim et al. [115] investigated the catalytic ability of MW, rich in calcite, dolomite, and quartz, for the low-temperature pyrolysis of waste cooking oil into bio-jet fuel. At 380 °C with 3 wt.% MW the process yielded 56.5% liquid fuel with hydrocarbons accounting for ~80%, primarily in the jet fuel C8–C16 range. Importantly, MW reduced carboxylic acids from 49% (catalyst-free pyrolysis) to <4%, while enhancing cyclic hydrocarbon content up to 35%. The combination of CaO and MgO active sites facilitated deoxygenation and C–O bond cleavage, improving hydrocarbon selectivity. The study indicates that MW, being an abundant, low-cost material, can be used as a catalyst for sustainable jet fuel production, offering a novel way for valorizing industrial waste. Tamim et al. [116] developed nickel-activated marble waste (Ni/MW) nanoparticles as efficient catalysts for the pyrolysis of WCO into hydrocarbons. MW, mainly calcite with traces of dolomite and quartz, was impregnated with 5–20 wt.% Ni and calcined at 550 °C. The optimized 5% Ni/MW catalyst achieved 95% WCO conversion and 60% biofuel yield at 380 °C, outperforming unmodified MW (76%). Hydrocarbon selectivity increased to 91.7% with diesel-range products dominating (82.3%) and n-C15 as the major fraction (39.9%). The catalyst showed >92% conversion after four reuse cycles. The Ni activation transformed MW into nanoparticle structures, enhancing the surface area, basicity, and catalytic stability.

#### 4. Biomass-Derived Platform Molecules Transformation into Value-Added Products

Depolymerization of biomass via hydrolysis, pyrolysis, cracking, and hydrothermal liquefaction results in very important substances, suitable for the preparation of bio-based products that can substitute similar petroleum-derived substances in the chemical industry. Catalytic transformation of the initial biomass-derived molecules to value-added products has drawn the attention of researchers. Biomass platform molecules upgrading is realized through catalytic hydrogenation, oxidation, oxidative cyanation, isomerization, condensation, etherification, hydrolysis, dehydration, and depolymerization. New catalysts have been developed for such reactions. Among them, heterogeneous catalysts based on natural minerals are eco-friendly and low-cost ones.

##### 4.1. Hydrogenation of Bio-Based Molecules

Furfural (FUR) is a platform molecule from biomass, produced in more than 300,000 tons per year worldwide [117]. It can be upgraded to added-value products via catalytic reduction. Richel et al. [118] have reviewed the relevant bibliography concerning the recent advances in the reduction of FUR to furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyltetrahydrofuran under liquid and gas phase continuous flow systems using thermal or electrochemical activation and hydrogen or alcohol as reducing agent.

Jiménez-Gómez et al. [119] prepared Cu (15–60 wt.%) catalysts supported on natural bentonite and sepiolite and evaluated them in FUR hydrogenation in a gas–solid atmospheric pressure fixed-bed reactor in a temperature range 170–230 °C and obtained selectively only furfuryl alcohol (main product) and 2-methylfuran. A catalyst loaded with 45 wt.% Cu on bentonite exhibited the highest furfuryl alcohol yield (72%, at 210 °C and 5 h time on stream). The above group [120] also studied sepiolite-supported Ni (1–10 wt.%) catalysts prepared by various methods for hydrogenation of FUR. A low loading (2.5 wt.% Ni) catalyst proved the most active and quite stable at 190 °C for 5 h TOS. At higher temperatures, the activity and stability declined. As to the products obtained, furan, methylfuran,

and furfuryl alcohol were the main. The production of the first two declined with TOS, while that of the latter increased. The catalyst prepared by a grafting method exhibited the best catalytic performance due to the high Ni phase dispersion achieved. García et al. [121] studied Ni supported on two natural sepiolites and an attapulgite as catalysts in the transformation of levulinic acid into  $\gamma$ -valerolactone, comparing various  $H_2$  donors ( $HCOOH$  and  $H_2O$ ) at 120 and 180 °C. Water proved the best hydrogen donor when it was activated by Zn addition. Attapulgite and high surface area sepiolite resulted in very active Ni catalysts (2 wt.% Ni), ensuring a high active site population. In a more recent work, García et al. [122] used natural sepiolite as support for Pt, Zr, and Pt-Zr (Zr-Pt) catalysts to transform FUR to  $\gamma$ -Valerolactone. This transformation involves two hydrogenation steps, in which 2-propanol participates as a reduction agent. They found that a physical mixture of Zr- and Pt-containing catalyst exhibited the best catalytic performance for the studied reaction, higher than each catalyst alone and the corresponding bimetallic ones.

#### 4.2. Oxidation of Bio-Based Molecules

Oxidation of biomass-derived molecules is an important reaction for the production of green and sustainable chemicals. Wang et al. [123] studied the transformation of dihydroxyacetone into glycolic and formic acid using  $MnO_2$ /goethite catalysts. They found that dihydroxyacetone is initially decomposed into glycolic acid and hydroxymethyl ( $\cdot CH_2OH$ ) radicals. The latter are oxidized to formic acid.  $MnO_2$  affects the reaction mechanism, preventing their over-oxidation. Zhong et al. [124,125] used natural clay minerals palygorskite and halloysite nanotubes for preparing supported bimetallic Pt-Pd [124] and Pt-Au [125] catalysts, respectively, and studied the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) in  $H_2O$  in the absence and in the presence of bases. FDCA is a very important monomer for preparing biopolymers. They found that the synergy between natural supports and active metals, as well as metal alloying, resulted in complete conversion of reactant and 99% yield of the desired product. The same research group [126] studied also the catalytic performance of two Ru/palygorskite catalysts containing 1 wt.% Ru in oxidic ( $Ru^{3+}$ ) and metal ( $Ru^0$ ) state for HMF selective oxidation to 2,5-difuranylfuran (DFF). Over the oxidic catalyst high yield of DFF (98%) was achieved under mild conditions (catalyst: 50 mg; toluene: 10 mL; HMF: 0.5 mmol;  $O_2$  pressure: 10 bar; temperature: 110 °C), while over the metallic catalyst lower yield was obtained. The best catalytic performance of the oxidic catalyst was attributed to the higher dispersion and the oxidizing ability of  $Ru^{3+}$  species. Wang et al. [127] studied the same reaction using bimetallic AuPd catalysts supported on nitrogen-doped carbon, which was templated by halloysite nanotubes (HNTs). Under optimum reaction conditions (catalyst = 0.05 g;  $nHMF:nNa_2CO_3 = 1:4$ ; 100 °C; 24 h; 2.0 MPa  $O_2$ ), a catalyst containing 2 wt.% active metals in a molar ratio Au:Pd = 3:1, exhibited excellent FDCA yield (99.9%), good stability, and reusability. An analogous finding has been published by Chen et al. [128], who also studied HMF oxidation to FDCA using the same active metals combination and molar ratio supported on a  $ZrO_2$  layer deposited on HNTs. Citric acid (CA) assisted sol-gel method was used for support preparation with various CA to Zr ratios (0, 0.5, 1, and 2). The catalyst prepared with CA:Zr = 1 exhibited the best catalytic activity and FDCA yield (99.5%). Following the aforementioned approach, they substituted  $ZrO_2$  with  $TiO_2$  to prepare  $Au_2Pd_1/TiO_2-xCA@HNTs$  catalysts with varying oxygen vacancies [129]. Oxygen vacancies regulate strong interactions between noble metals and support, increasing the adsorption capacity of HMF and crucial intermediates and facilitating the adsorption and activation of molecular oxygen. In a next study [130], they synthesized AuPd supported on natural vermiculate catalysts (mole ratio of Au to Pd: 1/0, 0/1, 1/1, 1/2, 2/1, and 2.5/1) and evaluated them for HMF conversion towards FDCA. A catalyst with Au:Pd = 2:1 proved

the most effective for FDCA production (99.9% FDCA yield at 2 h, 2 MPa O<sub>2</sub>, and 100 °C), being also quite stable (90.1% FDCA yield after five catalytic cycles). Recently, Zhang et al. [131], paving their pathway of noble metal catalysts supported on TiO<sub>2</sub> templated by HNTs, studied a series of trimetallic catalysts (Au/Pd/Pt) for HMF oxidation to FDCA at almost STP conditions using air as oxygen source. 93.6% FDCA yield was achieved over the Au<sub>0.5</sub>Pd<sub>0.2</sub>Pt<sub>0.3</sub>/TiO<sub>2</sub>@HNTs catalyst, showing the outstanding performance of the ternary noble metal catalyst in comparison to bimetallic and monometallic ones.

#### 4.3. Dehydration of Bio-Based Saccharides

Bio-based monosaccharides with six C atoms (like glucose, fructose, etc.) constitute very important sources of platform molecules, like FUR, HMF, levulinic acid (LA), and alkyl levulinates (AlkLevs) production, which are exploited in modern biorefineries for fine chemicals and biofuels production [132]. Their conversion can be achieved over heterogeneous catalysts. Relative processes based on catalysts derived from natural minerals, being eco-friendly, low-cost, and easily scaled up, fulfill the principles of green and sustainable chemistry.

Yang et al. [133] studied the conversion of mono- (fructose and glucose) and polysaccharides (inulin and starch) into HMF over natural attapulgite modified by H<sub>3</sub>PO<sub>4</sub> in a biphasic process (2-butanol/water). The attapulgite modification increased its acidity and changed the relative population of Brønsted and Lewis acid sites. This effect resulted in enhanced yield of HMF 96.3% from fructose and 50.4% from starch, while the modified catalyst exhibited excellent stability for at least four consecutive catalytic cycles. Kiani et al. [134] also used H<sub>3</sub>PO<sub>4</sub> to modify natural bentonite in order to obtain an effective catalyst for glucose transformation to FUR in a mono-phasic water–dimethyl sulfoxide (DMSO) system, achieving 69.2% FUR yield at 170 °C after 60 min.

Adila et al. [135] studied the dehydration of ethanol to produce diethyl ether using natural zeolite from Klaten, Indonesia, as a catalyst. This natural zeolite containing 32.57% mordenite exhibited quite stable, even low performance (~2.5% yield).

#### 4.4. Isomerization of Bio-Based Saccharides

Hydrolysis of waste cellulose or starch-rich materials results in bio-based glucose. Glucose can be isomerized to fructose through enzymatic processes, which require several high-cost requirements for industrial application, like enzyme cost and precise pH and temperature adjustment. Fructose is a well-known sweetener and could be easily transformed into HMF. The development of a thermochemical catalytic process for the above isomerization with high-performance and based on low-cost heterogeneous catalysts should be a very important alternative to the existing enzymatic process. Ye et al. [136] tested natural bentonite as a low-cost catalyst for such a process. Brønsted base sites of the catalyst were found to be the active sites, resulting in 39.2% fructose yield at mild reaction conditions (110 °C, 60 min, water solvent). The regulation of the catalyst's base sites is a key factor in glucose isomerization. Ren et al. [137] tried to regulate the base site population and strength by doping natural albite with N-depositing chitosan on its surface, followed by calcination (700 °C). Doping increased the population of weak and moderate strength base sites and reduced that of the strong base sites, being the majority on the undoped calcined albite. Fructose yield of 38.9% was achieved at 90 °C, 30min, in water over the N-doped albite catalyst. Long et al. [138] using natural dolomite and synthetic mixed CaO-MgO proved that moderate basicity is necessary for obtaining high fructose yield under mild conditions. The calcination protocol adopted regulates the base properties of dolomite. Thus, a catalyst which underwent calcination at 650 °C for 3 h and then at 700 °C for 3 more hours proved the best one, achieving 35.9% fructose yield at 35 °C for 60 min.

#### 4.5. Other Transformation Reactions of Bio-Based Molecules

As already mentioned, glycerol is a biodiesel byproduct produced in huge amounts worldwide (10% of biodiesel). Its molecule has three hydroxyl groups, which provide a diverse reactivity to obtain a variety of valuable compounds. In an effort to exploit this low-cost byproduct, various routes have been examined: dehydration, hydrogenolysis, oxidation, steam reforming, esterification, and etherification. The latter reaction can happen using glycerol as the only reactant, resulting in di- and triglycerol. These short-chain oligomers are used in cosmetics, polymers, food additives, paints, inks, etc. Barros et al. [139] studied the glycerol self-etherification to produce short-chain oligomers using natural dolomite as a catalyst. Using 2% calcined dolomite (800 °C) at a reaction temperature of 220 °C for 24 h, they achieved 77% glycerol conversion with enhanced di-glycerol selectivity (51%), while the tri-glycerol selectivity was low (3%).

Levulinic acid and levulinates are used as fine chemical intermediates, fuel additives, medicine, etc., for production. Tian et al. [140] tried to develop a recyclable and environmentally friendly catalyst, using natural attapulgite modified by H<sub>2</sub>SO<sub>4</sub>. Sulfated attapulgite was evaluated for the conversion of furfuryl alcohol to ethyl levulinate in ethanol. The concentration of sulfuric acid used for attapulgite modification affected the catalyst's texture, structure, sulfur content, acidity, formation of Brønsted and Lewis acid sites, and finally catalytic performance. The catalyst prepared with 1% H<sub>2</sub>SO<sub>4</sub> proved the best one, resulting in an ethyl levulinate yield of 95.4% at 160 °C in 3 h, exhibiting excellent reusability and easy regeneration. Lai et al. [141] studied the preparation of methyl levulinate using glucose as feedstock and a bifunctional catalyst consisting of phosphotungstic acid supported on metal (M: La<sup>3+</sup>, Ce<sup>3+</sup>, Er<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>)/Si-pillared natural montmorillonite. The catalyst modified by Zr<sup>4+</sup> and containing 20 wt.% phosphotungstic acid showed the best performance, achieving 65.8% yield of methyl levulinate at 170 °C for 4 h.

Acid (H<sub>2</sub>SO<sub>4</sub>) modified natural minerals (attapulgite, kaolin, and clinoptilolite) were used by Meng et al. [142] as catalysts for the aldol condensation reaction of bio-based cyclopentanone under solvent-free conditions. It was found that the attapulgite-based catalyst, with the highest acidity, exhibited the best catalytic performance (59% dimer yield and 24.3% trimer yield at the reaction temperature of 150 °C in 4 h).

Zhang et al. [143] also used mineral attapulgite as support to prepare Ni (5–30 wt.%) catalysts by deposition-precipitation for reductive amination of bio-based aldehydes and ketones. Catalysts containing 10–15 wt.% Ni and reduced at 550 °C, exhibited the highest catalytic performance for the conversion of 2-hydroxytetrahydropyran into valuable 5-amino-1-pentanol (94% yield). Furthermore, the catalyst with 10 wt.% Ni loading exhibited good activity and stability in the same reaction of several other biomass-derived aldehydes and ketones.

#### 4.6. Terpenes Upgrading

Terpenes, abundant in essential oils and forestry byproducts, represent a renewable platform for the production of high-value biofuels and chemicals. Their complex, cyclic, and unsaturated structures make them attractive precursors for jet fuel components, lubricants, and fine chemicals, though they require selective upgrading to meet fuel standards. Catalytic strategies—including isomerization, hydrogenation, and solvent-assisted transformations—have been widely employed, often using natural minerals and zeolite-based supports to enhance activity, selectivity, and catalyst stability. In parallel, the development of sustainable fuel additives plays a critical role in improving combustion efficiency and reducing greenhouse gas emissions. Nanostructured catalysts expand the possibilities for scalable and eco-friendly production. This section reviews recent advances in terpenes upgrading and the synthesis of bio-based fuel additives, highlight-

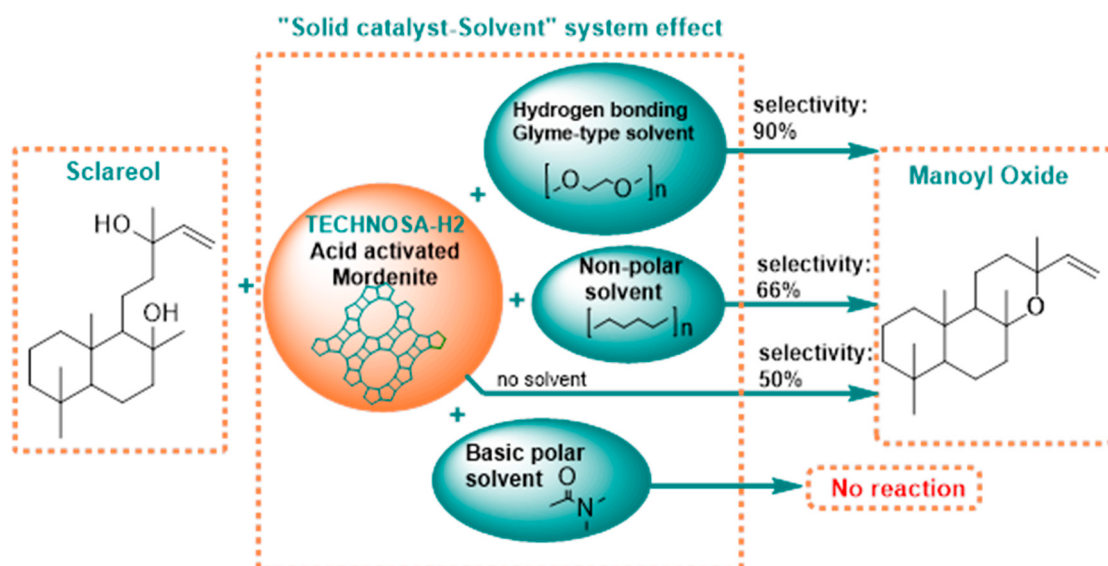
ing the role of mineral-derived catalysts in bridging renewable resources with practical energy applications.

Lycourghiotis et al. [144] investigated the activation of natural mordenite, sourced from volcanic soils in Greece, through treatment with different acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, CH<sub>3</sub>COOH) for the catalytic transformation of limonene into p-cymene, an added-value product. Acid treatments removed exchangeable cations from the natural mordenite, particularly sodium, thereby increasing surface area, acidity, and microporosity while preserving the fibrous crystalline framework. Among the samples, HCl-treated mordenite (TECHNOSA-H2) demonstrated the highest catalytic activity, achieving 65% p-cymene yield at 140 °C, with a limonene-to-catalyst ratio of 15 and 7 h reaction time. The study highlights the importance of natural minerals' acid treatment to transform them into efficient mineral-based solid acid catalysts for terpene upgrading, providing a cost-effective and sustainable pathway for p-cymene production from limonene. In this frame, Makarouni et al. [145] investigated the transformation of limonene into p-cymene using acid-activated natural mordenite treated by sulfuric acid as a heterogeneous catalyst and atmospheric oxygen as a green oxidant. The sulfuric acid treatment removed sodium oxides and opened micropores, drastically increasing surface area and generating strong acid sites without destroying the fibrous framework of mordenite. The catalyst promoted limonene isomerization inside micropores, followed by a non-catalytic oxidation step with oxygen, yielding high amounts of p-cymene while limiting polymeric by-products. The novelty of this work lies in demonstrating a two-step mechanism (catalytic isomerization and non-catalytic oxidation) using only natural minerals and air as a benign oxidant, which offers a sustainable route for terpene upgrading. The influence of thermal treatment (calcination) of natural mordenite and its acid-activated derivatives on their structural, textural, and acidity properties was also investigated [146]. This study revealed that calcination does not change the structure and morphology of mineral nanoparticles. However, it diminishes the Brønsted acidity in all cases. Concerning the textural characteristics of the studied samples, it was found that they depend on the acid activation mode adopted (HCl: no change; H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH: considerable decrease in specific surface area (SSA); HNO<sub>3</sub>: increase in SSA).

Moving beyond mordenite, Lycourghiotis et al. [147] explored montmorillonite as an alternative natural mineral catalyst, offering enhanced mesoporosity and distinct acid site distributions. This work investigates the transformation of limonene into high-value products, such as isomers ( $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene) and p-cymene, using acid-activated natural montmorillonite (treated with HCl or HNO<sub>3</sub>). Acid activation removed Na<sup>+</sup> and Ca<sup>2+</sup> ions from interlayer regions, increased mesoporosity (3–3.5 nm), and generated Brønsted acid sites. These sites catalyzed limonene isomerization, while final aromatization to p-cymene proceeded via oxidative dehydrogenation by atmospheric oxygen as a green oxidant. Optimization of conditions (100 °C, 20 h, limonene/catalyst ratio 15:1) enabled >90% yield of desired products with <1% polymer formation. Overall, acid-activated montmorillonite provides a sustainable catalytic route for producing aromatics and terpene isomers from renewable limonene.

In addition to limonene valorization, Makarouni et al. [148] shifted the focus toward di-terpenes, employing solvent-assisted mordenite catalysis to produce manoyl oxide. They developed a sustainable one-step catalytic system for producing manoyl oxide (MO), a di-terpenoid precursor of forskolin and ambrox, using acid-activated mordenite zeolite. The acid-activated mineral (TECHNOSA-H2) was tested with different solvents for the above reaction. The process employed sclareol (from *Salvia sclarea*) as the feedstock, undergoing catalytic cyclodehydration at 135 °C under atmospheric pressure (Figure 8). Without solvents, yields were limited (~50%), but the introduction of glyme-type solvents (diglyme,

triglyme, tetraglyme) drastically improved selectivity, achieving up to 90% yield in MO. Mechanistic analysis revealed that solvent polarity and hydrogen bonding interactions lowered the activation energy barrier (62.7 kJ/mol with glymes vs. 93.5 kJ/mol with dodecane). Catalyst acidity was identified as a key performance factor, with the strongest acid-activated mordenite producing the highest MO yields. This zeolite–solvent system offers an environmentally friendly and scalable pathway for terpenoid upgrading.



**Figure 8.** Schematic representation of the manoyl oxide production from sclareol over acid-activated mordenite [148].

Finally, Makarouni et al. [149] studied the catalytic performance of TECHNOSA-H2 for the synthesis of ethers (di-furfuryl ether and furfuryl ethyl ether) and acetals (citral propylene glycol acetal and citral diethyl acetal) from furfuryl alcohol and citral, respectively. They found that TECHNOSA-H2, a catalyst derived from natural mordenite, is quite promising for acetalization, isomerization, and etherification reactions, as well as in cases where reactant shape selectivity is crucial.

## 5. Conclusions and Future Perspectives

Biomass valorization leads to biofuels and value-added chemicals that can substitute the corresponding petroleum-based products, reducing the carbon footprint, ensuring domestic production, and minimizing/exploiting organic wastes in a circular economy philosophy. New catalytic processes emerge in modern biorefineries established worldwide, usually based on traditional refinery catalysts. However, the cost of such catalysts is unaffordable for industrial applications based on biomass processing [150]. Natural mineral-based catalysts seem to be a promising, eco-friendly, and low-cost solution to tackle this problem. This article attempts to highlight the potential of natural mineral-based catalysts for various processes in a biorefinery.

Catalytic processes like pyrolysis, gasification, and reforming are usually the first steps of any kind of biomass treated in a biorefinery. The reviewed articles showed that natural minerals suitably activated (calcination, acid treatment, etc.) can accelerate such processes in situ or ex situ due to their high acidity/basicity. Dolomite is a popular natural mineral for these processes, used either as a catalyst and CO<sub>2</sub> absorbent or as a catalytic support.

Biodiesel, a first-generation biofuel coming from fatty biomass, is produced industrially using mainly homogeneous catalysts. The reviewed studies clearly demonstrate the versatility of natural minerals and clays as catalysts and catalytic supports for transforming

the homogeneous process to the more environmentally benign heterogeneous one. Montmorillonite, mordenite, palygorskite, halloysite, and particularly dolomite have proven effective after targeted modifications such as sulfonation, metal impregnation, or acid/base activation. These strategies enhance acidity–basicity balance, surface area, and stability, enabling the simultaneous esterification of FFAs and transesterification of triglycerides in diverse feedstocks. These findings show that low-cost, abundant minerals can bridge laboratory research and industrial application, offering sustainable catalytic solutions for large-scale biodiesel production. Future work should emphasize catalyst durability, feedstock flexibility, and integration with biorefinery systems to accelerate commercialization.

HVO or green (renewable) diesel is a second-generation biofuel produced via fatty biomass hydrotreatment. Mordenite, clinoptilolite, montmorillonite, palygorskite, and dolomite, when modified through dealumination, acid/base activation, or transition-metal loading, consistently enhanced dispersion of active phases and reduced coke deposition. These systems achieved high conversion of biodiesel, waste cooking oil, and other lipid feedstocks into diesel-range hydrocarbons with excellent selectivity, stability, and reusability. The diversity of feedstocks—from palm oil and sludge palm oil to chicken fat and spent coffee ground oil further highlights the adaptability of mineral-based catalysts. These advances indicate that mineral-supported catalysts are scalable, sustainable solutions for green diesel production, though future work should refine resistance to deactivation and bridge the gap from pilot studies to commercial deployment.

Catalytic cracking of fatty biomass, particularly when employing zeolite and other mineral based catalysts, provides a promising pathway for producing high-quality biofuels without external hydrogen input. Natural zeolites such as mordenite and clinoptilolite and other minerals like montmorillonite, dolomite and marble waste, have shown excellent activity in deoxygenation and hydrocarbon upgrading, yielding diesel-range alkanes and light aromatics while reducing oxygenates. Metal promotion (Ni, Mo, Fe, Zn) further enhances selectivity, stability and coke resistance.

Heterogeneous catalysts based on natural minerals proved suitable for the upgrading of biomass platform molecules through catalytic hydrogenation, oxidation, oxidative cyanation, isomerization, condensation, etherification, hydrolysis, dehydration, and depolymerization. Ni and Cu catalysts supported on mordenite, sepiolite, and attapulgite have been studied as hydrogenation catalysts. MnO<sub>2</sub> and noble metals (Pt, Au, Pd, Ru) supported on goethite, palygorskite, and halloysite nanotubes have been examined as oxidation catalysts. Attapulgite, mordenite, and bentonite have been tested as saccharide dehydration catalysts. Bentonite, albite, and dolomite have been used for isomerization reactions.

Finally, recent advances in terpene upgrading highlight the transformative role of natural minerals and zeolites as cost-effective and sustainable catalysts. Acid activation, metal doping and solvent-assisted strategies have enabled high selectivity toward p-cymene, terpene isomers, and di-terpenoid derivatives.

Regulation of mineral-based catalysts' texture is a key factor in their catalytic performance. Mesoporosity is desired as it facilitates the mass transfer of large biomolecules inside the catalyst particles. Most natural minerals are microporous materials, and their pores are filled with various impurities. Suitable treatments (acid-base-washing and/or calcination) can empty micropores and create new mesopores, resulting in materials with high surface area and hierarchical pore structure.

The use of natural materials, like biomass as feedstock and natural minerals for catalysts' preparation, makes the corresponding industrial processes green and domestic. However, the complexity and composition instability of such materials raise significant challenges. Concerning natural minerals, they contain several impurities that depend on their geographical origin. Such impurities affect their catalytic behavior, making their pre-

treatment necessary without secure success. A new trend on this subject adopts the dilution of clay minerals, the purification of the solution derived, and the synthesis of new materials with precisely regulated structural, textural, and chemical characteristics [151,152]. On the other hand, long-term stability tests under industrial conditions, addressing catalyst deactivation (coking, sintering), the scalability of modification procedures, and a comparative techno-economic analysis of these natural mineral catalysts versus conventional synthetic ones are necessary for industrial application of the corresponding catalysts.

Coking is the main reason for catalyst deactivation during the biomass valorization processes. Minerals are usually thermally constant or have been stabilized by calcination at high temperatures. Thus, they could be easily regenerated via mild combustion of carbonaceous deposits. In this concept, the sintering of the active phase becomes the most difficult reversible deactivation process for the catalysts supported on natural minerals, followed by leaching phenomena due to the severe reaction conditions applied. Future studies focused on these issues should be performed to address them.

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