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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 minimization/exploitation of 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 to the above valorization. Natural zeolites and clays can be used as catalysts/CO_2 adsorbents and catalytic supports in various biorefinery processes (pyrolysis, gasification, hydrothermal liquefaction, esterification/transesterification, hydrotreatment, cracking, isomerization, oxidation, condensation etc.). Acid/base and textural properties of these materials are key factors for their catalytic performance and can be easily regulated by suitable treatments discussed in this article. The application of natural minerals in biorefinery processes makes them greener, cost-affordable and easily scalable.

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

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 counted to be about 1.65 trillion barrels, which means that with today's consumption rate are predicted to be finished up to 2070 [1]. Additionally, the natural gas reserves are counted 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] describes the global carbon budgets and the environmental consequences of fossil fuels consumption proving the urgent need for their replacement.

In this frame, biomass and organic residues appear to be valuable alternatives of mineral crude oil. The research in such sources 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 consuming demand for eco-friendly and biodegradable products.

The complex, unstable and variable composition of the biomass, which depends on its source, make its upgrading challenging. 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 [16]. To reduce the cost of relevant processes, natural mineral catalysts have been investigated. For example, lignocellulose conversion methods based on such catalysts have been already applied in several pilot and demonstration plants for the production of platform chemicals globally [17]. 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 [18].

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.

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 EU [19]. 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 [20].

Pyrolysis is a thermochemical process, in which biomass is heated at moderate temperatures (300 °C to 800 °C) in totally inert atmosphere to produce bio-oil, biochar, and syngas [21]. Gasification is also a thermochemical process aiming to 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 almost inert atmosphere containing controlled amount of oxygen and/or steam [22]. 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 low Higher Heating Value (HHV), high acidity and low stability. These characteristics exclude its application as 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 [23].

2.1. Biomass Pyrolysis

As already mentioned, pyrolysis enables the decomposition of a wide range of waste biomass into bio-oil (being raw material for obtaining valuable chemicals and fuels), syngas and char reducing simultaneously 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

[24]. Catalysts can be used inside of pyrolysis reactor (in-situ) or in a next reactor downstream (ex-situ). Wang et al. [25] 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 [24]. 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. [26] concluded that the co-pyrolysis of biomass with plastic is resulting 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 of the yield and the quality of liquid fuel obtained. Fifteen years ago, Kumar et al. [27] published one 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 fast heating rate of the reactor at pyrolysis temperature of 450°C, and using 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. [28] 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 temperature 460-480°C. Salan et al. [29] 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 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 improved also fuel characteristics especially in the presence of clinoptilolite catalyst. Gandidi et al. [30] 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. [31] 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. [27]. However, Vo et al. [32] studying the co-pyrolysis of baboo and polystyrene in a fluidized bed reactor (in-situ catalytic pyrolysis) found that the catalyst used plays key role in the quality of the produced bio-oil. In this sense, dolomite proved to be more effective catalyst than HZSM-5, red mud, and Fe_2O_3. The same group [33] using the above reactor system studied also fast pyrolysis of cashew nut shells (a waste biomass with high carbon content and low oxygen content) using dolomite as catalyst and CO_2 absorbent. They investigated the operation conditions of the process and found that concerning the dolomite catalytic performance, it has a substantial effect in the pyrolysis of biomass. More precisely, dolomite enhances dehydration, decarboxylation, and aromatization reactions, and increases syngas production.

Charusiri [34] has studied fast pyrolysis of residues from paper mill industry to bio-oil and value-added chemicals using dolomite as catalyst (1-5 wt. %) in a continuous pyrolyzer (Fig. 1).

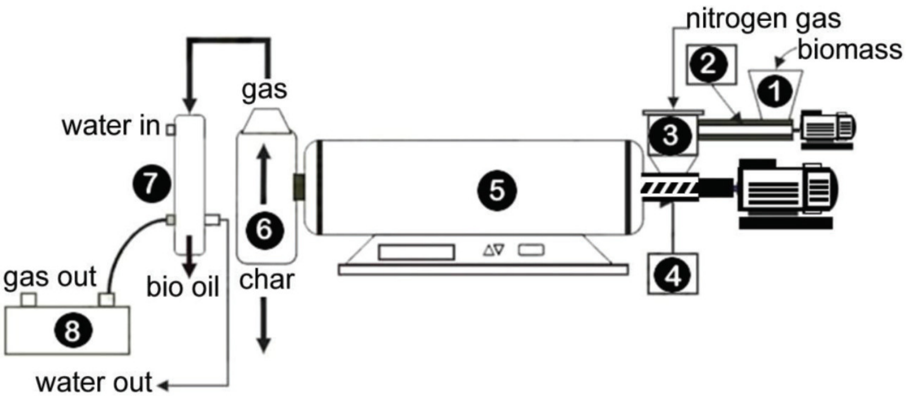

Figure 1. Schematic diagram for the continuous pyrolyzer: 1) hooper1 2) nitrogen gas feeding 3) hooper2 4) under-screw feeder 5) pyrolyzer 6) gas chamber 7) condenser 8) gas collector [34].

The bio-oil obtained under the best condition 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 infer the necessity of further upgrading in order to meet the transportation fuels standards. Veses et al. [35] using a similar type of pyrolyzer (auger reactor), compared sepiolite, bentonite, attapulgite and red mud as catalysts for pyrolysis of wood biomass. The optimum bio-oil production achieved at a temperature of 450 °C and catalyst to biomass ratio (1:6, in weight). Increase of the later results in reduction of bio-oil production and increase of char yield. All the catalysts studied improved the properties (viscosity, acidity, oxygen content and calorific value) of the obtained bio-oil.

Mohamed et al. [36] 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 it also increased the pyrolysis rate and conversion percentage, reducing the activation-energy of pseudo-lignin decomposition. Clinoptilolite used as 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. [37] 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. [38] 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 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 in 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 pyrolysis catalyst and CO_2-trap.

Song et al. [39] 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. [40] studied the ex-situ catalytic

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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 ratio 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. [41] showed that MgO materials derived via griding 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 (acids reduction, ketonization and aldol condensation) resulting in CO_2 formation instead of CO and water 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. [42] 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. [43] 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. [44] 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 dehydration leading to lower CO and CO_2 emissions, higher H_2/CO ratios and greater selectivity toward light aromatics (C_5–C_{11}). 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. [45] 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_2 release and aliphatic hydrocarbons through dehydrogenation. Red mud enhanced decarboxylation yielding lighter cyclic ketones. A catalytic run reduced oxygenates and raised 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. [46] explored the dual role of dolomite as both a CO_2 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_2-free, H_2-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_2 sources.

Duanguppama et al. [47] 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, increasing thus the light bio-oil yield. Zeolite catalyst facilitated mainly deoxygenation reactions, resulting in bio-oil with high hydrocarbons content. However, the catalysts configurations did not influence the yield of the whole process. Aljeradat et al. [48] used various Jordanian minerals as catalysts for the treatment of date kernels 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 -Vásconez et al. [49] investigated 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_3-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. [50] 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, autogenous 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, $FeSO_4 \cdot 7H_2O$, K_2CO_3, MgO, synthetic hydrotalcite, and ground colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)). 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 exported by Ma et al. [51], using commercial clay minerals (montmorillonite, dolomite, kaolinite and sand) for HTL of potato starch. Wu et al. [52] used montmorillonite coming from natural bentonite under mild conditions (montmorillonite:water:cellulose = 0.6:10:1, 200 °C, 2–24 h) and succeeded hydrothermal carbonization of cellulose resulting in 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. [53] 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 studied for hydrothermal liquefaction of biomass. Zhu et al. [54] 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 specific surface area of that of CoMo/Al_2O_3. Chen et al. [55] studied also Co catalysts supported on acid (1M HCl, for 12h) 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. [56] using bentonite clay as catalyst (Fig.2). The use of bentonite improved the bio-oil and biochar quality in both processes.

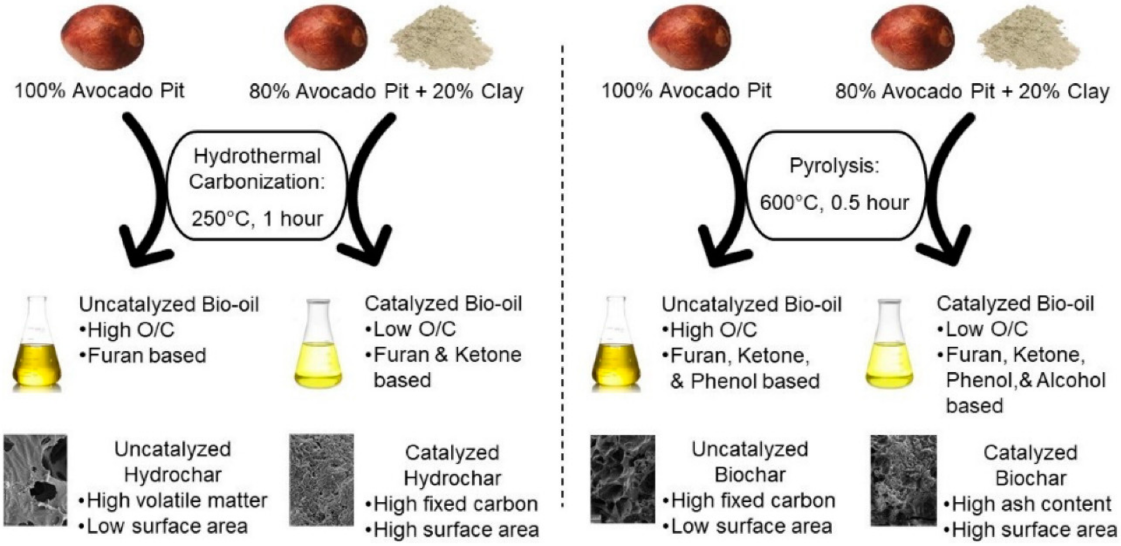


Figure 2. Schematic representation of hydrothermal carbonization and pyrolysis of avocado pit with and without bentonite clay catalyst (conditions and properties of the products) [56].

2.2. Biomass Gasification

The conversion of biomass to syngas is an attractive biomass valorization process, because of its universal character (independence of product on biomass kind). The major problem in gasification process is tar formation. Coping with this problem can be succeeded using suitable catalysts. Recently Ciuffi et al. [57] have published a critical review article concerning gasification of plastics. In this article co-gasification of plastics with biomass has been also 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 [58]. De Andrés et al. [59] compared the behavior of the two minerals (dolomite, olivine) with that of alumina as catalysts in 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. [60]. Catalytic minerals provoked reduction of CH_4 and light organic molecules (≤ C5) 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_2 production among the minerals studied. In a very interesting article, Zhou et al. [61] 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 increasing conversion, H_2 concentration, and syngas yield in the products. The high H_2 yield is attributed to tar cracking taking place on dolomite surface. On the other hand, the lower coke formation on used dolomite surface in comparison with that on used olivine, confirms the ability of dolomite particles in tar catalytic cracking. Dolomite is also easily regenerated inside the pressurized fluidized bed gasifier. They investigated also 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. [62] used waste from aluminium industry, the red mud (RM), as catalyst for the gasification of palm kernel shell wastes (PKS) at 800°C. As can be seen in Fig. 3, the increasing addition of RM promoted the conversion mainly of biochar and slightly that of bio-oil to non-condensable gases.

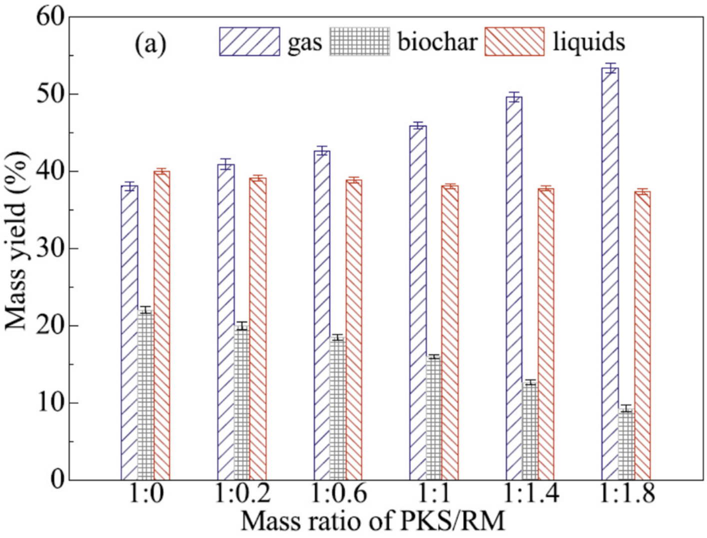
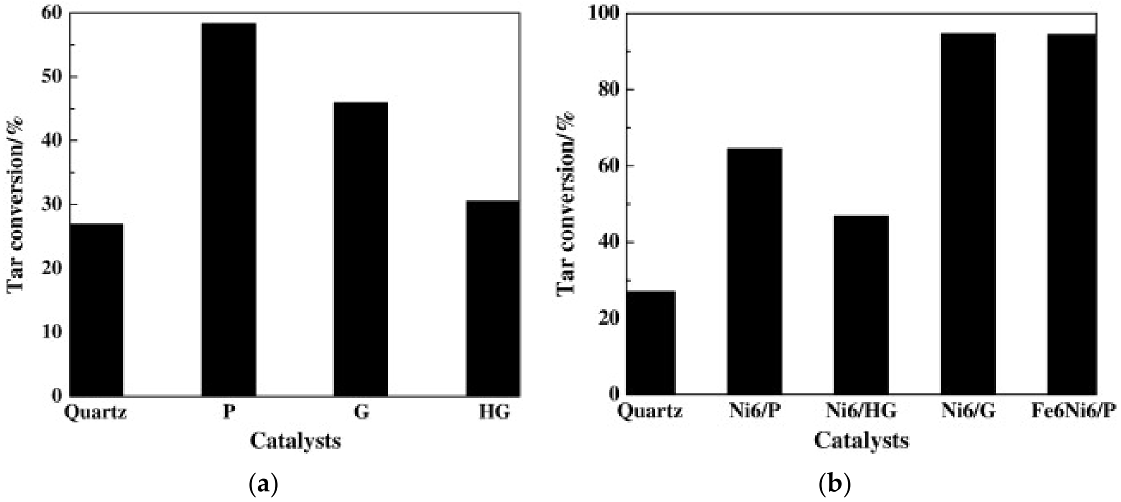


Figure 3. Mass yields of products obtained from fast pyrolysis of PKS at 800°C and various PKS/RM ratios [62].

Nickel catalysts are also suitable for tar elimination during biomass gasification. Liu et al. [63] 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_2 production. The same group [64] 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.



(**a**) (**b**)

Figure 4. (**a**) Tar conversion achieved over quartz, palygorskite (P), goethite (G) and hydrothermally synthesized goethite (HG); (**b**) Tar conversion achieved over Ni and Ni-Fe catalysts supported on quartz, palygorskite (P), goethite (G) and hydrothermally synthesized goethite (HG). Experimental conditions: fixed-bed reactor; WHSV=2.7 h^{-1}; temperature 700 °C and time 20 min [64].

As can be seen in Fig. 4, 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 of Fe_xO_y existed in its structure after calcination. Nickel addition improves the activity of the minerals studied. The Ni catalyst supported on goethite (Ni6/G) exhibits the highest activity and yield of gases followed by the corresponding bimetallic catalyst supported on palygorskite (Fe6Ni6/P).

Chiodo et al. [65] compared dolomite, MgO and a commercial Ni/Al_2O_3 – CaO catalyst for the gasification of citrus peel residues to obtain hydrogen rich syngas. Dolomite proved the best catalyst, while Ni catalyst seems to be affected by coke formation and sintering upon reaction. Puig-Gamero et al. [66] studied, also, dolomite as catalyst for steam co-gasification of olive pomace, coal and petroleum coke. The presence of dolomite resulted in enhanced H_2/CO ratio, reactivity and low H_2S, NO and SO_2 emissions. Dolomite was proved by Tian et al. [67] 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. [68] studied natural olivine ($(Mg,Fe)_2SiO_4$) as catalyst for bio-oil gasification. They found that metallic iron contained in this material is its active component. Reduction of natural material with H_2 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_2/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. [69] studied a Ni based catalyst supported on natural clay composed by 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 catalyst resulted in tar reduction and increase of H_2 content. The increase of 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 [70]. CLR of biofuels is considered as a promising method to produce syngas. Xu et al. [71] compared M_xO_y (M=Cu, Fe and Ni) catalysts supported on dolomite for CLR process of toluene used as biomass representative molecule. Iron and nickel oxide catalysts proved more effective than copper one 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_2/CO ratios (~ 2.0) under different reaction conditions.

Veses et al. [72] 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 (Fig.5) using the inexpensive and widely available dolomite as cracking catalyst results in the production of a valuable syngas fraction. This research group studied also 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_2, CO, and CH_4, with a heating value of ~18–20 MJ/Nm^3. Dolomite emerged as the most efficient and low-cost catalyst [73]. Similar results have been obtained by the same group using the aforementioned processes and spent green tea waste as feedstock [74]. These studies highlights the potential of natural mineral catalysts for producing clean fuels and chemicals while providing a sustainable solution for managing challenging waste streams.

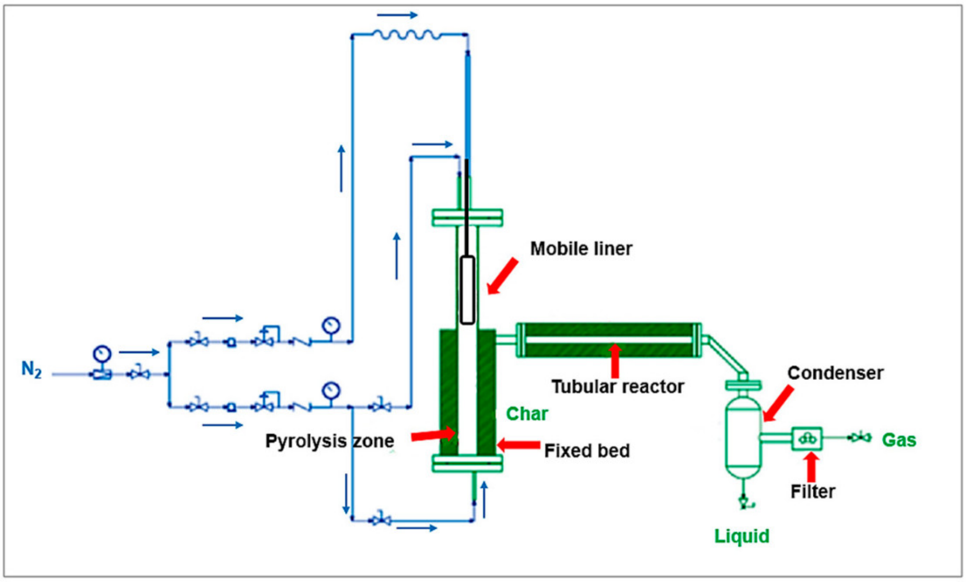


Figure 5. Schematic diagram of a two-stage pyrolysis setup: Pyrolysis temperature 550°C; N_2 as carrier gas; Catalytic cracking temperature in tubular reactor from 400 to 900°C [72–74].

Yang et al. [75] prepared catalysts for reforming the pine pyrolysis gas using mineral diatomite as precursor to prepare foam ceramic and then loaded it with Fe_2O_3 or $CeCl_3$. The diatomite-based foam ceramic increased the pyrolysis gas (CH_4, H_2, and CO_2) yield in expense of liquid yield. The catalyst containing Fe_2O_3 proved to be the best one.

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. [76] studied the upgrading of raw bio-oil produced by flash pyrolysis of pine sawdust using calcined natural dolomite (850°C for 5h) as catalyst in a U-shaped continuous working reactor (Fig. 6) co-fed with bio-oil and steam (Steam: C ≈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 significant reduction of the O/C ratio in the bio-oil obtained, removing the carboxylic acids and sugars and acting as CO_2 sorbent. The same group in a more recent work [77] using less steam-to-carbon mass ratio (Steam: C ≈ 3), revealed that, at short time on stream, the upgraded bio-oil was free of acids and heavy phenols and rich of light ketones (≤C5). However, carbonation of dolomite and coke formation on its surface alter the composition of the upgraded bio-oil and deactivate the catalyst.

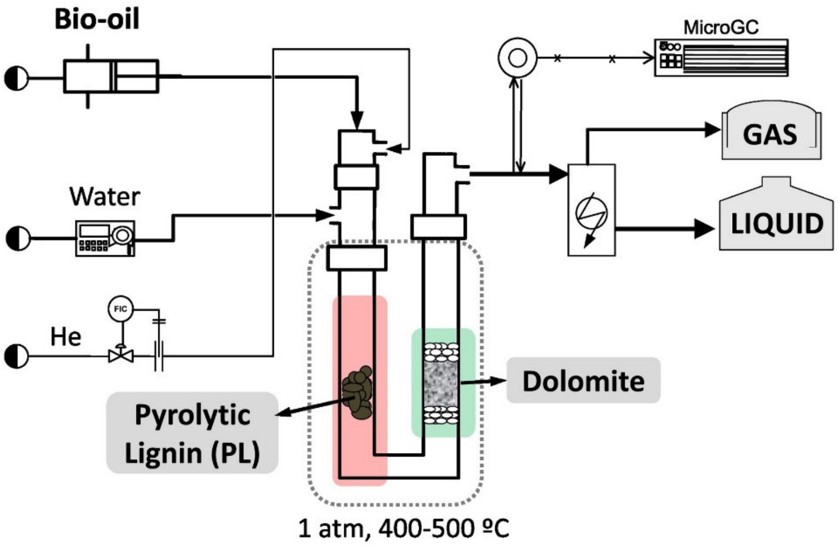


Figure 6. Schematic diagram of a U-shaped tubular reactor used for upgrading of raw bio-oil in the presence of calcined natural dolomite [76,77].

Glycerol is a by-product derived from biodiesel production. Its price has decreased dramatically because of the increase of this fuel production worldwide. Thus, the exploitation of this bio-based by-product is urgent. Cruz et al. [78] studied crude glycerol and animal fat mixtures steam reforming over activated alumina and dolomite (fixed bed reactor, 700 & 750 °C). Dolomite produced ~10 vol% more H_2 favoring the water-gas shift reaction. Villegas-Bolaños et al. [79] 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. [80] used natural palygorskite (attapulgite) 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. [81] prepared also 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 [82]. Indeed, more than 50% of the research articles reviewed in this chapter concern the use of dolomite either as catalyst/CO_2 absorbent [30–34,37,38,40,43–47,51,58–61,65–67,72–74,76–78,82] or catalyst support [69,71].

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 to be 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. [83] optimized FAME production from waste cooking oil using a montmorillonite clay as 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. [84] developed a bifunctional 30%Sn-MMT-SO_3H catalyst from natural montmorillonite for efficient biodiesel production from Jatropha curcas oil. The catalyst prepared via Sn^{4+} ion exchange and sulfonation, retained a layered nanosheet structure (145 m^2/g surface area, 5.8 nm pores 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 in advantage the catalytic potential of montmorillonite Tiwari et al. [85] extended its application by designing a Sn_1-TPA/K-10 catalyst, further enhancing both Brønsted and Lewis acidity. The study developed a highly active 20% Sn_1-TPA/K-10 catalyst by partially exchanging protons of tungstophosphoric acid (TPA) with Sn^{2+} and supporting it on montmorillonite K-10. This design enhanced both Brønsted and Lewis acidity (2.21 mmol/g) and maintained 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_1-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. [86] focuses on activated natural mordenite (ANM) used as support for dual basic metal oxides (Na_2O–K_2O 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_2O–K_2O/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_2O–K_2O/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. [87] 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 enhanced 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. [88] investigated CaO-modified dolomite as a heterogeneous basic catalyst for 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. [89] 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 Fig. 7.

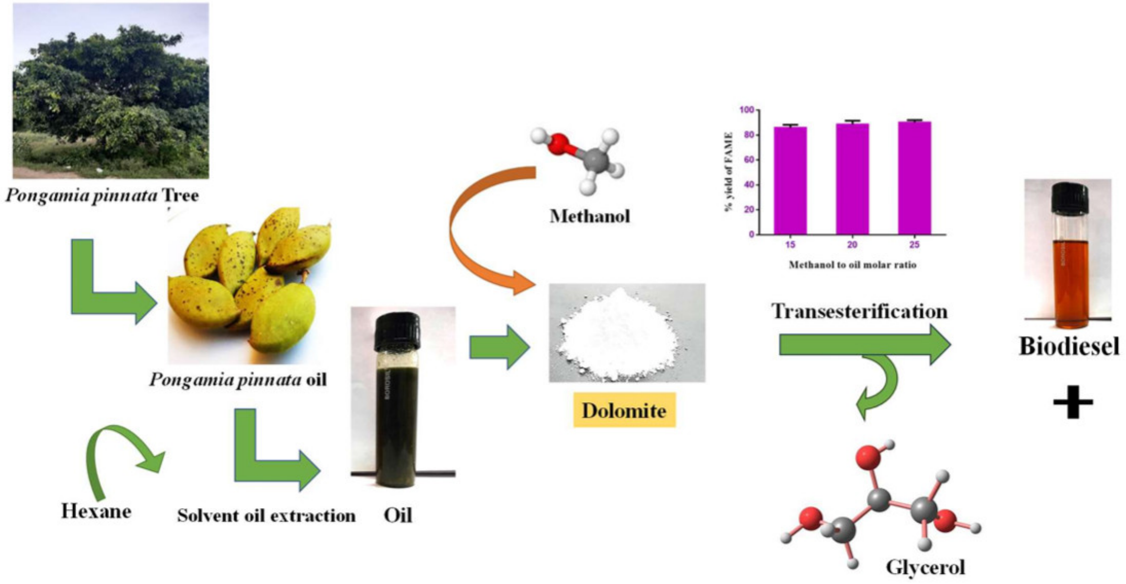


Figure 7. Schematic representation of biodiesel production from *Pongamia pinnata* oil using dolomite as transesterification catalyst [89].

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. [90] designed a cerium-incorporated dolomite catalyst to address 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 to 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_2, increased basicity (2.21 mmol/g), and a mesoporous structure (19.34 m^2/g) while Ce^{3+} 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. [90] demonstrated how rare-earth doping enhances dolomite's stability, Subramani et al. [91] advanced its application to both laboratory and pilot scales proving industrial viability. Specifically, Subramani et al. [91] 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, FTIR and NMR) validated biodiesel quality, while the study highlights dolomite's role in reducing waste and enabling sustainable biodiesel commercialization.

Korkut and Bayramoglu [92] 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). 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. [93] 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 $CaO\text{-}SiO_2$ 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. [94]. This paper demonstrated a copper-impregnated industrial waste dolomite catalyst (Cu@dolomite) for biodiesel production from *Madhuca indica* oil emphasizing on scalability and sustainability. Catalyst characterization (XRD, BET, SEM-EDX) confirmed high $CaCO_3$/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. The set–up used in the process is shown in Fig. 8.

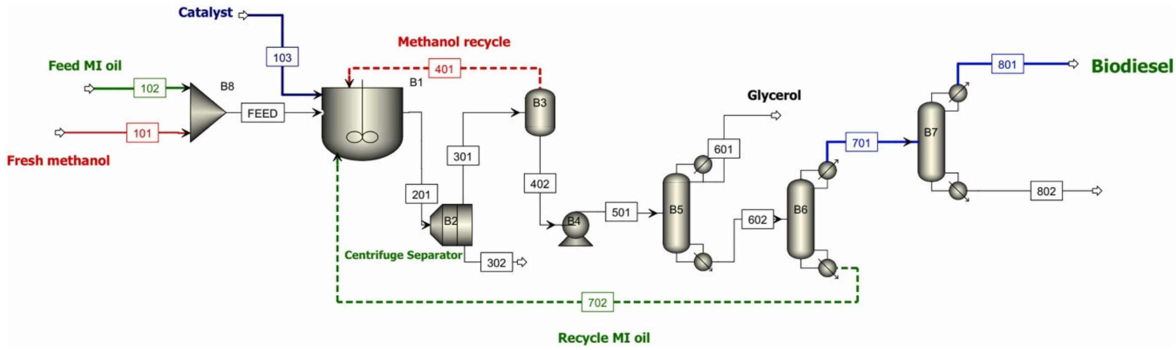


Figure 8. The process flow diagram for biodiesel production from *Madhuca indica* oil using Cu@dolomite catalyst [94] (CSTR: B1, centrifugal separator: B2, flash column: B3, pump: B4 and three distillation columns arranged in series: B5-B7).

A detailed techno-economic analysis via Aspen Plus (1,000 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 NOx confirming biodiesel's suitability as a diesel substitute. This study is worth noting for its integrating 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. [95] functionalized palygorskite with ionic liquids achieving efficient esterification performance. They developed a novel heterogeneous poly ionic 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_3-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 morphology as an effective scaffold for ionic liquid catalysts, offering a scalable route for solid acid design.

An interesting study comes from Casiello et al. [96]. 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. [97] 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 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.

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 catalysts' 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. [98] 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 m^2/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 (~6.8 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. In Figure 1 we can see a Reaction Network of biodiesel upgrading to HVO. This work demonstrated that mordenite, an abundant and low-cost zeolitic material, is an effective support for selective deoxygenation catalysts concerning the biodiesel upgrading to green diesel.

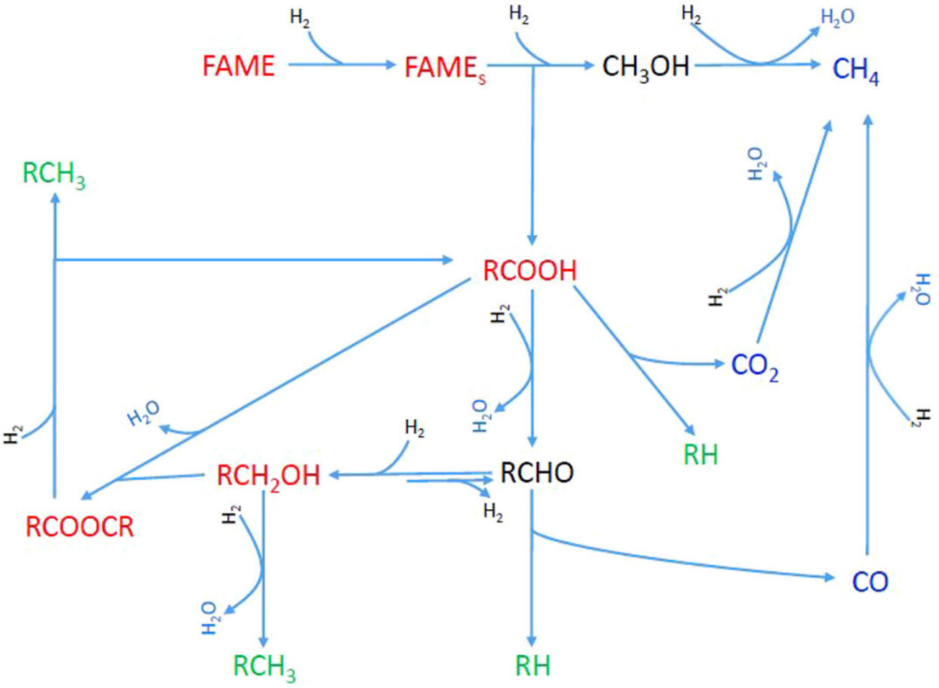


Figure 9. Proposed reaction network for biodiesel upgrading to HVO over Ni−Mordenite catalysts [98].

Taking into account the above encouraging results Fani et al. [99] studied acid- and acid–base-activated mineral mordenite (MO_A, MO_{AB}) as supports for 30 wt. % Ni catalysts in biodiesel selective deoxygenation to HVO. Double activation improved mesoporosity (14 nm), Ni dispersion (~7 nm particles) and balanced acidity resulting to 94 wt. % diesel-range hydrocarbons after 9 h at 350 °C and 40 bar H_2. Kinetic analysis confirmed pseudo-first-order behavior with an activation energy of 64.4

kJ/mol. MO_{AB}-based catalysts showed lower coke formation and sintering, demonstrating the importance of zeolite textural engineering for coke-resistant SDO catalysts.

The work of Putra et al. [100] deals with mixed-phase mineral zeolites (mordenite & 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_2, and 2 h, Fe/NZ achieved 89% conversion and 76% diesel-range hydrocarbons selectivity (C15–C18) 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. [101] continued their studies on zeolites investigating dealuminated and NH_4^+-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_2 and 2 h) it was achieved 52% conversion and 70% selectivity to C15 alkanes via decarbonylation resulting to diesel-range fuel with cetane numbers of 71–77. This work highlights NH_4^+-form zeolites as selective, mild-acidity catalysts for a sustainable, non-metal-based pathway green diesel production.

Aside from mordenite-rich zeolites, clinoptilolite phases have also been valorized. Kurniawan et al. [102] evaluated Indonesian Lampung, Bayah and Tasikmalaya zeolites (clinoptilolite, mordenite phases) as supports for $NiMo/Al_2O_3$-zeolite catalysts for hydrocracking waste cooking oil (WCO). Acid dealumination raised Si/Al ratios (up to 13.6) and surface areas (Bayah: 191 m^2/g). On the $NiMo/Al_2O_3$ (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, reducing thus, the reliance on imported supports and valorizing WCO.

Beside zeolitic systems, montmorillonite clays have also attracted attention due to their tunable acidity and high surface reactivity. Lycourghiotis et al. [103] 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 (Fig.9). Detailed characterization (XRD, TEM, XPS, H_2-TPR, NH_3-TPD) revealed strong Ni–Mo synergy at 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. [104] 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_2, 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_3-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. [105] 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_2, 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.

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_2 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. [106] 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. [107] optimized the catalytic cracking of palmitic acid using Fe^{3+}-modified mineral mordenite from Indonesia to produce aviation fuel components. The Fe^{3+} exchange enhanced Brønsted and Lewis acidity (81.66 and 26.77 mmol/g), increased the surface area (198 m^2/g) and reduced pore size (7.36 nm) compared to parent mordenite, while preserving the crystalline structure. Under cracking at 310 ^{o}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^+- unmodified mordenite, Fe^{3+}-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. [108] 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. Fig. 10 shows the proposed RTO pyrolysis mechanism over dolomite illustrating decarboxylation/decarbonylation pathways and product distribution.

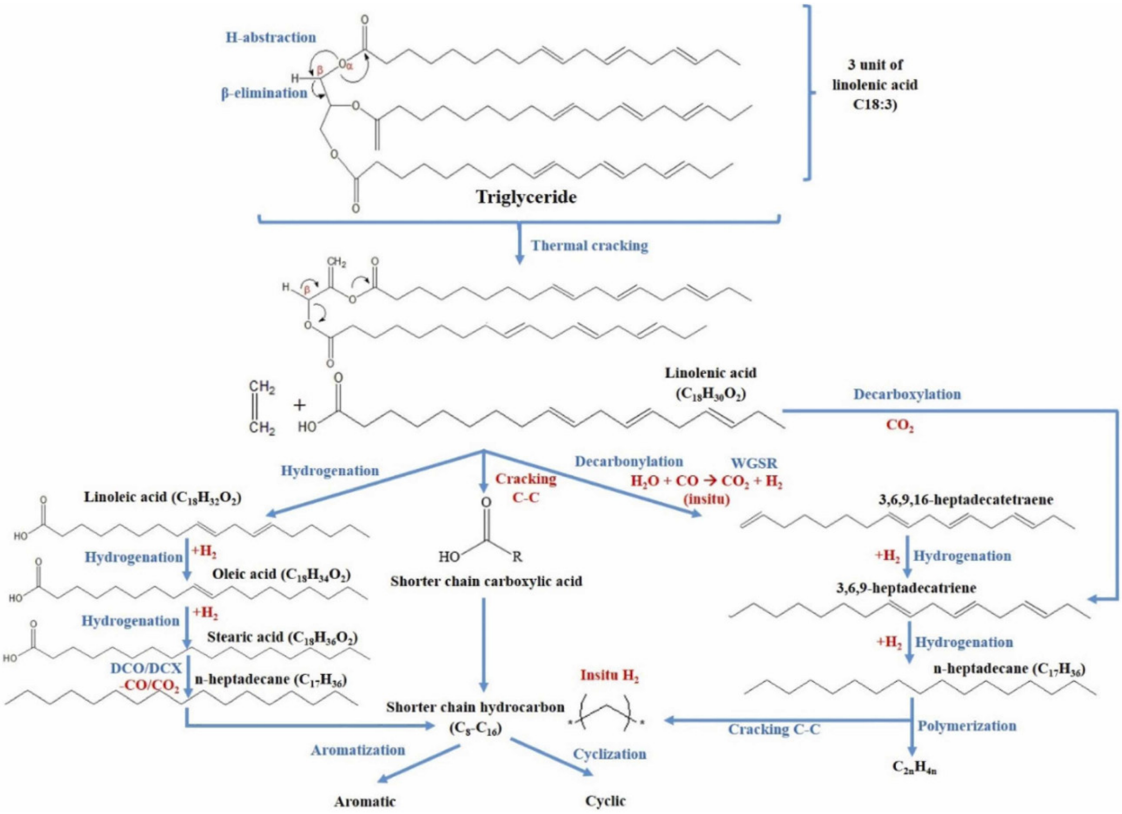


Figure 10. Proposed reaction network of RTO catalytic pyrolysis/deoxygenation over dolomite catalyst [108].

Hafriz et al. [109] investigated catalytic pyrolysis of WCO using Malaysian dolomite as a deoxygenation catalyst. Upon calcination at 900 °C under N_2, dolomite was transformed into active MgO–CaO phases, significantly enhancing basicity, porosity, and CO_2 adsorption. The catalyst achieved 76.5% liquid hydrocarbon yield (C8–C24), 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. [110] 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_2-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 (C13–C20 hydrocarbons) from WCO. Ali et al. [111] 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 enhanced 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. [112] 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_2 flow. Optimum conditions (410 °C, 60 min, 5.5 wt% catalyst, 175 cm^3/min N_2) yielded >98% WCO conversion, high hydrocarbon selectivity (C_8–C_{24}), 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. Fig. 11 illustrates a schematic representation of the semi-batch reactor set-up used for catalytic deoxygenation of WCO.

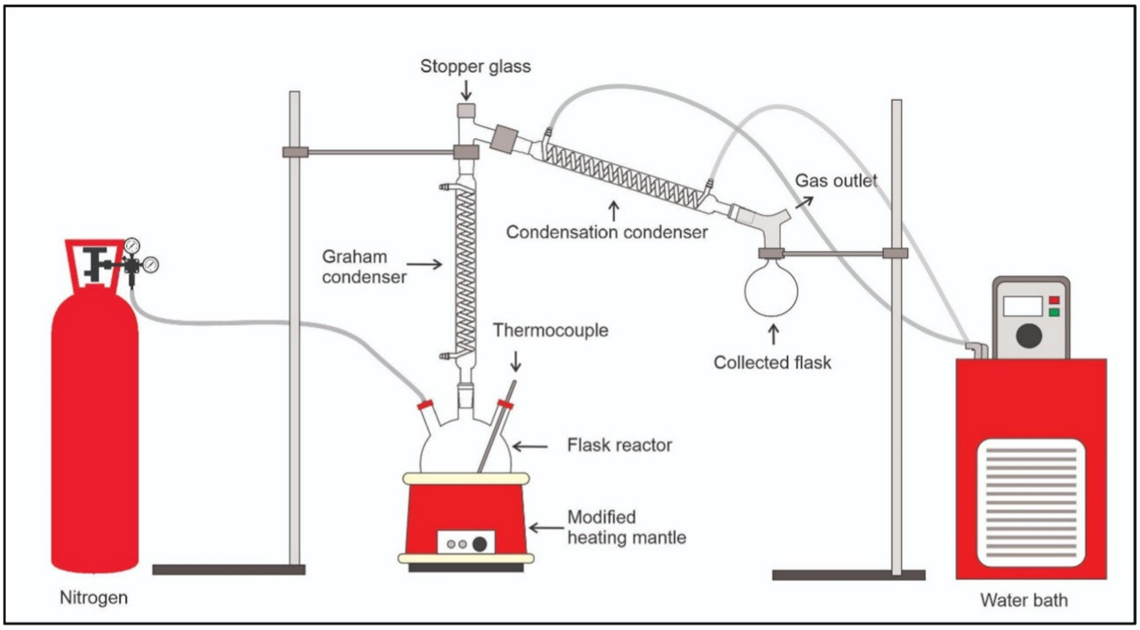


Figure 11. Semi-batch reactor set-up for catalytic deoxygenation of WCO [109–112].

Kanchanatip et al. [113] explored the catalytic performance of Thai dolomite modified with varying $MgCO_3$ 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. [114] 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 catalyst for sustainable jet fuel production offering a novel way for valorizing industrial waste. Tamim et al. [115] 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, hydrothermal liquefaction, results in very important substances, suitable for preparation of bio-based products that can substitute similar petroleum derived substances in chemical industry. Catalytic transformation of the initial biomass derived molecules to value-added products has drawn the attention of the 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 [116]. It can be upgraded to added-value products via catalytic reduction. Richel et al. [117] 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. [118] prepared Cu (15-60 wt. %) catalysts supported on natural bentonite and sepiolite and evaluated them in FUR hydrogenation in 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 5h time on stream). The above group [119] studied also 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 two first declined with TOS, while that of the latter increased. Catalyst prepared by a grafting method exhibited the best catalytic performance due to the high Ni phase dispersion achieved. García et al. [120] studied Ni supported on two natural sepiolites and an attapulgite as catalysts in the transformation of levulinic acid into γ-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 high active sites population. In a more recent work García et al. [121] used natural sepiolite as support of Pt, Zr and Pt-Zr (Zr-Pt) catalysts to transform FUR to γ-Valerolactone. This transformation involves two hydrogenation steps, in which 2-propanol participates as 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. Oxydation of Bio-Based Molecules

Oxidation of biomass-derived molecules is an important reaction for production of green and sustainable chemicals. Wang et al. [122] 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 rection mechanism preventing their over-oxidation. Zhong et al. [123,124] used natural clay minerals palygorskite and halloysite nanotubes for preparing supported bimetallic Pt–Pd [123] and Pt-Au [124] catalyst, 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 metals alloying resulted in complete conversion of reactant and 99% yield of the desired product. The same research group [125] 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 -diformylfuran (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 oxidic catalyst was attributed to the higher dispersion and the oxidizing ability of Ru^{3+} species. Wang et al. [126] studied the same reaction using a bimetallic AuPd catalysts supported on nitrogen-doped carbon which was templated by halloysite nanotubes (HNTs). Under optimum reaction conditions (catalyst = 0.05 g; nHMF: $n$$Na_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, following the mechanism showed in Fig. 12.

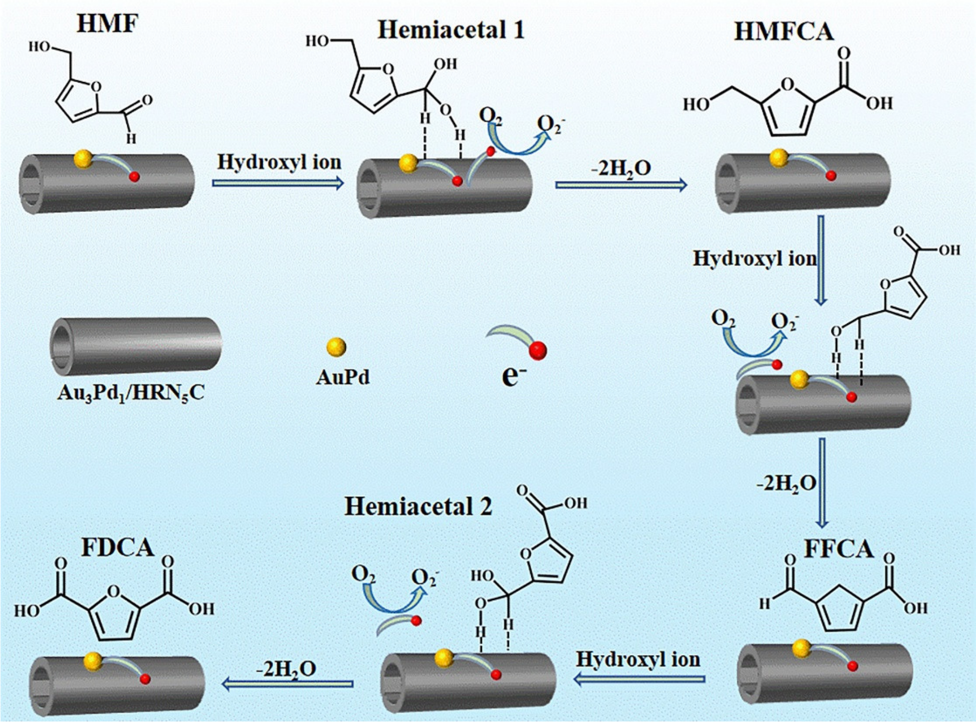


Figure 12. A tentative mechanism proposed by Wang et al. [126] for HMF oxidation to FDCA over catalysts studied.

An analogous finding has been published by Chen et al. [127], who studied also HMF oxidation to FDCA using the same active metals combination and molar ratio supported on ZrO_2 layer deposited on HNTs. Citric acid (CA) assisted sol-gel method was used for supports 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 by TiO_2 to prepare Au_2Pd_1/TiO_2-xCA@HNTs catalysts with varying oxygen vacancies [128].

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 [129], 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_2, and 100 ◦C) being also quite stable (90.1% FDCA yield after five catalytic cycles). Recently, Zhang et al. [130], paving their pathway of noble metals catalysts supported on TiO_2 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 $Au_{0.5}Pd_{0.2}Pt_{0.3}/TiO_2$@HNTs catalyst showing the outstanding performance of 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 [131]. 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. [132] studied the conversion of mono- (fructose and glucose) and polysaccharides (inulin and starch) into HMF over natural attapulgite modified by H_3PO_4 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 modified catalyst exhibited excellent stability for at least four consecutive catalytic cycles. Kiani et al. [133] used also H_3PO_4 to modify natural bentonite in order to obtain an effective catalyst for glucose transformation to FUR in mono-phasic water–dimethyl sulfoxide (DMSO) system, achieving 69.2% FUR yield at 170 °C after 60 min.

Adila et al. [134] studied the dehydration of ethanol to produce diethyl ether using natural zeolite from Klaten, Indonesia, as 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 appear 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. [135] tested natural bentonite as low-cost catalyst for such a process. Brønsted base sites of the catalyst found to be the active sites resulting in 39.2% fructose yield at mild reaction conditions (110 °C, 60min, water solvent). The regulation of catalyst’s base sites is a key factor in glucose isomerization. Ren et al. [136] 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. [137] using natural dolomite and synthetic mixed CaO-MgO proved that moderate basicity is necessary for obtaining high fructose yield under mild conditions. Calcination protocol adopted regulates the base properties of dolomite. Thus, a catalyst which underwent calcination at 650 ◦C for 3 hours 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 production by-product 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. [138] studied the glycerol self-etherification to produce short-chain oligomers using natural dolomite as catalyst. Using 2% calcined dolomite (800 °C) at 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 used fine chemical intermediates, fuel additives, medicine, etc. production. Tian et al. [139] tried to develop a recyclable and environmentally friendly catalyst, using natural attapulgite modified by H_2SO_4. Sulfated attapulgite was evaluated for conversion of furfuryl alcohol to ethyl levulinate in ethanol. The concentration of sulfuric acid used for attapulgite modification affected catalyst's texture, structure, sulfur content, acidity, formation of Brønsted and Lewis acid sites and finally catalytic performance. The catalyst prepared with 1% H_2SO_4 proved the best one resulting in ethyl levulinate yield of 95.4% at 160 °C in 3h, exhibiting excellent reusability and easy regeneration. Lai et al. [140] studied the preparation of methyl levulinate using glucose as feedstock and a bifunctional catalyst consisted by phosphotungstic acid supported on metal (M: La^{3+}, Ce^{3+}, Er^{3+}, Cu^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+})/Si-pillared natural montmorillonite. The catalyst modified by $Zr^{4+}$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_2SO_4) modified natural minerals (attapulgite, kaolin, and clinoptilolite) were used by Meng et al. [141] as catalysts for 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. [142] used also 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 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, highlighting the role of mineral-derived catalysts in bridging renewable resources with practical energy applications.

Lycourghiotis et al. [143] investigated the activation of natural mordenite, sourced from volcanic soils in Greece, through treatment with different acids (HCl, H_2SO_4, HNO_3, CH_3COOH) 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. [144] 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 offer 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 investigated also [145]. 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_2SO_4 and CH_3COOH: considerable decrease of specific surface area (SSA); HNO_3: increase of SSA).

Moving beyond mordenite, Lycourghiotis et al. [146] 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 (α-terpinene, γ-terpinene, terpinolene) and p-cymene, using acid-activated natural montmorillonite (treated with HCl or HNO_3). Acid activation removed Na^+ and Ca^{2+} 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. [147] 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 (Fig. 13). 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.

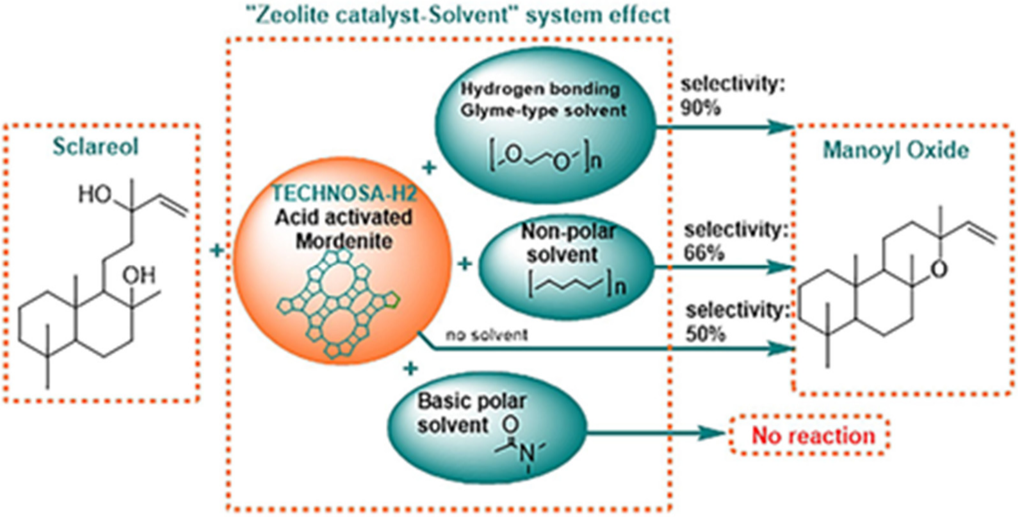


Figure 13. Schematic representation of the manoyl oxide production from sclareol over acid-activated mordenite [147].

Finally, Makarouni et al. [148] 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 reactants shape selectivity is crucial.

5. Conclusions

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 minimization/exploitation of 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 [149]. 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 catalyst and CO_2 absorbent or as 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 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 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_2 and noble metals (Pt, Au, Pd, Ru) supported on goethite, palygorskite, halloysite nanotubes have been examined as oxidation catalysts. Attapulgite, mordenite and bentonite have been tested as saccharides 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.

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References

1. https://www.worldometers.info/oil/ accessed 19-06-2025
2. https://www.worldometers.info/gas/ accessed 19-06-2025
3. Friedlingstein, P.; O'Sullivan, M.; Jones, M.W.; Andrew, R.M. et al. Global Carbon Budget 2024, *Earth Syst. Sci. Data* **2025**, *17*, 965–1039. https://doi.org/10.5194/essd-17-965-2025
4. Ning, P.; Yang, G.; Hu, L. et al. Recent advances in the valorization of plant biomass. *Biotechnol Biofuels* **2021**, *14*, 102. https://doi.org/10.1186/s13068-021-01949-3
5. Bulushev, D.A.; Ross, J.R.H. Perovskite Oxide Catalysts for the Conversion of Biomass and Biomass-Derived Compounds. *ACS Catal.* **2023**, *13*, 7548–7583. https://doi.org/10.1021/acscatal.2c06147.

6. Mohammad, M.; Rahman, M.M.; Rashid, U.; Taufiq-Yap, Y.H. Biochar-Based Heterogeneous Catalysts for Biodiesel Production: A Review. *ACS Omega* **2023**, *8*, 11234–11253. https://doi.org/10.1021/acsomega.2c07909.
7. Tang, Y.; Li, H.; Gao, H.; Zhang, Q. Biomass-Derived Carbon Materials as Catalysts and Catalyst Supports in Green Chemistry: Synthesis, Properties, and Applications. *Green Chem.* **2024**, *26*, 3325–3350. https://doi.org/10.1039/D4GC00606B.
8. Zhang, Y.; Liu, X.; Wang, H.; Zhao, J. Recent Advances in Metal-Based Catalysts for Biomass Valorization: From Transition Metals to Noble Metals. *Catalysts* **2024**, *14*, 40. https://doi.org/10.3390/catal14010040.
9. Patel, S.; Kalia, V.C.; Sharma, D.K. Thermochemical Conversion of Waste Biomass for Biofuels Production: A Critical Review. *Renew. Energy Focus* **2024**, *46*, 100919. https://doi.org/10.1016/j.ref.2024.100919.
10. Nguyen, H.M.; Tran, N.D.; Le, T.H. Bio-Waste Derived Catalysts for Biodiesel Production and Biomass Valorization: Circular Bioeconomy Perspectives. *Energy Convers. Manag* **2024**, *297*, 117536. https://doi.org/10.1016/j.enconman.2024.117536.
11. Güleç, F.; Parthiban, A.; Umenweke, G. C.; Musa, U.; Williams, O.; Mortezaei, Y.; Suk-Oh, H.; Lester, E.; Ogbaga, C. C.; Gunes, B.; Okolie, J. Progress in lignocellulosic biomass valorization for biofuels and value-added chemical production in the EU a focus on thermochemical conversion processes. *Biofpr* **2024**, *18(3)*, 755-781. https://doi.org/10.1002/bbb.2544
12. Joshi, N.C.; Sinha, S.; Bhatnagar, P.; Nath, Y.; Negi, B.; Kumar, V.; Gururani, P. A concise review on waste biomass valorization through thermochemical conversion. *Curr. Res. Microb. Sci.* **2024**, *6*, 100237. https://doi.org/10.1016/j.crmicr.2024.100237
13. Joshi, M.; Manjare, S. Chemical approaches for the biomass valorisation: a comprehensive review of pretreatment strategies. *Environ Sci Pollut Res* **2024**, *31*, 48928–48954. https://doi.org/10.1007/s11356-024-34473-6
14. Alazaiza, M.Y.D.; Alzghoul, T.M.; Ramu, M.B.; Nassani, D.E. Catalysis in Biofuel Production and Biomass Valorization: Trends, Challenges, and Innovations Through a Bibliometric Analysis. *Catalysts* **2025**, *15*, 227. https://doi.org/10.3390/catal15030227.
15. Akhtar, M.S.; Naseem, M.T.; Ali, S.; Zaman, W. Metal-Based Catalysts in Biomass Transformation: From Plant Feedstocks to Renewable Fuels and Chemicals. *Catalysts* **2025**, *15*, 40. https://doi.org/10.3390/catal15010040
16. Hurst, G.; González-Carballo, J.M.; Tosheva, L.; Tedesco, S. Synergistic Catalytic Effect of Sulphated Zirconia—HCl System for Levulinic Acid and Solid Residue Production Using Microwave Irradiation. *Energies* **2021**, *14*, 1582. https://doi.org/10.3390/en14061582
17. Hurst, G.; Teklemariam, A.; Brierley, S.; De Rienzo, M.A.D.; Tedesco, S. Lignocellulosic biomass conversion to levulinic acid via acid catalysis: Current methods, opportunities and challenges for self-sustaining biorefineries. *Int. J. Thermofluids* **2025**, *27*, 101175. https://doi.org/10.1016/j.ijft.2025.101175
18. Ochirkhuyag, A.; Temuujin, J. The Catalytic Potential of Modified Clays: A Review. *Minerals* **2024**, *14*, 629. https://doi.org/10.3390/min14060629
19. Bio-based industry and biorefineries in the EU. Available online: https://knowledge4policy.ec.europa.eu/visualisation/bio-based-industry-biorefineries-eu_en (accessed on 28-08-2025).
20. Baidoo, E.B.; Tulashie, S.K.; Alale, E.M.; Munumkum, C.A.; Acquah, D.; Agudah, P.Q.; Asante, P.A. Revolutionizing bioenergy production: a review on sustainable biomass feedstock. *BIOMASS BIOENERG.* **2025**, *201*, 108113. https://doi.org/10.1016/j.biombioe.2025.108113
21. Konyannik, B.Y.; Lavie, J.D. Valorization techniques for biomass waste in energy Generation: A systematic review. *Bioresour. Technol.* **2025**, *435*, 132973. https://doi.org/10.1016/j.biortech.2025.132973
22. Setioputro, N.T.; Muchammad, M.; Yohana, E.; Syaiful, S.; Ariyanto, H.D.; Kosim, M. Effect of soaked biomass on gasification temperature performance in an open-downdraft gasifier. *Bioresour. Technol.* **2025**, *415*, 131651. https://doi.org/10.1016/j.biortech.2024.131651
23. Lopez, G.; Artetxe, M.; Amutio, M.J.; Bilbao, A.J.; Olazar, M. Recent advances in the gasification of waste plastics. A critical overview. *Renew. Sustain. Energy Rev.* **2018**, *82*, 576–596. https://doi.org/10.1016/j.rser.2017.09.032

24. Barahmand, Z.; Wang, L.; Holm-Nielsen, J.B.; Eikeland, M. Significance of pyrolysis in the circular economy: An integrative review of technologies, potential chemicals, and separation techniques. *Fuel*, **2025**, *398*, 135539. https://doi.org/10.1016/j.fuel.2025.135539
25. Wang, K.; Johnston, P.A.; Brown, R.C. Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. *Bioresour. Technol*. **2014**, *1(173)*, 124-131. http://dx.doi.org/10.1016/j.biortech.2014.09.097
26. Zulkafli, A.H.; Hassan, H.; Ahmad, M.A.; Din, A.T.M.; Wasli, S.M. Co-pyrolysis of biomass and waste plastics for production of chemicals and liquid fuel: A review on the role of plastics and catalyst types. *Arab. J. Chem.* **2023**, *16*, 104389. https://doi.org/10.1016/j.arabjc.2022.104389
27. Kumar, G.; Panda, A.K.; Singh, R.K. Optimization of process for the production of bio-oil from eucalyptus wood. *J. Fuel Chem. Technol.* **2010**, *38(2)*, 162-167. https://doi.org/10.1016/S1872-5813(10)60028-X
28. Kosivtsov, Y.; Sulman, E.; Lugovoy, Y.; Kosivtsova, A.; Stepacheva, A. Experimental Investigation of the Biomass Catalytic Pyrolysis Process to Produce the Combustible Gases with the High Calorific Value. *Bull. Chem. React. Eng. Catal.* **2015**, *10(3)*, 324-331. https://doi.org/10.9767/bcrec.10.3.8869.324-331
29. Salan, T.; Alma, M.H.; Altuntaş, E. The fuel properties of pyrolytic oils obtained from catalytic pyrolysis of non-recyclable pulper rejects using activated natural minerals. *Energy Sources Part A*, **2018**, *41(12)*, 1460–1473. https://doi.org/10.1080/15567036.2018.1548522
30. Gandidi, I.M.; Sukarni, S.; Permanasari, A.A.; Purnami, P.; Abdullah, T.A.T.; Johari, A.; Pambudi, N.A. Production of Light Fraction-Based Pyrolytic Fuel from Spirulina platensis Microalgae Using Various Low-Cost Natural Catalysts and Insertion. *Energy Engineering* **2024**, *121(12)*, 3635-3648. https://doi.org/10.32604/ee.2024.054943
31. Merdun, H.; Sezgin, İ.V. Products distribution of catalytic co-pyrolysis of greenhouse vegetable wastes and coal. *Energy* **2018**, *162*, 953-963. https://doi.org/10.1016/j.energy.2018.08.004
32. Vo, T.A.; Ly, H.V.; Hwang, I.; Hwang, H.T.; Kim, J.; Kim, S.-S. Enhancement of biofuel quality via conventional and catalytic co-pyrolysis of bamboo with polystyrene in a bubbling fluidized bed reactor: Coupled experiments and artificial neural network modeling. *Fuel* **2023**, *346*, 128403. https://doi.org/10.1016/j.fuel.2023.128403
33. Vo, T.A.; Kim, J.; Hwang, H.T.; Kim, S.-S. Fast pyrolysis of cashew nut shells in a bubbling fluidized bed reactor for producing high-heating value bio-oil using dolomite as a catalyst and carbon capture sorbent. *Fuel* **2024**, *364*, 131024. https://doi.org/10.1016/j.fuel.2024.131024
34. Charusiri, W. Fast Pyrolysis of Residues from Paper Mill Industry to Bio-oil and Value Chemicals: Optimization Studies. *Energy Procedia* **2015**, *74*, 933-941. https://doi.org/10.1016/j.egypro.2015.07.724
35. Veses, A.; Aznar, M.; López, J.M.; Callén, M.S.; Murillo, R.; García, T. Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials. *Fuel* **2015**, *141*, 17-22. https://doi.org/10.1016/j.fuel.2014.10.044
36. Mohamed, B.A.; Ellis, N.; Kim, C.S.; Bi, X. Understanding catalytic effects of bentonite/clinoptilolite on biomass pyrolysis. *Renew. Energy* **2019**, *142*, 304-315. https://doi.org/10.1016/j.renene.2019.04.117
37. Rijo, B.; Soares Dias, A.P.; de Jesus, N.; Pereira, M.F. Home Trash Biomass Valorization by Catalytic Pyrolysis. *Environments* **2023**, *10*, 186. https://doi.org/10.3390/environments10100186
38. Sandoval-Rangel, L.; Ramírez-Murillo, C.J.; Dimas-Rivera, G.L.; De La Rosa, J.R.; Lucio-Ortiz, C.J.; Ahmad, E.; Nigam, K.D.P.; Montesinos-Castellanos, A.; Mendoza, A. Enhancing the quality of products from slow pyrolysis of an agro-industrial biomass waste with natural mineral additives. *Ind. Crops Prod.* **2024**, *216*, 118798. https://doi.org/10.1016/j.indcrop.2024.118798
39. Song, Q.; Zhao, H.; Jia, J.; Yang, L.; Lv, W.; Bao, J.; Shu, X.; Gu, Q.; Zhang, P. Pyrolysis of municipal solid waste with iron-based additives: A study on the kinetic, product distribution and catalytic mechanisms. *J. Clean. Prod*. **2020**, *258*, 120682. https://doi.org/10.1016/j.jclepro.2020.120682
40. Syazaidah, I.; Bakar, M.S.A.; Reza, M.S.; Azad, A.K. Ex-situ catalytic pyrolysis of chicken litter for bio-oil production: Experiment and characterization. *J. Environ. Manage*. **2021**, *297*, 113407. https://doi.org/10.1016/j.jenvman.2021.113407
41. Stefanidis, S.D.; Karakoulia, S.A.; Kalogiannis, K.G.; Iliopoulou, E.F.; Delimitis, A.; Yiannoulakis, H.; Zampetakis, T.; Lappas, A.A.; Triantafyllidis, K.S. Natural magnesium oxide (MgO) catalysts: A cost-

effective sustainable alternative to acid zeolites for the in situ upgrading of biomass fast pyrolysis oil. *Appl. Catal. B: Environ*. **2016**, *196*, 155-173. https://doi.org/10.1016/j.apcatb.2016.05.031

42. Karod, M.; Hubble, A.H.; Maag, A.R. et al. Clay-catalyzed in situ pyrolysis of cherry pits for upgraded biofuels and heterogeneous adsorbents as recoverable by-products. *Biomass Convers. Biorefin*. **2024**, *14(7)*, 7873–7885. https://doi.org/10.1007/s13399-022-02921-3
43. Bisen, D.; Lanjewar, R.; Chouhan, A.P.S. et al. Catalytic co-pyrolysis of rice husk and high-density polyethylene using dolomite for enhancement of bio-oil production and quality. *Environ. Sci. Pollut. Res.* **2025**, *32*, 15676–15694. https://doi.org/10.1007/s11356-025-36600-3
44. Ly, H.V.; Lim, D.-H.; Sim, J.W. et al. Catalytic pyrolysis of tulip tree (Liriodendron) in bubbling fluidized-bed reactor for upgrading bio-oil using dolomite catalyst. *Energy* **2018**, *162*, 564-575. https://doi.org/10.1016/j.energy.2018.08.001
45. Ly, H.V.; Tran, Q.K.; Kim, S.-S. et al. Catalytic upgrade for pyrolysis of food waste in a bubbling fluidized-bed reactor. *Environ. Pollution* **2021**, *275*, 116023. https://doi.org/10.1016/j.envpol.2020.116023
46. Mysore Prabhakara, H.; Bramer, E.A.; Brem, G. Role of dolomite as an in-situ CO_2 sorbent and deoxygenation catalyst in fast pyrolysis of beechwood in a bench scale fluidized bed reactor. *Fuel Process. Technol.* **2021**, *224*, 107029. https://doi.org/10.1016/j.fuproc.2021.107029
47. Duanguppama, K.; Pannucharoenwong, N.; Echaroj, S.; Pham, L.K.H.; Samart, C.; Rattanadecho, P. Integrated catalytic pyrolysis and catalytic upgrading of Leucaena leucocephala over natural catalysts. *J. Energy Inst.* **2023**, *106*, 101155. https://doi.org/10.1016/j.joei.2022.101155
48. Aljeradat, R. A.; Aljbour, S. H.; Jarrah, N. A. Natural minerals as potential catalysts for the pyrolysis of date kernels: effect of catalysts on products yield and bio-oil quality. *Energy Sources Part A* **2021**, *47(2)*, 2003485. https://doi.org/10.1080/15567036.2021.2003485
49. Venegas-Vásconez, D.; Orejuela-Escobar, L.; Valarezo-Garcés, A.; Guerrero, V.H.; Tipanluisa-Sarchi, L.; Alejandro-Martín, S. Biomass Valorization through Catalytic Pyrolysis Using Metal-Impregnated Natural Zeolites: From Waste to Resources. *Polymers* **2024**, *16*, 1912. https://doi.org/10.3390/polym16131912
50. Nazari, L.; Yuan, Z.; Souzanchi, S.; Ray, M.B.; Xu, C. Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils. *Fuel* **2015**, *162*, 74-83. https://doi.org/10.1016/j.fuel.2015.08.055
51. Ma, Q.; Wang, K.; Sudibyo, H.; Tester, J.W.; Huang, G.; Han, L.; Goldfarb, J.L. Production of upgraded biocrude from hydrothermal liquefaction using clays as in situ catalysts. *Energy Convers. Manag*. **2021**, *247*, 114764, https://doi.org/10.1016/j.enconman.2021.114764
52. Wu, L.M.; Tong, D.S.; Li, C.S.; Ji, S.F.; Lin, C.X.; Yang, H.M.; Zhong, Z.K.; Xu, C.Y.; Yu, W.H.; Zhou, C.H. Insight into formation of montmorillonite-hydrochar nanocomposite under hydrothermal conditions. *Appl. Clay Sci.* **2016**, *119(1)*, 116-125. https://doi.org/10.1016/j.clay.2015.06.015
53. Sudibyo, H.; Cabrera, D.V.; Widyaparaga, A.; Budhijanto, B.; Celis, C.; Labatut R. Reactivity and Stability of Natural Clay Minerals with Various Phyllosilicate Structures as Catalysts for Hydrothermal Liquefaction of Wet Biomass Waste. *Ind. Eng. Chem. Res.* **2023**, *62*, 12513–12529. https://doi.org/10.1021/acs.iecr.3c01681
54. Zhu, Y.; Zhao, Y.; Tian, S.; Zhang, X.; Wei, X. Catalytic hydrothermal liquefaction of sewage sludge: Effect of metal support heterogeneous catalysts on products distribution. *J. Energy Inst.* **2022**, *103*, 154-159. https://doi.org/10.1016/j.joei.2022.04.008
55. Chen, J.; Wang, D.; Lu, X. Effect of Cobalt(II) on Acid-Modified Attapulgite-Supported Catalysts on the Depolymerization of Alkali Lignin *Ind. Eng. Chem. Res.* **2022**, *61*, 1675−1683. https://doi.org/10.1021/acs.iecr.1c04695
56. Karod, M.; Pollard, Z.A.; Ahmad, M.T.; Dou, G.; Gao, L.; Goldfarb, J.L. Impact of Bentonite Clay on In Situ Pyrolysis vs. Hydrothermal Carbonization of Avocado Pit Biomass. *Catalysts* **2022**, *12*, 655. https://doi.org/10.3390/catal12060655
57. Ciuffi, B.; Chiaramonti, D.; Rizzo, A.M.; Frediani, M.; Rosi, L. A Critical Review of SCWG in the Context of Available Gasification Technologies for Plastic Waste. *Appl. Sci.* **2020**, *10*, 6307. https://doi.org/10.3390/app10186307

58. Mohammed, M.A.A.; Salmiaton, A.;Wan Azlina,W.A.K.G.; Mohammad Amran, M.S.; Fakhru'L-Razi, A.; Taufiq-Yap, Y.H. Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1258–1270. https://doi.org/10.1016/j.rser.2010.10.003
59. De Andrés, J.M.; Narros, A.; Rodríguez, M.E. Behaviour of dolomite, olivine and alumina as primary catalysts in air-steam gasification of sewage sludge. Fuel 2011, 90, 521–527. https://doi.org/10.1016/j.fuel.2010.09.043
60. Alper, D.; Babayiğit, E.; Zengin, G.E.; Okutan, H.C.; Sarıoğlan, A. The catalytic influence of low-cost natural minerals on sewage sludge gasification for hydrogen production. *Int. J. Hydrogen Energy* **2025**, *142*, 966-980. https://doi.org/10.1016/j.ijhydene.2025.03.009
61. Zhou, C.; Rosén, C.; Engvall, K. Use of in-bed primary catalyst in pressurized biomass fluidized bed gasification: Strategies for optimal use. *Fuel* **2025**, *393*, 134997. https://doi.org/10.1016/j.fuel.2025.134997
62. Chang, G.; Shi, P.; Guo, Y.; Wang, L.; Wang, C.; Guo, Q. Enhanced pyrolysis of palm kernel shell wastes to bio-based chemicals and syngas using red mud as an additive. *J. Clean. Prod.* **2020**, *272*, 122847. https://doi.org/10.1016/j.jclepro.2020.122847
63. Liu, H.; Chen, T.; Zhang, X.; Li, J.; Chang, D.; Song, L. Effect of Additives on Catalytic Cracking of Biomass Gasification Tar over a Nickel-Based Catalyst. *Chin. J. Catal.* **2010**, *31*, 409–414. https://doi.org/10.1016/S1872-2067(09)60061-9
64. Liu, H.; Chen, T.; Chang, D.; Chen, D.; Frost, R.L. Catalytic cracking of tars derived from rice hull gasification over goethite and palygorskite. *Appl. Clay Sci.* **2012**, *70*, 51-57. https://doi.org/10.1016/j.clay.2012.09.006
65. Chiodo, V.; Urbani, F.; Zafarana, G.; Prestipino, M.; Galvagno, A.; Maisano, S. Syngas production by catalytic steam gasification of citrus residues. *Int. J. Hydrogen Energy* **2017**, *42(46)*, 28048-28055. https://doi.org/10.1016/j.ijhydene.2017.08.085
66. Puig-Gamero, M.; Lara-Díaz, J.; Valverde, J.L.; Sanchez-Silva, L.; Sánchez, P. Dolomite effect on steam co-gasification of olive pomace, coal and petcoke: TGA-MS analysis, reactivity and synergistic effect. *Fuel* **2018**, *234*, 142-150. https://doi.org/10.1016/j.fuel.2018.07.014
67. Tian, Y.; Zhou, X.; Lin, S.; Ji, X.; Bai, J.; Xu, M. Syngas production from air-steam gasification of biomass with natural catalysts. *Sci. Total Environ.* **2018**, *645*, 518-523. https://doi.org/10.1016/j.scitotenv.2018.07.071
68. Latifi, M.; Berruti, F.; Briens, C. Jiggle bed reactor for testing catalytic activity of olivine in bio-oil gasification. *Powder Technol.* **2017**, *316*, 400-409. https://doi.org/10.1016/j.powtec.2016.11.057
69. Šuhaj, P.; Haydary, J.; Husár, J.; Steltenpohl, P.; Šupa, I. Catalytic gasification of refuse-derived fuel in a two-stage laboratory scale pyrolysis/gasification unit with catalyst based on clay minerals. *Waste Management* **2019**, *85*, 1-10. https://doi.org/10.1016/j.wasman.2018.11.047
70. Adanez, J.; Abad, A.; Garcia-Labiano, F.; Gayan, P.; de Diego, L.F. Progress in Chemical-Looping Combustion and Reforming technologies. *Prog. Energy Combust. Sci.* **2012**, *38(2)*, 215-282. https://doi.org/10.1016/j.pecs.2011.09.001
71. Xu, T.; Xu, F.; Moyo, G.G.; Sun, Y.; Chen, Z.; Xiao, B.; Wang, X.; Hu, Z. Comparative study of MxOy (M = Cu, Fe and Ni) supported on dolomite for syngas production via chemical looping reforming with toluene. *Energy Convers. Manag.* **2019**, *199*, 111937. https://doi.org/10.1016/j.enconman.2019.111937
72. Veses, A.; Sanahuja-Parejo, O.; Callén, M.S.; Murillo, R.; García, T. A combined two-stage process of pyrolysis and catalytic cracking of municipal solid waste for the production of syngas and solid refuse-derived fuels. *Waste Management* **2020**, *101*, 171-179. https://doi.org/10.1016/j.wasman.2019.10.009
73. Veses, A.; Sanahuja-Parejo, O.; Martínez, I. et al. A pyrolysis process coupled to a catalytic cracking stage: A potential waste-to-energy solution for mattress foam waste. *Waste Manag.* **2021**, *120*, 415-423. https://doi.org/10.1016/j.wasman.2020.09.052
74. Ben Abdallah, A.; Ben Hassen Trabelsi, A.; Veses, A.; García, T.; López, J.M.; Navarro, M.V.; Mihoubi, D. Enhancing the Production of Syngas from Spent Green Tea Waste through Dual-Stage Pyrolysis and Catalytic Cracking. *Catalysts* **2023**, *13*, 1334. https://doi.org/10.3390/catal13101334
75. Yang, C.; Pang, Y.; Li, G.; Chen, Y.; Li, H. Degradation of biomass tar catalyzed by Fe/Ce supported on diatomite-based foam ceramics. *Biomass Conv. Bioref.* **2024**, *14*, 21107–21120. https://doi.org/10.1007/s13399-023-04124-w

76. Valle, B.; Aramburu, B.; Santiviago, C.; Bilbao, J.; Gayubo, A.G. Upgrading of Bio-Oil in a Continuous Process with Dolomite Catalyst. *Energy Fuels* **2014**, *28(10)*, 6419-6428. https://doi.org/10.1021/ef501600f
77. Valle, B.; García-Gómez, N.; Remiro, A.; Gayubo, A.G.; Bilbao, J. Cost-effective upgrading of biomass pyrolysis oil using activated dolomite as a basic catalyst. *Fuel Process. Technol*. **2019**, *195*, 106142. https://doi.org/10.1016/j.fuproc.2019.106142
78. Cruz, A.; Ramalho, E.; Ribeiro, A.; Pilão, R. Effect of catalyst on the producer gas composition from co-gasification of glycerol/fat mixtures. *Energy Reports*, **2022**, *8*, 139-144. https://doi.org/10.1016/j.egyr.2022.01.104
79. Villegas-Bolaños, P.A.; Gallego, J.; Dorkis, L.; Márquez, M.A. Glycerol valorization using Colombian olivine as a catalyst. *Heliyon* **2023**, *9*, e15561. https://doi.org/10.1016/j.heliyon.2023.e15561
80. Wang, Y.; Wang, C.; Chen, M.; Tang, Z.; Yang, Z.; Hu, J.; Zhang, H. Hydrogen production from steam reforming ethanol over Ni/attapulgite catalysts - Part I: Effect of nickel content. *Fuel Process. Technol*. **2019**, *192*, 227-238. https://doi.org/10.1016/j.fuproc.2019.04.031
81. Chen, Y.; Chen, T.; Liu, H.; Zhang, P.; Wang, C.; Dong, S.; Chen, D.; Xie, J.; Zou, X.; Suib, S.L.; Li, C. High catalytic performance of the Al-promoted Ni/Palygorskite catalysts for dry reforming of methane. *Appl. Clay Sci*. **2020**, *188*, 105498. https://doi.org/10.1016/j.clay.2020.105498
82. Del Grosso, M.; Sridharan, B.; Tsekos, C.; Klein, S.; de Jong, W. A modelling based study on the integration of 10 MWth indirect torrefied biomass gasification, methanol and power production. *Biomass Bioenergy* **2020**, *136*, 105529. https://doi.org/10.1016/j.biombioe.2020.105529
83. Dong, L.; Sharma, P.; Abass, R.R. et al. Optimization of biofuel production from biomass using montmorillonite catalyst by development of predictive models. *J. Mol. Liq.* **2024**, *403*, 124768. https://doi.org/10.1016/j.molliq.2024.124768
84. Chen, L.; He, L.; Zheng, B.; Wei, G.; Li, H.; Zhang, H.; Yang, S. Bifunctional acid-activated montmorillonite catalyzed biodiesel production from non-food oil: Characterization, optimization, kinetic and thermodynamic studies. *Fuel Process. Technol.* **2023**, *250*, 107903. https://doi.org/10.1016/j.fuproc.2023.107903
85. Tiwari, M.S.; Dicks, J.S.; Keogh, J.; Ranade, V.V.; Manyar, H. G. Direct conversion of furfuryl alcohol to butyl levulinate using tin exchanged tungstophosphoric acid catalysts. *J. Mol. Catal.* **2020**, *488*, 110918. https://doi.org/10.1016/j.mcat.2020.110918
86. Sumari, S.; Sulistyoningsih, D.A.; Aisyah, F.; et al. Catalytic transesterification of kapok seed oil by dual metal oxide (Na_2O-K_2O; MgO-CaO) impregnated active-natural mordenite under ultrasonic irradiation. *Energy Sources A: Recovery Util. Environ. Eff.* **2023**, *45(3)*, 6885-6900. https://doi.org/10.1080/15567036.2023.2217771
87. SathyaSelvabala, V.; Varathachary, T.K.; Selvaraj, D.K.; Ponnusamy, V.; Subramanian, S. Removal of free fatty acid in Azadirachta indica (Neem) seed oil using phosphoric acid modified mordenite for biodiesel production. *Bioresour. Technol.* **2010**, *101(15)*, 5897-5902. https://doi.org/10.1016/j.biortech.2010.02.092
88. Çakırca, E.E.; Tekin, G.N.; İlgen, O.; Akın, A.N. Catalytic activity of CaO-based catalyst in transesterification of microalgae oil with methanol. *Energy & Environment* **2019**, *30(1)*, 176-187. https://doi.org/10.1177/0958305X18787317
89. Sudalai, S.; Devanesan, M.G.; Arumugam, A. Dolomite as A Potential Source of Heterogenous Catalyst for Biodiesel Production from Pongamia pinnata. *Nat. Environ. Pollut. Tech.* **2024**, *23(4)*, 2391-2396. https://doi.org/10.46488/NEPT.2024.v23i04.042
90. Niu, S.; Zhang, X.; Ning, Y.; et al. Dolomite incorporated with cerium to enhance the stability in catalyzing transesterification for biodiesel production. *Renew. Energy* **2020**, *154*, 107-116. https://doi.org/10.1016/j.renene.2020.03.003
91. Subramani, S.; Sambath, R.; Ponnuvel, A. et al. Pilot scale production of biodiesel from *Madhuca indica* and comparative techno-economic analysis. *Environ Sci Pollut Res* **2025**. https://doi.org/10.1007/s11356-025-36043-w
92. Korkut, I.; Bayramoglu, M. Selection of catalyst and reaction conditions for ultrasound assisted biodiesel production from canola oil. *Renew. Energy* **2018**, *116*, 543-551. https://doi.org/10.1016/j.renene.2017.10.010

93. Vargas, E.M.; Neves, M.C.; Tarelho, L.A.; Nunes, M.I. Solid catalysts obtained from wastes for FAME production using mixtures of refined palm oil and waste cooking oils. *Renew. Energy* **2019**, *136*, 873-883. https://doi.org/10.1016/j.renene.2019.01.048
94. Sudalai, S.; Vairaprakash, P.; Devanesan, M.G.; Arumugam, A. Sustainable biodiesel production from Madhuca indica oil using a functionalized industrial waste as a catalyst: Ready to scale-up approach. *Ind. Crop. Prod.* **2023**, *193*, 116233. https://doi.org/10.1016/j.indcrop.2022.116233
95. Zhang, W.; Li, M.; Wang, J. et al. Heterogeneous poly (ionic liquids) catalyst on nanofiber-like palygorskite supports for biodiesel production. *Appl. Clay Sci.* **2017**, *146*, 167-175. https://doi.org/10.1016/j.clay.2017.05.031
96. Casiello, M.; Savino, S.; Massaro, M. et al. Multifunctional halloysite and hectorite catalysts for effective transformation of biomass to biodiesel. *Appl. Clay Sci.* **2023**, *242*, 107048. https://doi.org/10.1016/j.clay.2023.107048
97. Sudalai, S.; Prabakaran, S.; Devanesan, M.G.; Arumugam, A. Process Optimization for *Madhuca indica* Seed Kernel Oil Extraction and Evaluation of its Potential for Biodiesel Production. *Nat. Env. Poll. Tech.* **2024**, *23(4)*, 2335-2345. https://doi.org/10.46488/NEPT.2024.v23i04.037
98. Fani, K.; Lycourghiotis, S.; Bourikas, K.; Kordouli, E. Biodiesel upgrading to renewable diesel over nickel supported on natural mordenite catalysts. *Ind. Eng. Chem. Res.* **2021**, *60(51)*, 18695-18706. https://doi.org/10.1021/acs.iecr.1c02560
99. Fani, K.; Lycourghiotis, S.; Bourikas, K.; Kordouli, E. Influence of natural mordenite activation mode on its efficiency as support of nickel catalysts for biodiesel upgrading to renewable diesel. *Nanomaterials* **2023**, *13(10)*, 1603. https://doi.org/10.3390/nano13101603
100. Putra, R.; Lestari, W.W.; Wibowo, F.R.; Susanto, B.H. Fe/Indonesian natural zeolite as hydrodeoxygenation catalyst in green diesel production from palm oil. *Bull. Chem. React. Eng. Catal.* **2018**, *13(2)*, 245-255. https://doi.org/10.9767/bcrec.13.2.1382.245-255
101. Putra, R.; Lestari, W.W.; Susanto, B.H.; Kadja, G.T. Green diesel rich product (C-15) from the hydrodeoxygenation of refined palm oil over activated NH^{4+}-Indonesian natural zeolite. *Energy Sources A: Recovery Util. Environ. Eff.* **2022**, *44(3)*, 7483-7498. https://doi.org/10.1080/15567036.2022.2113934
102. Kurniawan, A.A.; Rustyawan, W.; Ibadurrohman, M. Performance Test of Various Indonesian Natural Zeolites as Composite Components of NiMo/Al_2O_3-Zeolite Catalysts for Hydrocracking Used Cooking Oil into Biohydrocarbons. *Bull. Chem. React. Eng. Catal.* **2025**, *20(1)*, 99-108. https://doi.org/10.9767/bcrec.20254
103. Lycourghiotis, S.; Kordouli, E.; Zafeiropoulos, J.; Kordulis, C.; Bourikas, K. Mineral montmorillonite valorization by developing Ni and Mo–Ni catalysts for third-generation green diesel production. *Molecules* **2022**, *27(3)*, 643. https://doi.org/10.3390/molecules27030643
104. Lycourghiotis, S.; Kordouli, E.; Sygellou, L.; Bourikas, K.; Kordulis, C. Nickel catalysts supported on palygorskite for transformation of waste cooking oils into green diesel. *Appl. Catal., B* **2019**, *259*, 118059. https://doi.org/10.1016/j.apcatb.2019.118059
105. Lycourghiotis, S.; Kordouli, E.; Kordulis, C.; Bourikas, K. Transformation of residual fatty raw materials into third generation green diesel over a nickel catalyst supported on mineral palygorskite. *Renew. Energy* **2021**, *180*, 773-786. https://doi.org/10.1016/j.renene.2021.08.059
106. Zamri, M.F.M.A.; Shamsuddin, A.H.; Ali, S.; Bahru, R.; Milano, J.; Tiong, S.K.; Fattah, I.M.R.; Raja Shahruzzaman, R.M.H. Recent Advances of Triglyceride Catalytic Pyrolysis via Heterogenous Dolomite Catalyst for Upgrading Biofuel Quality: A Review. *Nanomaterials* **2023**, *13*, 1947. https://doi.org/10.3390/nano13131947
107. Abdulloh, A.; Rahmah, U.; Permana, A.J. et al. Cracking optimization of palmitic acid using Fe^{3+} modified natural mordenite for producing aviation fuel compounds. *Chem. Chem. Technol.* **2023**, *17(3)*, 625–635. https://doi.org/10.23939/chcht17.03.625
108. Buyang, J.D.; Hasanah, L.; Rahmayeni, R.; Sulhatun, S.; Putri, R.N. Catalytic pyrolysis of *Reutealis trisperma* oil using dolomite catalyst. *J. Anal. Appl. Pyrol.* **2023**, *169*, 105852. https://doi.org/10.1016/j.jaap.2022.105852
109. Hafriz, R.S.R.M.; Salmiaton, A.; Yunus, R.; Taufiq-Yap, Y.H. Green Biofuel Pro-duction via Catalytic Pyrolysis of Waste Cooking Oil using Malaysian Dolomite Catalyst. *Bull. Chem. React. Eng. Catal.* **2018**, *13(3)*, 489-501. https://doi.org/10.9767/bcrec.13.3.1956.489-501

110. Hafriz, R.S.R.M.; Nor Shafizah, I.; Arifin, N.A. et al. Effect of Ni/Malaysian dolomite catalyst synthesis technique on deoxygenation reaction activity of waste cooking oil. *Renew. Energy* **2021**, *178*, 128–143. https://doi.org/10.1016/j.renene.2021.06.074
111. Ali, S.H.; Hafriz, R.S.R.M.; Shamsuddin, A.H.; Salmiaton, A. Production of liquid biofuel from sludge palm oil (SPO) using heterogeneous catalytic pyrolysis. *J. Appl. Sci. Eng.* **2022**, *26(4)*, 529-538. http://dx.doi.org/10.6180/jase.202304_26(4).0009
112. Hafriz, R.S.R.M.; Arifin, N.A.; Salmiaton, A. et al. Multiple-objective optimization in green fuel production via catalytic deoxygenation reaction with NiO-dolomite catalyst. *Fuel* **2022**, *308*, 122041. https://doi.org/10.1016/j.fuel.2021.122041
113. Kanchanatip, E.; Chansiriwat, W.; Palalerd, S. et al. Light biofuel production from waste cooking oil via pyrolytic catalysis cracking over modified Thai dolomite catalysts. *Carbon Resour. Convers.* **2022**, *5*, 177–184. https://doi.org/10.1016/j.crcon.2022.05.001
114. Tamim, R.; Prasetyoko, D.; Jovita, S. et al. Low temperature pyrolysis of waste cooking oil using marble waste for bio-jet fuel production. *Renew. Energy* **2024**, *232*, 121135. https://doi.org/10.1016/j.renene.2024.121135
115. Tamim, R.; Prasetyoko, D.; Jovita, S. et al. Ni-activated marble waste nanoparticles for catalyzed pyrolysis of waste cooking oil into hydrocarbon. *Renew. Energy* **2025**, *248*, 123128. https://doi.org/10.1016/j.renene.2025.123128
116. Nhien, L.C.; Long, N.V.D.; Lee, M. Novel hybrid reactive distillation with extraction and distillation processes for furfural production from an actual xylose solution. *Energies* **2021**, *14 (4)*, 1152. https://doi.org/10.3390/en14041152
117. Richel, A.; Maireles-Torres, P.; Len, C. Recent advances in continuous reduction of furfural to added value chemicals. *Curr. Opin. Green Sustain. Chem.* **2022**, *37*, 100655. https://doi.org/10.1016/j.cogsc.2022.100655
118. Jiménez-Gómez, C.P.; Cecilia, J.A.; Moreno-Tost, R.; Maireles-Torres, P. Selective Furfural Hydrogenation to Furfuryl Alcohol Using Cu-Based Catalysts Supported on Clay Minerals. *Top. Catal.* **2017**, *60*, 1040–1053. https://doi.org/10.1007/s11244-017-0804-2
119. Guerrero-Torres, A.; Jiménez-Gómez, C.P.; Cecilia, J.A. et al. Ni supported on sepiolite catalysts for the hydrogenation of furfural to value-added chemicals: influence of the synthesis method on the catalytic performance. *Top. Catal.* **2019**, *62*, 535–550. https://doi.org/10.1007/s11244-019-01168-z
120. García, A.; Sanchis, R.; Llopis, F.J.; Vázquez, I.; Pico, M.P.; López, M.L.; Álvarez-Serrano, I.; Solsona, B. Ni Supported on Natural Clays as a Catalyst for the Transformation of Levulinic Acid into γ-Valerolactone without the Addition of Molecular Hydrogen. *Energies* **2020**, *13*, 3448. https://doi.org/10.3390/en13133448
121. García, A.; Saotta, A.; Miguel, P.J. et al. Promoter Effect of Pt on Zr Catalysts to Increase the Conversion of Furfural to γ-Valerolactone Using Batch and Continuous Flow Reactors: Influence of the Way of the Incorporation of the Pt Sites. *Energy Fuels* **2024**, *38(11)*, 9849-9861. https://doi.org/10.1021/acs.energyfuels.4c01174
122. Wang, J.; Dai, X.; Wang, H. et al. Dihydroxyacetone valorization with high atom efficiency via controlling radical oxidation pathways over natural mineral-inspired catalyst. *Nat. Commun.* **2021**, *12*, 6840. https://doi.org/10.1038/s41467-021-27240-5
123. Zhong, X.; Wei, Y.; Sadjadi, S. et al. Base-free oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid over palygorskite-supported bimetallic Pt–Pd catalyst. *Appl. Clay Sci.* **2022**, *226*, 106574. https://doi.org/10.1016/j.clay.2022.106574
124. Zhong, X.; Yuan, P.; Wei, Y. et al. Coupling Natural Halloysite Nanotubes and Bimetallic Pt–Au Alloy Nanoparticles for Highly Efficient and Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. *ACS Appl. Mater. Interfaces* **2022**, *14(3)*, 3949-3960. https://doi.org/10.1021/acsami.1c18788
125. Zhong, X.; Yuan, P.; Sadjadi, S. et al. Palygorskite-supported ruthenium catalysts for the efficient selective oxidation of 5-hydroxymethylfurfural to 2, 5-diformylfuran. *Appl. Clay Sci.* **2023**, *242*, 107023. https://doi.org/10.1016/j.clay.2023.107023

126. Wang, F.; Yan, C.; Jiang, R. et al. Highly efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over halloysite nanotubes-templated nitrogen-doped carbon supported bimetallic AuPd catalyst. *Appl. Clay Sci.* **2023**, *235*, 106872. https://doi.org/10.1016/j.clay.2023.106872
127. Chen, Y.; Sun, L.; Li, Y. et al. Oxygen Vacancy-Induced Metal–Support Interactions in AuPd/ZrO_2 Catalysts for Boosting 5-Hydroxymethylfurfural Oxidation. *Inorg. Chem.* **2023**, *62(37)*, 15277-15292. https://doi.org/10.1021/acs.inorgchem.3c02473
128. Liu, Y.; Chen, Y.; Li, Y.; Guan, W.; Xia, Q.; Cao, M.; Huo, P.; Zhang, Y. Oxygen vacancy-driven strong metal-support interactions on AuPd/TiO_2 catalysts for high-efficient air-oxidation of 5-hydroxymethylfurfural. *Chem. Eng. J.* **2023**, *476*, 146874. https://doi.org/10.1016/j.cej.2023.146874
129. Li, H.; Li, Y.; Xia, Q.; Liu, Y.; Guan, W.; Chen, Y. Efficient Catalytic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid Using a Natural Mineral Vermiculite-Loaded Gold–Palladium Bimetallic Catalyst. *Catalysts* **2024**, *14*, 949. https://doi.org/10.3390/catal14120949
130. Zhang, Y.; Liu, Y.; Xia, Q. et al. Ambient temperature catalyzed air-oxidation of 5-hydroxymethylfurfural via ternary metal and oxygen vacancies. *G. E. E.* **2025**, *10(7)*, 1568-1582. https://doi.org/10.1016/j.gee.2025.02.003
131. Silva, M.J.d.; da Silva Andrade, P.H. The Heteropolyacid-Catalyzed Conversion of Biomass Saccharides into High-Added-Value Products and Biofuels. *Processes* **2024**, *12*, 2587. https://doi.org/10.3390/pr12112587
132. Yang, F.; Weng, J.; Ding, J. et al. Effective conversion of saccharides into hydroxymethylfurfural catalyzed by a natural clay, attapulgite. *Renew. Energ.* **2020**, *151*, 829-836. https://doi.org/10.1016/j.renene.2019.11.084
133. Kiani, F.; Mazloom, G.; Ghani, M. et al. Acid-modified mineral bentonite as catalyst for efficient furfural formation from glucose. *Biomass Conv. Bioref.* **2024**, *14*, 11617–11631. https://doi.org/10.1007/s13399-022-03243-0
134. Adila, Z.; Trisunaryanti, W.; Triyono, T. Modification of Natural Zeolite from Klaten, Indonesia Using Ammonium Chloride by Ion-Exchange and Its Application as Catalyst in Ethanol Dehydration to Produce Diethyl Ether. *Indones. J. Chem.* **2024**, *24(2)*, 505 – 518. https://doi.org/10.22146/ijc.90279
135. Ye, X.; Shi, X.; Jin, B.; Zhong, H.; Jin, F.; Wang, T. Natural mineral bentonite as catalyst for efficient isomerization of biomass-derived glucose to fructose in water. *Sci. Total Environ.* **2021**, *778*, 146276. https://doi.org/10.1016/j.scitotenv.2021.146276
136. Ren, J.; Ye, X.; Shi, X.; Xu, H.; Wu, L.; Wang, T. N-Doped natural albite mineral as green solid catalyst for efficient isomerization of glucose into fructose in water. *React. Chem. Eng.* **2022**, *7*, 1786. https://doi.org/10.1039/d2re00112h
137. Long, S.; Huang, Z.; Du, Q.; Tang, P.; Xian, X.; Du, F.; Li, Y. Glucose isomerization into fructose with CaO-MgO mixed oxides and dolomite(ore)-derived base CaO/MgO catalysts in water under mild conditions. *Fuel* **2024**, *370*, 131754. https://doi.org/10.1016/j.fuel.2024.131754
138. Barros, F.J.S.; Cecilia, J.A.; Moreno-Tost, R. et al. Glycerol Oligomerization Using Low Cost Dolomite Catalyst. *Waste Biomass Valor.* **2020**, *11*, 1499–1512. https://doi.org/10.1007/s12649-018-0477-5
139. Tian, H.; Shao, Y.; Liang, C. et al. Sulfated attapulgite for catalyzing the conversion of furfuryl alcohol to ethyl levulinate: Impacts of sulfonation on structural transformation and evolution of acidic sites on the catalyst. *Renew. Energ.* **2020**, *162*, 1576-1586. https://doi.org/10.1016/j.renene.2020.09.113
140. Lai, F.; Yan, F.; Wang, Y. et al. Tungstophosphoric acid supported on metal/Si-pillared montmorillonite for conversion of biomass-derived carbohydrates into methyl levulinate. *J. Clean. Prod.* **2021**, *314*, 128072. https://doi.org/10.1016/j.jclepro.2021.128072
141. Meng, X.; Su, H.; Song, R.; Su, J.; Bian, J. Solvent-Free Aldol Condensation of Cyclopentanone with Natural Clay-Based Catalysts: Origin of Activity & Selectivity. *Catalysts* **2023**, *13*, 530. https://doi.org/10.3390/catal13030530
142. Zhang, J.; Yang, J.; Li, X. et al. Natural attapulgite supported nano-Ni catalysts for the efficient reductive amination of biomass-derived aldehydes and ketones. *Green Synth. Catal.* **2024**, *5(1)*, 42-50. https://doi.org/10.1016/j.gresc.2023.02.003
143. Lycourghiotis, S.; Makarouni, D.; Kordouli, E.; Bourikas, K.; Kordulis, C.; Dourtoglou, V. Activation of natural mordenite by various acids: Characterization and evaluation in the transformation of limonene into p-cymene. *Mol. Catal.* **2018**, *450*, 95-103. https://doi.org/10.1016/j.mcat.2018.03.013

144. Makarouni, D.; Lycourghiotis, S.; Kordouli, E.; Bourikas, K.; Kordulis, C.; Dourtoglou, V. Transformation of limonene into p-cymene over acid activated natural mordenite utilizing atmospheric oxygen as a green oxidant: A novel mechanism. *Appl. Catal. B: Environ.* **2018**, *224*, 740-750. https://doi.org/10.1016/j.apcatb.2017.11.006
145. Lycourghiotis, S.; Makarouni, D.; Kordouli, E.; Bourikas, K.; Kordulis, C.; Dourtoglou, V. The Influence of Calcination on the Physicochemical Properties of Acidactivated Natural Mordenite. *CCAT* **2020**, *9(2)*, 138-147. https://doi.org/10.2174/2211544709999200430003940
146. Lycourghiotis, S.; Makarouni, D.; Kordouli, E.; Bourikas, K.; Kordulis, C.; Dourtoglou, V. Transformation of limonene into high added value products over acid activated natural montmorillonite. *Catal. Today* **2020**, *355*, 757-767. https://doi.org/10.1016/j.cattod.2019.04.036
147. Makarouni, D.; Kordulis, C.; Dourtoglou, V. Solvent-Driven Selectivity on the One-Step Catalytic Synthesis of Manoyl Oxide Based on a Novel and Sustainable "Zeolite Catalyst–Solvent" System. *Catal. Lett.* **2022**, *152(5)*, 1298-1307. https://doi.org/10.1007/s10562-021-03721-6
148. Makarouni, D.; Dimitriadi Evgenidi, C.; Kordulis, C.; Dourtoglou, V. Catalytic conversion of biomass-derived compounds to high added value products using an acid treated natural mordenite. *Sustain. Chem. Pharm.* **2023**, *33*, 101125. https://doi.org/10.1016/j.scp.2023.101125
149. Balasubramanian, S.; Shanmugam, R.; Basha, A.C.; Sriariyanun, M.; Shanmugam, S.R.; Venkatachalam, P. An Overview of Solid Acid Catalysts in Lignocellulose biorefineries. *Catalysts* **2025**, *15*, 432. https://doi.org/10.3390/catal15050432