

# An Evaluation of Catalyst Applications in Bio-Oil Upgrading and Biomass Pyrolysis

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**Abstract** – Biomass has been offered as a sustainable replacement to fossil fuels since it can be converted into chemicals and liquid fuels. Recent years have seen a surge in interest in the feasibility of combining biomass rapid pyrolysis and bio-oil catalytic upgrading to produce liquid biofuels. There would be no progress in this process without the catalysts. Although progress has been achieved, problems with catalyst selectivity and inactivation persist despite these efforts. Many catalysts have proven effective, leading to notable advancements in the processes of petroleum refining. As petroleum refining and biomass conversion share a similar reaction pathway and substrate, the lessons learned from catalyst applications in the former might pave the way for breakthroughs in the latter. This article provides a concise comparison of numerous catalysts used in the refining of petroleum and the manufacture of biofuels. In this paper, pyrolysis and bio-oils upgrading are investigated as potential applications for petroleum refining catalysts.

**Keywords** – Fluid Catalytic Cracking (FCC), High-Density Olefins (HDO), Crude Distillation Unit (CDU), Hydro-Denitrogenation (HDN).

## I. INTRODUCTION

Several studies have examined the integration of biorefineries with petrochemical infrastructure, particularly with regard to improving the conversion of biomass to petroleum refinery catalyst. These studies are crucial for optimizing biofuel production processes and enhancing their quality. For catalysts to be developed with the high specificity and sustained activity requisite for bio-oil upgrading, both fundamental and applied research are needed. Due to developments in nanomaterials over the last several decades, a new strategy for synthesizing the high-performance catalyst utilized in the petroleum refinery is now possible, allowing for unequalled molecular-level knowledge and control over catalyst. These methods have the potential to advance the development of a catalyst for application in a biorefinery. As the high-density olefins (HDO) hydrodeoxygenation process generates a lot of water, scientists such as Sung, Yang, Park, and Jon [1] are looking at potential alternatives to the traditional alumina support for hydrotreating catalysts. Selecting the proper reaction conditions and properly preparing the catalysts are just as critical as selecting the suitable noble electrocatalyst for the HDO process. ZSM-5 has the right cracking catalyst capabilities to transform bio-oil into hydrocarbon biofuels; its primary drawbacks are its deactivation and poor yield.

In order to minimize the deposition of carbon and enhance the lifecycle of catalysts, it may become necessary to develop unique methods of changing the ZSM-5 zeolites surface elements. According to Tahmasebpour, Rahimvandi Noupour, and Badamchizadeh [2], it is hoped that the inclusion of metals similar to those used in fluid catalytic cracking (FCC) catalysts would be effective. Synthesis and use of certain mix crystal zeolites with unique features in the petroleum refinery may shed light on the possibility of bio-oil catalytic cracking. The best method for making biofuel involves integrating existing technology with a new catalyst. Bio-oils hydrogenation first would significantly minimize unstable component, and as a result, lessen carbon accumulation on catalysts; this may lead researchers to consider coupling noble

metals hydrogenation reactors with HDO catalysts or catalytic cracking catalysts. It is recommended to pick the best reaction procedures for manufacturing biofuels and chemicals based on the petroleum refining procedure. To improve catalyst activity and longevity, more work has to be put into developing efficient catalysts for deoxygenating bio-oils. Catalyst inactivation and regeneration should be explored systematically. In particular, it is important to stress sophisticated characterisation of the employed catalysts at various phases of deactivation and to thoroughly explore the deactivation process. It is crucial to fully assess the role of pollutants in bio-oils on catalyst inactivation.

According to Cai, Liu, Tang, Tan, and Cao [3], energy consumption is on the rise, but finite fossil fuel reserves and increasing public concern about the environment mean that alternatives must be sought out if we are to keep up with demand and ensure sustainable growth.

With its high rate of availability and reduced price, biomass is typically visualized as the sole viable carbon source capable of producing renewable chemicals or liquid fuels. Wheat straw, forest leftovers, maize stover, wood chips, and even rubbish have all been the subject of intensive efforts to be transformed into drop-in-fuels. Rapid pyrolysis is seen as an outstanding strategy for biomass conversions to bio-oils, and there have been encouraging developments in the manufacturing of petroleum-based fuels from biomass. However, the most pressing challenge is enhancing bio-oil to create high-quality fuel. Bio-oil produced by rapid pyrolysis may contain anywhere from three hundred to four hundred different chemicals. These chemicals include a wide variety of acids, ketones, ethyl alcohol, esters, aldehydes, and aromatic compounds.

Due to its increasing high viscosity, high levels of acidity, high oxygen levels, and incompatibility with fuels derived from petroleum, bio-oil must be modified in order to become more suited to the present fuel and chemical manufacturing infrastructures. Catalysts serve a crucial role in the production of high-quality renewable fuels throughout the upgrading process. Hydrotreating, catalytic cracking, and 8-hydrodeoxygenation are just a few of the catalytic processes being explored with this objective in mind. Catalyst advancement will lead to widespread use of biomass-based renewable fuels.

To this end, the use of a heterogeneous catalyst might help overcome technical and scientific hurdles in order to mass-produce biofuels at a reasonable cost. Hydrocracking, FCC, hydrotreating, and other methods utilize heterogeneous catalyst that has found significant success in the oil refinery industry. ZSM-5 integrating different zeolites are employed in the process of FCC including other petroleum refining procedures because they are an effective catalyst. A crucial part of the modern petrochemical industry is played by hydrotreating catalysts. Sulfur, nitrogen, metals, and oxygen are all eliminated from the system with the help of CoMo, NiW, and NiMo catalysts. The bio-oils fractions have certain similarities with the petroleum ones. To fulfill the standard for blending with petroleum-derived fuels, the quality of pyrolysis bio-oil may be enhanced with the use of certain catalysts used in petroleum refining. Using catalysts developed for petroleum refining, scientists have tried several times to modify biomass and boost the quality of bio-oil.

Catalysts utilized in the upgrading of bio-oils require a critical form of treatment and conversion due to the oil's unique acidity and oxygen content contrasted to saturated hydrocarbons. To make biofuels and chemicals, for example, heterogeneous catalysts may be used to convert biomass. To some extent, this is analogous to what has been done in oil refineries, where catalysts play a crucial part in both the refining and processing of petroleum and chemical products. In the futuristic biorefinery, biomass feed-stocks will be transformed to chemical, energy and fuel products, and heterogeneous catalysts are anticipated to play major roles in this process. So, the future advancement of catalysts in bio-oil upgrading and biomass conversion may be illuminated by a comparison of heterogeneous catalysts employed in both processes.

In this review, we will present a discussion of the history and importance of heterogeneous catalysts in the petroleum refining industry and provide a brief summary of their operation. Several of the most promising pathways for biomass conversion will be highlighted, including hydrodeoxygenation (HDO), hydrotreating, and fluid catalytic cracking. The catalysts applied in the present FCC, hydrotreating, and HDO processes for bio-oil upgrading will next be studied and compared to those used in petroleum refining. To address the objective of the research, this paper has been organized as follows: Section II provides a discussion of catalyst application in petroleum refinery. Section III focuses on discussing the catalysts in petroleum refinery. Section IV is about catalysts for bio-oil upgrading and pyrolysis. In Section V, a survey of the applications of petroleum technology in biomass conversion is provided. Finally, Section VI draws conclusive remarks to the article.

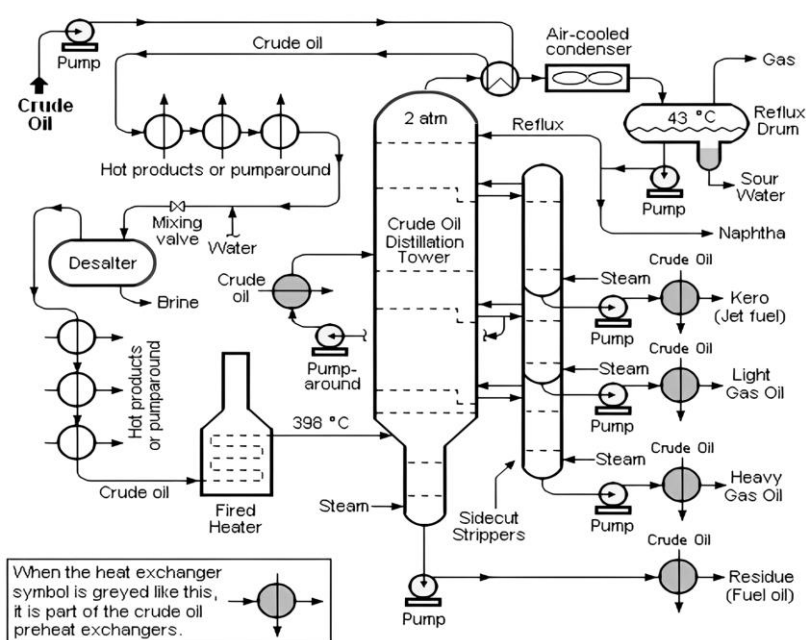
## II. HISTORICAL ANALYSIS

Islamic chemists distilled crude oil, and their methods are explained in detail in texts like those authored by Muhammad ibn Zakarya Rzi (c. 865–925). As petroleum was mined locally, it was used to pave Baghdad's streets. Modern-day Baku, Azerbaijan, is located on oil reserves that were first developed in the 9<sup>th</sup> century. Both the Italian traveller Marco Polo (in the 13<sup>th</sup> century) and Islamic geographical expert Abu al-Hassan (in the 10<sup>th</sup> century) mentioned the vastness of these fields and their ability to produce hundreds of shiploads of oil. Scientists in the Islamic world also refined crude oil to create explosives for use in warfare [4]. Predating the nineteenth century, civilizations as diverse as Egypt, China, Babylon, Rome, the Philippines, and the areas surrounding the Caspian Sea had all discovered and made use of petroleum in various forms. In 1846, a Canadian chemist, Abraham Gessner, discovered a way to extract kerosene from firewood, ushering in the modern age of the petroleum sector. Soon after, Ignacy Lukasiewicz in 1854 started generating kerosene from different oil wells he drilled by hand in the Polish town of Krosno. Due to the abundance of oil in Romania, the country's first significant petroleum refinery was built at Ploesti in 1856.

In 1858, John Miller Williams dug the first oil well in Canada. Edwin Drake's discovery of oil in 1859 at Titusville, Pennsylvania marked the beginning of the American petroleum industry. Throughout the 1800s, the business progressively expanded, chiefly generating kerosene for oil lights. The fast expansion of the petroleum business may be traced back to the early twentieth century, when the vehicle became widely used. Big oil "booms" in Oklahoma, Texas, and California quickly overtook the earlier discoveries in Ontario and Pennsylvania.

In the early 1940s, before the onset of World War II, most American petroleum refineries were nothing more than oils distillation firms (typically known as environmental CDU). In addition to thermal cracking devices like visbreakers, certain refineries also possessed vacuum distillation facilities (units for lowering oil viscosity, viscosity breakers). All of the several different refining techniques that will be mentioned below were created either during the war itself or very quickly afterwards. Within a decade after the end of wars, the worldwide oil industry had developed to the point of economic viability [5]. The rising demand for gasoline and jet fuel drove the expansion of refineries globally and the development of new technologies to meet that need. Construction of new refineries in the United States came to a halt somewhere in the 1980s for a variety of complicated economic and political reasons. U.S. refineries have been modernizing and expanding their facilities to meet stricter environmental standards for air and water pollution, crude oil processing, and product gasoline octane.

The crude distillation unit (CDU) [6] is often the first to be put into operation in oil refineries. The CDU separates crude oil into its various boiling range components before sending them on to the refinery. Due to the somewhat greater working pressure than conventional air pressure, the CDU is known to be the atmosphere distillation unit. **Fig 1** depicts the operation of a conventional crude oil distilling facility. Through the heat exchanger, certain amounts of hot distillation fraction and other fractions are utilized to pre-heat the incoming crude oil. Desalination removes the sulphates (sodium chloride). Following the desalter, some of the distillation fractionation and other streams are heated further, and this heat is exchanged with the crude oil to increase its temperature. From there, it is heated to a temperature of approximately 398 °C in a fuel-fueled heater (burning heater) before being pumped into the distilling unit's base.



**Fig 1.** Simplified Flowchart of the Distillation Process for Crude Oil Used in Petroleum Refineries

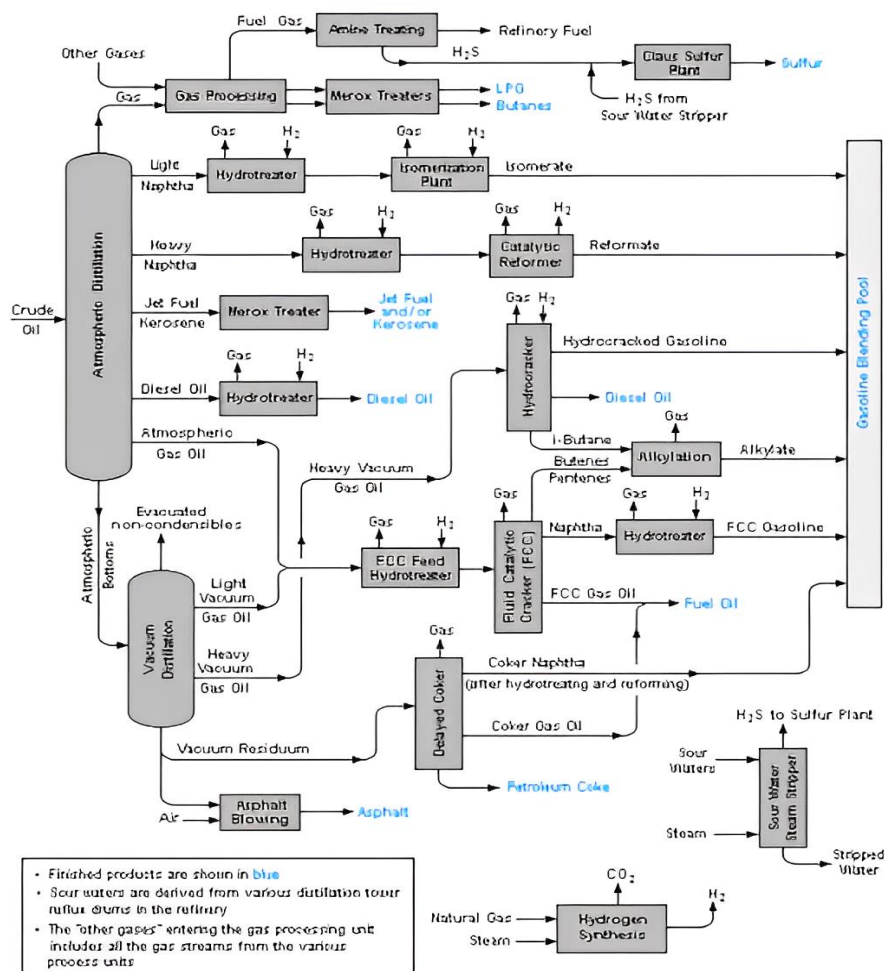
Both the entering crude oil and a secondary condenser, cooled by air or water, contribute to the cooling and condensation process in the tower-mounted distillation apparatus. **Fig 1** is a graphic depicting how a pumparound system is used to remove extra heat from the distillation column. Naphtha is shown as the percentage that is distilled from the distillation column's overhead distillate. Sidecuts refer to the distillation fractions that are taken from the sides of the column at varying heights. A heat exchange between the entering crude oil and the sidecuts (light gas oil, heavy gas oil, and kerosene) cools each of the sidecuts. Before proceeding with further processing, all of the fractions (sidecuts, bottom residue, and overhead naphtha) are kept in transitional tanks.

**Fig 2** presents a conventional petroleum refinery, which showcases the processes of refining include the channels of movement of products between the input substrate and the end-user products. The oil refinery layout seen here is only one of potentially hundreds of possible arrangements. Also missing from the figure are the typical utilities provided by a refinery, such as heat, electrical power, and cooling water, in addition to the storage tanks utilized for both finished products, and crude oil feedstock.

### III. CATALYSTS IN PETROLEUM REFINERY

### *Distillation of Naphtha and Kerosene*

The drilling of the first oil wells occurred in 1858 in Ontario, Canada, and in 1859 in Pennsylvania, Titusville, United States, ushering in the era of petroleum refinement. Until that time, petroleum was only accessible in minute amounts through seepage of subterranean oil in different parts of the planet. But, because of its scarcity, petroleum was once again relegated to the realm of medicine and the arts. Larger-scale processing systems were motivated by the detection of "rock oils" in Pennsylvania, which led to a significant increase in the availability of crude oil. Traditionally, crude oil was refined using primitive devices called "stills," which included boiling the crude oil combination in a tank and then compressing the resultant vapours into liquid fractionation. Originally, kerosene was the main output because it was more readily available, burned cleaner, and had more uniform quality compared to animal fat or whale oil.



**Fig 2.** An Illustration of the Schematic Flow of a Conventional Petroleum Refinery

Straight run naphtha, a precursor to unrefined gasoline, was the still's lowest-boiling raw output (petrol). To begin with, it was mostly used in the business sector as a solvent. Initially, higher-boiling materials were mostly novelties despite their usefulness as lubricants and fuel oils. By 1890, Russian refineries were pumping out massive amounts of kerosene and fuel oils thanks to the rapid improvement of oil-drilling technology. In the latter part of the nineteenth century, when the internal combustion engine was developed, a little market was opened up for crude naphtha. However, with the introduction of motor vehicles at the onset of the century came a surge in demand for premium gasoline, and with it, a place for the less volatile petroleum fractions that had previously been relegated to kerosene. Continuous distillation of crude oil was created as the need for fuel for automobiles increased.

### Conversion to Light Fuels

Automobile fuel requirements began to outstrip kerosene demands in 1910, prompting refiners to seek for ways to increase gasoline production [7]. The initial technique, called thermal fracturing, comprised heating denser oils (with a relatively low demand) in pressurized heaters and shattering, or dividing, their large molecules into lightweight, more valuable fractions such as kerosene, light industrial fuels, and gasoline. Cracked gasoline, as opposed to gasoline made from the simple distillation of crude oil, is superior in terms of how it performs in automotive engines. Fuel additives containing

lead were developed in the late 1930s in response to the need to enhance the performance of more powerful aviation engines by increasing the combustion properties of gasoline.

Improvements in refining technology and the widespread use of catalysts throughout the 1930s and WWII resulted in a larger supply of higher-quality transportation fuels and a marked uptick in fuel quality. Catalytic pyrolysis of alkylation, heavy oils, isomerization, and polymerization were all innovations that helped the petroleum industry meet the demands of high-performance warplanes throughout the war and thereafter [8]. An increase need for jet fuel and premium lubricating lubricants emerged in the 1950s and 1960s. The need to refine more types of crude oil into finished goods has grown in importance as the market for petroleum products continues to expand. Because of the rise in popularity of higher-compression engines, catalytic reforming of naphtha has largely superseded thermal reforming as the primary method for improving fuel quality. Catalytic cracking in the presence of hydrogen, or hydrocracking, was designed to be a flexible method of production that could be used to boost output of either jet fuel or gasoline.

#### Environmental Concerns

In 1970, oil refining had already become an established industry all across the globe. Most of the world's refineries are situated in developed countries and process about 2.3 billion metric tons of crude oil annually (40 million barrels/day) to create finished petroleum products. However, when people throughout the globe learned about the negative effects of industrial dilapidation on the ecosystem, the petroleum refining sector became a focal point for reform. Several tons of elemental sulfur were produced when refineries installed hydrotreating equipment to remove sulphur dioxide from their products. There has been a rise in technological interest in the treatment of wastewater as well as the prevention of air pollution from hydrocarbons and combustion byproducts. Several processed goods also got the once-over. Commencing in the mid-1970s, the U.S. and later the rest of the world required petroleum refiners to find methods for manufacturing high-quality petroleum without using lead admixtures, and starting in the 1990s, gasoline refiners were required to invest heavily in the complete restructuring of diesel fuel in order to reduce ecological emissions. While it still processes about 4.6 billion metric tons of crude oil per year, the petroleum refining industry is now one of the most stringently governed production industries on earth, devoting a large portion of its resources to reducing its impact on the ecosystem (approximately 80 million barrels/day).

#### High-Conversion Oil Refinery Process

As can be seen in **Fig 3**, the process of contemporary petroleum refinery is rather involved, requiring and making significant use of several different kinds of heterogeneous catalyst, including hydro-cracking catalysts, hydrotreating catalysts, and FCC catalysts. **Table 1** displays the composition and characteristics of three different catalysts.

**Table 1.** Major Element of the Three Selected Catalysts

Catalysts	Metals	Support	Conditions of reactions	Functions	Feed
<b>Hydro-treating catalysts</b>	Pd/Pt; Co-Mo; Ni-Mo; Ni-W	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	$P = 1 \text{ to } 10 \text{ MPa}$ $T = 300 \text{ }^{\circ}\text{C to } 450 \text{ }^{\circ}\text{C}$	Saturation, hydrogenation; and HDM, HDO, HDN, and HDS	Lubricant wax, kerosene, gasoline, diesel
<b>FCC</b>	-	ZSM-5, Ultra-stable Y	$P = 0.1 \text{ to } 0.3 \text{ MPa};$ $T = 450 \text{ }^{\circ}\text{C to } 550 \text{ }^{\circ}\text{C}$	Aromatization, isomerization, cracking	VR, CGO, VGO, AR
<b>Hydro-cracking catalyst</b>	Ni-W; Co-Mo; Ni-Mo	$\beta, Y$	$P = 10 \text{ to } 15 \text{ MPa}$ $T = 260 \text{ }^{\circ}\text{C to } 400 \text{ }^{\circ}\text{C}$	Cracking and hydrogenation; isomerization	HAGO, AGO, DAO, CGO, VGO

Heavy oil's rising popularity necessitates the employment of FCC catalysts to increase the output of high-level octane gasoline. Catalysts for hydrotreating and hydrocracking are used to eliminate contaminants from petroleum feedstocks and saturate the olefin, resulting in higher grade fuels. As regulations get stricter to safeguard the environment, the catalysts for hydrotreating and hydro-cracking become increasingly valuable.

#### Catalytic Cracking Catalysts

The fischer-tropsch process is a crucial step in the production of petroleum. It is often used to refine lower-value crude oil fractions like alkanes and residues into more lucrative end products like gasoline, olefin, and others. The fluid catalytic cracking unit's "hearts" are the reactor and regenerator. Cracked products are created when hydrocarbon feedstock comes into touch with hot and small catalysts in the reactor. While this is happening, the FCC catalyst becomes coked and inactive. When the wacked catalysts have been removed from the broken products by cyclones, they are sent to a regenerator, where they are rejuvenated by smoldering coke in oxygen at 650 °C to 760 °C. The catalysts that have been recycled are then added to the reactor. For the FCC procedure to take place, the acidity sites are necessary for supplying the active sites, which are responsible for the various reactions that take place, such as cracking, hydrocarbons transfer,

interesterification, and calcining. X zeolite was an early FCC catalyst utilised in cracking of gas oils. The removal of lead from gasoline accelerates the importance of using high-octane fuels. A super-duper Y zeolite catalyst was developed as a result of the discovery of a dealuminated method to remove metal subatomic particles from the zeolite structure.

As USY zeolite is more resistant to heat and water, it is used to make almost all FCC catalysts used in today's petroleum refineries. In order to meet the rising demand for light olefins, ZSM-5 is being used as an addition in FCC catalyst in order to boost the yield of octane and olefins rating of gasoline. ZSM-5 zeolite is used for cracking high molecular fractions to light olefins. Light olefin synthesis is favored by the low hydrogen transfer activity of ZSM-5 zeolite, which in turn reduces the generation of n-paraffins. When it comes to production yield and gas and gasoline compositions, ZSM-5 zeolite's surface acidity and particle density play a major role. Cracking and isomerization activities of ZSM-5 increased with increasing total acidity.

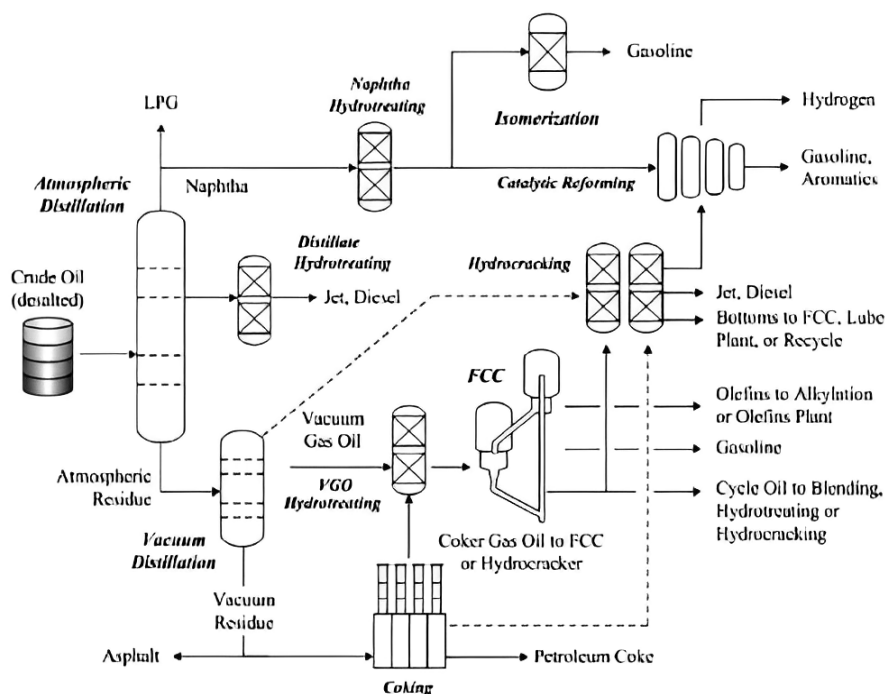


Fig 3. Oil Refinery Design with A Focus on Maximum Conversion

### Hydrocracking Catalysts

Hydrocracking refers to the process by which sulfur and nitrogen are removed from a hydrocarbon mixture and the heavier hydrocarbon fraction is cracked into smaller, more manageable molecules. In addition, hydrogen causes olefins and aromatics to become saturated. The hydrocracking method involves two distinct chemical reactions: pre-treatment and cracking. Sulfur, nitrogen, organometallic compounds, halides, and oxygen are all eliminated during the pre-treating procedure. Throughout the course of the cracking reaction, many different processes will occur, including cracking, isomerization, saturation of aromatics, creation of polynuclear aromatics, and coke formation. When a carbon-to-carbon covalent bond is ended and hydrogen is integrated, the carbon-to-carbon double bond is formed, which may then be used as fuel. Temperature and hydrogen play crucial roles in hydrocracking since all hydrocracking procedures necessitate hydrogen contacts with reactors at a pressure more than 7.0 MPa and temperatures up to 470 °C.

Both an acidity site and hydrogenation dehydrogenation sites are needed in conventional hydro-cracking catalysts. Both the former (providing the structure's stability) and the latter (forming the structure's shape) are made of metal. Cracking reactions occur at the acidity sites, whereas the transfers of hydrocarbon are set in motion at the hydrogenation dehydrogenation site. Excessive acidic site activity will likely cause the catalyst to coke and become inactive. A well-tuned equilibrium between two activity sites is necessary for the creation of an effective hydrocracking catalyst. Hydrocracking catalysts have come a long way from their early days, when acid function was fulfilled by using acidic clays and amorphous silica alumina. Union Carbide Company employees in the 1940s and 1950s synthesized the first artificial equivalent of the natural mineral by introducing synthetic X and Y zeolites.

To increase the selectivity of zeolite-based hydrocracking catalysts [9] and hence generate superior middle distillates, a number of techniques for modifying zeolites have been developed. According to research conducted by Union Carbide, a reduction in zeolite's acidity, as determined by the reductions in UCS (Unit Cell Size), could reduce catalytic activity and enhance selectivity to jets and fuel products [10]. A higher degree of specificity toward denser products can be attributed to a reduced amount of acid amine groups and an increase in the range between them as a result of vigorous

hydrothermaltreatment. The mesoporous zeolite Y created using steam dealumination improves accessibility while maintaining high activity and stability.

In addition, the Y zeolite's Si/Al ratio may be controlled by the de-alumination process, making it a very flexible zeolite that can be used to modify the selectivity of a catalyst incorporating zeolite. Crack ingactivity drops and diesel becomes more selective as its Al concentration drops. The zeolite structure-function criteria have been better understood thanks to recent developments in zeolite research. By fine-tuning the catalyst composition and production processes, highly active hydrocracking catalysts have been developed. Because of this, their acidity and framework composition may be fine-tuned to better suit their intended purpose. In hydrocracking, for example, Y zeolites have found several uses, from maximizing naphtha output to churning out high-quality distillates, illuminating the extent of these developments. The science of making hydro-cracking catalysts has progressed thanks to increased insight into optimizing the use of amorphous and zeolitic acidic constituents and their combination with the hydroformylation elements.

#### *Hydrotreating Catalysts*

Hydrotreating catalysts in a petroleum refinery are used for hydrogenation and pollutant removal. Catalysts for traditional hydrotreating typically consist of group VI and VIII metals supported by alumina. Before this catalyst can be employed in the hydrotreating process, it must first undergo sulfidation. Sulfided CoMo and NiMo are common catalysts used in hydrotreatment. Hydrogenation ( $H_2$ ) and Hydro-denitrogenation (HDN) reactions benefit most from a NiMo catalyst, whereas HDS reactions favor those catalyzed by a CoMo catalyst. For hydrocracking, hydrogenation of aromatics at low  $H_2S$  conversion, and concentrations of alkylated dibenzo thiophenes, NiW substances show great promise. As noble metallic substances are among the most energetic in hydrogenation reactions, they have garnered a lot of interest. These catalysts, however, are easily poisoned by sulfur compounds. It's interesting to note that sulfided CoW catalysts don't appear to work well in industrial hydrotreating procedures.

Several high-quality evaluations condense the vast majority of the written work on hydrotreating catalysts. The activity of hydrotreating catalysts is determined by two factors: regulates the active phase's distribution and form by interactions with the trivalent sulfide and the support.  $Al_2O_3$  is the most typical form of support due to its stringent form of affinity with Mo, resulting in a highly dispersed and stable active state.  $SiO_2$  and  $TiO_2$  are two other supports that have been investigated and examined by a wide range of experts. In general, the weak Mo-support contact in  $SiO_2$  leads to poor  $MoS_2$  dispersion, and thus, limited HDS activity.  $TiO_2$  has been proven to be a suitable substrate for HDS catalysts due to its improved interaction with Mo over  $Al_2O_3$ . The noteworthy difference in activity between  $Mo/TiO_2$  and  $Mo/Al_2O_3$  has been ascribed to variations in shape, dispersion, or sulfidability. It has been hypothesized that heat-treated Ti-species, which have been sulfided and/or reduced, play the role of promoter and therefore boost the activity.

$TiO_2$ -promoted catalysts have a far less promotion effect than  $Al_2O_3$ -promoted catalysts, which is an intriguing fact in and of itself. Two distinct CoMoS structures on  $CoMo/Al_2O_3$  have been postulated, leading to the conclusion that CoMoS is the active stage of HDS catalyst. The first stage is postulated to be constituted primarily of  $MoS_2$  cellular membranes linking with the support via Mo-O-Al interactions, and to exhibit inadequate sulfidation. The other stage is assumed to be completely sulfided and consists of layered  $MoS_2$  particles, interacting tenuously with the assistance via interactions of van der Waals. It seems that the kind of reactant determines the extent to which these two forms of phase differ in their activity.

#### IV. CATALYSTS FOR BIO-OIL UPGRADING AND FOR PYROLYSIS

To create biofuels that are up to par with transportation fuel standards, the biomass conversion process must include a wide variety of heterogeneous catalysts, much like petroleum refining. However, no adequate catalysts have been developed so far to convert the biomass in an efficient and cost-effective manner. Many attempts have been made in this field, with promising outcomes. We anticipate that commercial heterogeneous catalysts used in petroleum refinery will speed up and broaden the development of biorefinery catalyst. Hydrodeoxygenation and catalytic cracking are two of the most popular techniques used to create biofuels. A number of researchers have tried out various zeolites and hydrogenation catalysts.

#### *Catalytic Cracking Catalysts*

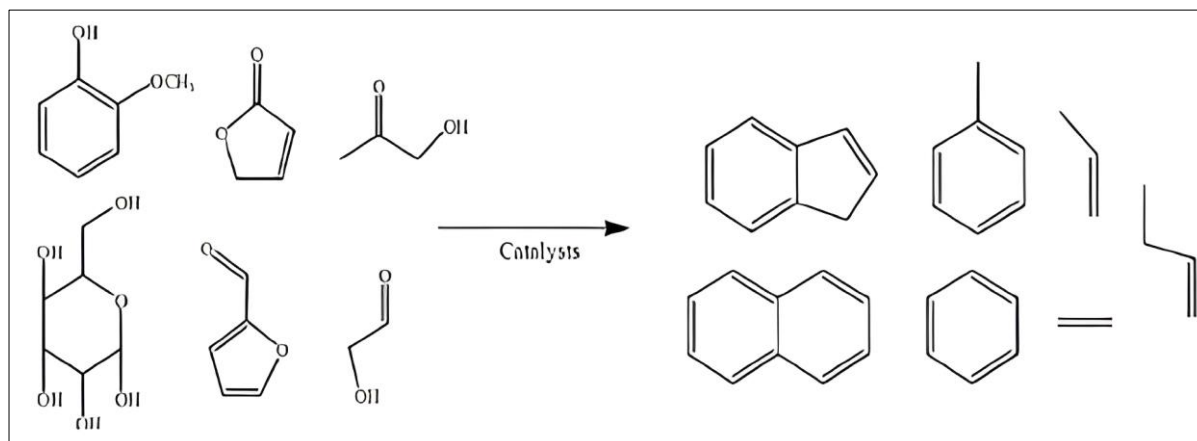
Upgrading bio-oils with the right catalysts may lower the oxygen content and improve the thermal stability. Due to the absence of  $H_2$  and the similarity of the reaction conditions to those of pyrolysis, catalytic cracking is the favored method. Hydrocarbons, water, aqueous organics, gases, and coke are the major products, all of which have considerable processing and economic benefits. The primary drawbacks of this process are the low hydrocarbon yields and the large coke yields; however, they may be enhanced by using a strong performance catalyst under the right circumstances. **Fig 4** depicts the catalytic cracking process's reaction route.

Zeolites, also employed in the refining of petroleum, are the primary catalysts in the catalytic cracking process. Zeolites such as SAPO, MCM-41, ZSM-5, Y, silica-alumina, and SBA-15 were employed in the process for bio-oils deoxygenation. In comparison to  $SiO_2-Al_2O_3$ , silicalites, and ZSM-5 with silica-alumina, the quantity of liquid organic compounds produced by ZSM-5 is the largest, making it a promising catalyst. Also, most aromatics, the key commercial chemical product, are produced from ZSM-5. The procedure yields the gases carbon dioxide ( $CO_2$ ), carbon monoxide (CO), light alkanes (LAs), and light olefins (LOx). As with petroleum FCC catalyst, the bio-oil catalytic cracking process



produced a lot of coke (30-50 wt pct). Coked catalyst is regularly burnt off in the petroleum FCC process to replenish catalyst and supply process heat.

As a result of this, the creation of coke in the cracking process of catalytic bio-oil is really beneficial. The process, however, has not yet been shown to have a satisfactory thermal balance. Several model compounds have been studied to learn more about the bio-oil reaction pathway over ZSM-5 catalyst. At high temperatures over ZSM-5, alcohols are first transformed to olefins, and then paraffin and aromatics are formed. Due to its limited reactivity and heat breakdown into coking issues, phenol and 2-methoxyphenol are identified in only trace levels. Hydrogenation of acetic acid yields acetone, which has properties distinct from those of alcohols. To get to the gasoline-range paraffin, aromatics, and alkenes, acetone must be transformed to isobutene first. Acetic acid and acetone are more efficient feedstocks for coke production than alcohol. Hence, the development of efficient catalytic cracking catalysts is hampered by the fact that different chemicals in bio-oils exhibit different reaction pathways.



**Fig 4.** Catalytic Cracking Reaction Mechanism

By combining rapid pyrolysis with a catalyst, catalytic pyrolysis process offers a promising method for transforming biomass into valuable fuels and chemicals. Catalyst addition to pyrolysis has the potential to moderate reaction conditions and boost biomass conversion. Hydrocarbon content and pyrolysis bio-oil quality both increase despite a drop in bio-oil production. The production of bio-oils may be improved by increasing the heating rate and decreasing the residence duration. The catalytic fastpyrolysis method typically employs ZSM-5 as the catalyst. The most common components in both gases and liquids are olefins and aromatics.

Using catalytic fast pyrolysis with ZSM-5 accelerators, Huber and colleagues have made significant progress toward commercial manufacture of p-xylene from biomass. The enhancement of p-xylene selectivity is attributed to a simple zeolite surface modification process, and good yields are the byproduct of using optimal reaction conditions. Catalytic pyrolysis was shown to be a shape-sensitive technique, with active site types and pores design enhancements being the key determinants in obtaining high p-xylene specificity. ZSM-5 catalysts, thanks to their potent acidity, catalytic capacity, and structure selectivity, provide outstanding catalytic efficiency in the conversion of pyrolysis bio-oils into chemicals and biofuels.

ZSM-5 catalyst, however, has a few drawbacks, including poor yield, easycoking, and a short life. More and more interest has been shown in the possibility of using zeolite catalysts with a bigger pore size in catalytic rapid pyrolysis, whereby the catalyst deactivation rate may be lowered and a greater yield of organic oil can be obtained. The creation of coke and the deactivation of a catalyst are thought to be mitigated by using zeolites with bigger pore sizes, which would allow larger molecular products to flow through and convert more readily.

#### Hydrotreating Catalysts

Hydrotreating catalysts, similar to those used in petroleum refining, may be employed for oxygen removal and boost bio-oil quality produced during pyrolysis see **Fig 5** for the chemical pathway of the hydrotreating process. It may be used in conjunction with existing transportation fuels and has increased thermal stability. The inhydrotreating process involves a plethora of chemical reactions, including as hydrogenolysis, hydrogenation, hydrodeoxygenation, decarbonylation, cracking, and decarboxylation. Concurrent with the polymerization stage, coke is produced. Thus, it is important that these catalysts have more than one active site. Hydrotreating bio-oils require the development of high-performance catalysts. In this procedure, several heterogeneous catalysts were tested, including those employed in common petroleum hydrotreatment and noble-metal hydrogenation. Hydrotreating is broken down into two stages so that it may be performed at more controllable temperatures and pressures using sulfated NiMo and CoMo catalysts. Low-temperature hydrogenation of pyrolysis bio-oil is the initial step.

Hydrogenation stabilizes the thermally unstable bio-oil molecules, reducing thermal breakdown and consequent coke generation. The second step is a second hydrogenation, this time at a somewhat higher temperature. Enhanced bio-oils



with a high-octane rating and low oxygen content are feasible. At high temperatures, water creates instability in the support, which leads to deactivation of the catalyst. The increased oxygen concentration in pyrolysis bio-oils makes it more critical to account for water's influence on hydro-treating enzymes in the bio-oil procedure compared to the oil refinery procedure. The integration of noble metallic hydrogenation precursors with mesoporous materials catalyst has contributed greatly to the development of the two-step hydroprocessing process. Evidence suggests that using a noble solid catalyst during the first hydroformylation step can improve bio-oil solidity while reducing coking.

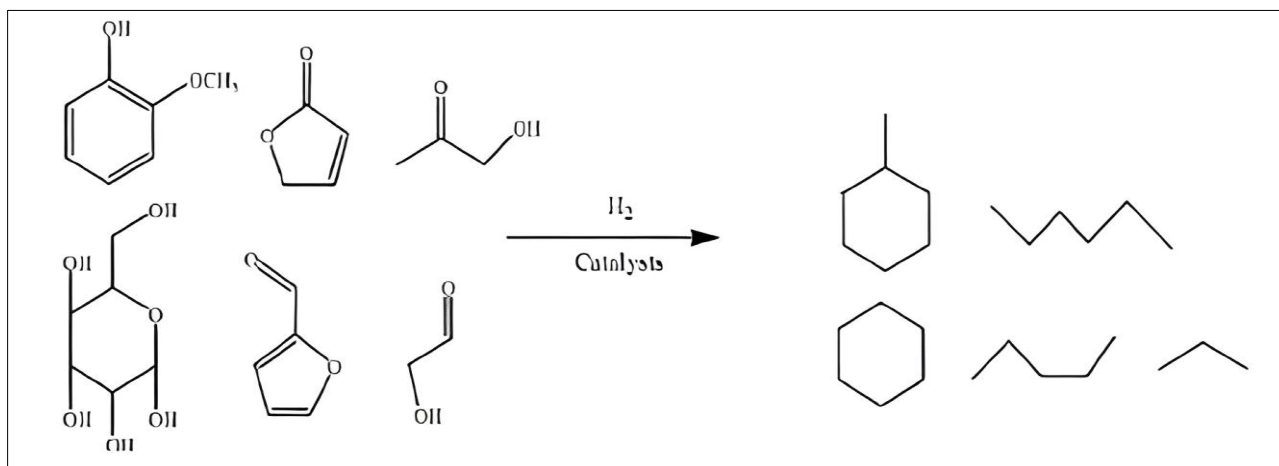
Due to the high activity of noble metacatalysts, both the temperature and pressure of the reaction may be maintained low. Pyrolysis yields bio-inherent oil with a higher hydrogen concentration in the first stage. The synthesized bio-oil is next converted into light olefins and aromatic compounds by employing a catalyst called ZSM-5. The liquids yields could be much as three-times more compared to that of traditional pyrolysis bio-oil pretreated with the identical ZSM-5 catalyst. The initial hydrogenation step in the zeolite's method converts the carbonyl and polyunsaturated carbon bond monomers in bio-oil into thermally stable compounds, lowering the probability of coke production. Hydrogenation has also been suggested as a means of increasing the liquid yield from bio-oil by increasing the H-to-C ratio that could increasingly saturate the double carbon-carbon bond and reduce the production of coke over zeolites. As a result of its strong C-O hydrogenation activity in addition to its low C-C bond breaking activity, Ru serves as the most selective and versatile substrates for the hydrogenation of acetic anhydride, while Pt serves as the most catalytic but has poor specificity.

#### Hydrodeoxygenation Catalysts

Saturated C-C bonds result from the hydrogenation process that occurs during the hydrotreatment of pyrolysis bio-oils that removes oxygen through the combination of hydrogen. As hydrogen is not needed to completely saturate phenol rings in HDO, it is the more efficient procedure. **Fig 6** depicts the chemical pathway of the HDO process. The HDN, HDM, and HDS processes are utilized to eliminate nitrogen, metals, and sulfur, from petroleum fractions during the refining process.

Saturation with olefins is also used to improve petroleum fuels quality. The HDO technique for bio-oils accomplishes its primary goals of improving the oil's stability and lowering its viscosity by removing oxygen and increasing its energy content. For use in biofuels, the oxygen concentration must be reduced to below 5wt%. Since aromatic unsaturation occurs in the presence of hydrogen during the HDO process, the upgraded bio-octane oil's number is not reduced, and the process does not need more hydrogen. Sulfided CoMo and NiMo hydro-treating materials are utilized in pyrolysis bio-oil HDO because the mechanism of HDO in bio-oil upgrading is almost identical to HDS in petroleum refining. In comparison to supported Nicatalysts and copper-chromite catalysts, these catalysts perform well for upgrading bio-oils. For specifics on the testing of commercial hydrotreating catalysts, one need only consult Elliott's study. For sulfided NiMo, and CoMo catalysts, higher catalytic activities must be continuously replenished by the addition of sulphur precursor or H<sub>2</sub>S. Nevertheless, there are a number of issues that arise when sulfur is used, most notably a loss of selectivity and the unintended sulfidation of certain oxygenated molecules.

In low concentrations, hydrogen sulfide has a beneficial effect on hydrogenation activity, but at greater quantities, it has an obviously inhibiting effect. As a result, strict regulation of sulfur levels is required. Hydrogen sulfide decreases the selectivity of the reaction toward the synthesis of catechol, as shown by the findings of the guaiacol dehydroxylation and hydrogenation of carbonyl. The reaction routes of major molecules are also determined using a large number of model bio-oil compounds. To guarantee that the framework bio-oil feedstocks have similar functional groupings as the pyrolysis oils, guaiacol combinations, including ethyldecanoate, and methylacetophenone are often utilized.



**Fig 5.** The Hydrotreating Process and Its Reaction Pathway

One may selectively and quickly convert a ketone group to a methylene grouping at reduced temperatures, but guaiacol and carboxylic groups require higher temperatures for hydrogenation. Differences exist between the chemical pathways of guaiacol and carboxylic groups. In contrast to the carboxylic group, this undergoes simultaneous hydrogenation and

decarboxylation, the guaiacol grouping only convert to catechol before converting to phenol. The catalyst is deactivated and guaiacol readily cokes on acidity sites. Enhancing the catalyst support acidity amounts to the synthesis of coke from guaiacol at a faster rate and also accelerates the hydrogenation and decarboxylation of ethyl decanoate.

HDO of guaiacol was used to evaluate the catalytic efficiency of NiMo and CoMo catalysts where the batch model. NiMo guaiacol conversion and the hydro-deoxygenation product quantity are both more than those of the CoMo catalyst at a reduced temperature, as shown by the findings. Therefore, NiMo catalyst exhibits high activities of the conversion of guaiacol than CoMo catalyst. Although while sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts are advantageous for the process of HDO, their instabilities on the substrate of alumina in the presence of high degrees of water is considered as a major drawback, and significant coking is seen due to the acidity of the alumina support. Several other types of catalysts are tried out, some of which include non-alumina substrates including molecular sieves, titanium and carbon. The activated low acidity of carbon decreases undesirable coke production, making it an ideal catalytic support for the HDO process. Compared to alumina-supported catalysts, the catalytic activity of carbon-based NiMo and CoMo catalysts for the HDO of carboxyl, methoxyl, and carbonyl groups is lower. Carbon supported catalysts may be altered by rearranging the sequence of heat or sulfidation treatment and metal impregnation. HDO activity for carboxy, and methoxy groups is enhanced, whereas HDO activity for carbonyl groups is suppressed, depending on the sequence in which Co and Mo are impregnated.

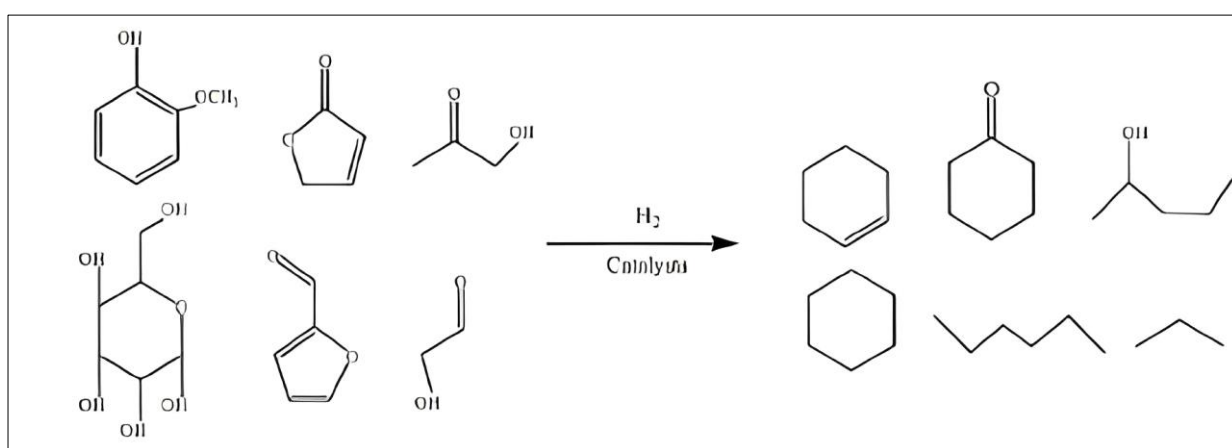


Fig 6. The HDO Reaction Pathway

In addition, the hydrogenation selectivity also increases. Metals emerge on the surface of catalysts as a result of a shift in impregnation order. Cobalt is shown to be deposited on the support surface, whereas molybdenum enters the pore structure to a greater depth. The active surface sites of catalysts are created when cobalt is first deposited on the support surface, establishing metallic sites for respective production of molybdenum. However, the wide pore structure of activated carbon results in a more diffused and accessible active phase, which in turn increases catalytic activity. Also being looked at as a support for CoMo catalysts in HDO of bio-oils is MCM-41 with varying amounts of Si/Al. The data demonstrates that as compared to CoMo/Al<sub>2</sub>O<sub>3</sub> and CoMo supported on structural mesoporous alumina, CoMo/MCM-41 possesses less catalytic activity. HDO of bio-oil additionally makes use of HMS, DMS-1, SBA-15, and SBA-16 as support. HDO catalytic supports for bio-oils were investigated, and it was noticed that DMS, SBA-15 and SBA-16 were significantly effective.

To produce less and less paraffin, the selectivity drops down as follows: For the record, SBA-15 is superior than SBA-16 [DMS] and HMS. It has been shown that metal catalysts are more active compared to sulfide CoMo catalysts within the hydrogenated reactions, even at less-reactive conditions. This leads to reduced coke production. To counteract the level of alumina instability at high levels of water, noble metal catalysts may be easily formulated on non-alumina substrates. Although the sulfur concentration of bio-oils is often lower than that of petroleum fractions, catalysts are considered as a preferential option in the process of HDO. The employment of metal catalyst for this process in bio-oils has been the subject of much research. For the hydrogenation of acetic acid and furfural, Ru/C is seen as a potential catalyst. Pd, Pt, and Rh catalysts supported on ZrO<sub>2</sub> are also studied for their potential use in the process of guaiacol hydrotreating, with the Rh/ZrO<sub>2</sub> catalyst demonstrating the highest activity. Pt/Al<sub>2</sub>O<sub>3</sub> is shown to have excellent activity in the bio-oil upgrading process, and this is only one of several noble metal catalysts that have been explored for use in this application. Nevertheless, because a variety of bio-oil models were utilized as feedstocks, it is difficult to draw firm conclusions about the impact of the support level on the performance of catalytic noble catalysts for HDO of bio-oils.

Due to the heat instability of bio-oil chemicals, the HDO reaction speeds up the breakdown and polymerization processes. As a result of this process, free radicals are produced, which soon clump together on the surface of catalysts, rendering them ineffective. Bio-oil alcohols may be thermally dehydrated to olefins, and this may be the root cause of polymerization problems under hydrotreatment conditions. The improved oil is more difficult to separate from water at milder

intensities. Even at a significantly lower temperature and hydrogen ecosystem with catalysts, polymerization is a prevalent phenomenology in the bio-oil HDO process. Yet, at relatively moderate temperatures, the tiny molecular bio-oils may be readily hydrogenated into molecules with reduced oxygen concentration. The two-step hydrogenation method is suggested to generate biofuels with reduced oxygen content due to these two factors. In the first stage, bio-oil obtained by pyrolysis is hydrotreated at low temperatures with the help of Ru catalysts. Hydrogenation reduces polymerization in bio-oils with small molecular weights. After the bio-oils have been hydrogenated, they are hydrotreated at a low temperature using a NiW catalyst. This procedure is advantageous because of the high liquid yield and low oxygen concentration. As compared to results obtained without the low temperature stage, somewhat less char/coke is produced. It has been shown that the HDO process requires a low-temperature stabilization step at relatively higher temperatures.

## V. APPLICATION OF PETROCHEMICAL TECHNOLOGY IN BIOMASS CONVERSION

Several attempts have been made to create sustainable biofuels by biomass conversion using already established refinery catalysts. When biofuels are produced in tandem with an already operational petroleum refinery, both the development time and economic efficiency of the project are reduced. If the pyrolysis bio-oil co-process can be successfully integrated with conventional petroleum refineries, the development of biofuels will speed up significantly, allowing them to more readily fulfill the rising demand for petroleum. Several well-known oil firms are already working to facilitate the commercialization of biofuels by adapting current petroleum refinery technology. Using biomass-based hydrogen or syngas, the hydrotreating hydro-cracking and FCC process are at least the petroleum refinery technologies that may be used to transform biomass into fuels and chemicals. F-T synthesizing, Methanol synthesizing, and other bio-products made from syngas obtained from biomass may replace syngas sourced from coal or natural gas. Use of syngas or hydrogen produced from biomass is beyond the scope of this article.

As was noted up above, FCC is a common method for transforming petroleum's heavy components into lighter hydrocarbons. Hydrotreating is an efficient technique for removing sulfur, nitrogen, metals, and oxygen from a variety of feedstocks via the process of hydrogenation. These two methods are now being implemented as a practical procedure for deoxygenating bio-oil produced by pyrolysis. The conventional catalysts used in each of these methods are also undergoing evaluation. Many areas of the FCC reactor were analyzed to determine the best way to co-feed pyrolysis bio-oil and VGO feedstock. Bio-oil feed-stocks and VGO feed stocks are shown to share hydrogen. Co-feeding glycerol and VGO feedstock was shown to have no appreciable effect on product selectivity. Petroleum and Glycerol hydro-carbon interact, leading to higher selectivity than would be expected from a simple additive effect. These findings point to the viability of co-feeding bio-oils and petroleum fractions in a commercial FCC reactor. Nevertheless, several findings show that bio-oils co-feeding with petroleum fraction would promptly block FCC reactors and create coke. Thus, additional work has to be done to elucidate the impact of bio-oil co-feeding with the fractions of petroleum on the process of FCC, notably on product distribution and FCC catalysts.

By fusing hydrotreating, a technique often utilized in the refining of petroleum, with upgrading, we get the HDO process. Hydrodeoxygenation of bio-oil has historically made use of a wide variety of conventional hydrotreating catalysts, e.g., NiMo, and CoMo catalysts and the noble metallic catalysts. The HDO bio-oil process and the petroleum refinery in the HDS process are distinct, but the differences between the two have been mapped out. When working with bio-feedstocks, which often have a low sulfur concentration, it is required to add sulfur-donor chemicals to maintain the catalyst's activity. Specifically, catalyst activity inhibition is seen throughout the bio-oil production HDO process. Hence, not only do standard hydroprocessing and conventional hydro-treating catalysts need to be modified, but also the processes themselves. Alterations to HDO could be visualized as an advancement of petroleum pre-processing but still within the field of petroleum processing in case the two are combined in a more workable manner. As a result of the significant dissimilarity between the constituents of bio-oil and petroleum, modifications to the traditional hydrotreating catalyst are possible.

## VI. CONCLUSION

Catalysts of several types have been developed with advances in preparation technology and are now routinely utilized in the procedures of petroleum refining to provide high-quality bio-fuels for transportation. In order to get more light olefins out of the larger molecules in crude oil, zeolites like MCM, ZSM-5, and USY family are utilized. In the meanwhile, the HDN, HDM, HDS and HDO processes utilize hydro-treatment catalysts integrating NiW, noble metal catalysts, and CoMo to enhance petroleum fuel quality based on ecological regulations. Hydrotreating catalyst, catalytic cracking catalyst, and HDO catalyst are just a few examples of the many types of catalysts being explored for the generation of chemicals and biofuels from biomass. In this article, ZSM-5 considered the most substantial catalyst for the process of catalytic cracking because it has the right qualities to turn pyrolysis bio-oils into usable biofuels. Effectual NiMo catalysts and CoMo employed in the refining of petroleum are also applied in the process of high-density olefins (HDO), which enhances the bio-oils quality. Moreover, HDO of bio-oils have promising applications for noble metal catalysts. Since that sulfur and other impurities are less abundant in bio-oil feedstock compared to petroleum feedstock, this grouping of catalyst could amount to significant advances. By combining the benefits of two distinct catalysts, certain successes have also been realized in a two-stage procedure. To reduce carbon depositions on HDO catalysts and boost hydrocarbon output,

hydrogenation catalysts are increasingly being integrated with HDO catalysts. A novel approach of deoxygenating bio-oil to produce high-yield commercial chemicals may be achieved by combining hydroprocessing with catalytic cracking.

#### Data Availability

No data was used to support this study.

#### Conflicts of Interests

The author(s) declare(s) that they have no conflicts of interest.

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#### Ethics Approval and Consent to Participate

The research has consent for Ethical Approval and Consent to participate.

#### Competing Interests

There are no competing interests.

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