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REVIEW ARTICLE

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Hydrocracking of non-edible vegetable oil and waste cooking oils for the production of light hydrocarbon fuels: A review

Sharron Ratshoshi | **Hembe Elie Mukaya** | **Diakanua Nkazi**

School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

Correspondence
Hembe Elie Mukaya, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2050, South Africa.
Email: elie.mukaya@gmail.com

Abstract

The high demand for biofuels by surfacing economies with environmental issues has resulted in a more in-depth search for new biofuel feedstocks. Non-edible oils have become the centre of investigation as biofuel feedstocks since they do not compete with food sources. This review evaluates hydrocracking as a biofuel production method and further elucidates different feedstocks, the effects of hydrocracking catalysts, and operating parameters to obtain optimum yields and selectivity of desired products. The bifunctional catalyst mechanism is also explained. The hydrocracking technique is found to be more advantageous than other biofuel production techniques such as transesterification and pyrolysis due to its ability to produce valuable products of better quality and with higher yields. Coke formation is one of the challenges faced by hydrocracking despite that it can be reduced by high hydrogen pressure; this will increase the cost of the entire process.

KEYWORDS

biodiesel, biofuel, bio-gasoline, bio-jet, catalyst, hydrocracking

1 | INTRODUCTION

Feedstock selectivity in the bio-refinery is one of the most dominant features that should be given attention to, including determining the economies, availability, and production yield of the biofuel. Vegetable oils are considered to be the most commonly used feedstocks, and due to their high energy density and availability as a renewable source, they are converted into liquid fuels.[1] It is widely known that different amounts of biofuels are produced from raw edible vegetable oil feedstocks such as sunflower and soybean, and from non-edible vegetable oils which include used vegetable oils and animal fats.[2] Edible vegetable oils are currently the main resource for biofuel production, although lately, a switch to non-edible vegetable oils is being considered. Non-edible vegetable oils are the leading option considering that they do not clash with the food security policy.[3] These vegetable oils cannot be directly used as liquid fuels because they are highly viscous and quite unstable, and they form carbon deposits in automobile engine parts. Thus, they will need to be upgraded into useful biofuels through different modern technologies.[4] Successful industrial biofuel production would be achieved whenever the technology used is properly selected and the selected feedstock is available in adequate quantities to guarantee a steady production process[5] and biofuel quality.[6] The production processes

Abbreviations: APR, aqueous phase reforming; DDS, direct desulphurization; FAME, fatty acid methyl ester; FFA, free fatty acids; FOG, fats, oils, or grease; HDO, hydrodeoxygenation; HTL, hydrothermal liquefaction; HVGO, heavy vacuum gas; LCO, light cycle oil; LHSV, liquid hourly space velocity; RA, ricinoleic acid; RON, research octane number; SRGO, straight-run gas oil; TG, triglycerides; WCO, waste cooking oil; WHSV, weight hourly space velocity.

that may be employed for biofuel production include transesterification/esterification, pyrolysis (catalytic cracking), gasification, microemulsion, and hydrocracking.[7–9] This review evaluates hydrocracking as the biofuel production method, and further elucidates the different feedstocks, effect of catalysts, and operating parameters to obtain optimum yield and selectivity of desired products. The hydrocracking technique is found to be more advantageous over other biofuel production techniques such as transesterification and pyrolysis due to its ability to produce valuable products of better quality and higher yields.[2]

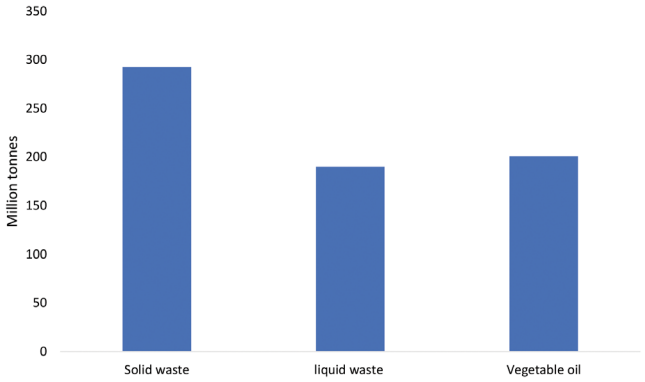

FIGURE 1 Feedstocks annual production yield in 2018.

2 | FEEDSTOCK MATERIAL

The biomass-derived feedstock is classified into three categories: 1) cellulosic biomass, 2) starch- and sugar-derived biomass, and 3) triglyceride-based biomass, also known as vegetable oils. These biomass-derived feedstocks are the current trend in biofuel technology.[10]

Cellulosic biomass has a crystalline recalcitrate structure that makes it hard for the biomass to be converted into fuel when compared to the starch-based biomass. Cellulosic biomass can be produced quickly and at lower costs than food crops, which is the economic advantage of this biomass over other agricultural feedstocks.[11] Sugar- and starch-based feedstocks are economically favourable compared to lignocelluloses and are dominating the industrial level. These starch- and sugar-based feedstocks include grains such as corn and sugarcane, respectively. Starch can easily be converted into fermentable sugars and these sugars can be converted into ethanol for large-scale affordable production. The disadvantage of starch- and sugar-based feedstocks is that they interfere with the human food chain.

Triglycerides (TG) occur mostly in animal fats and vegetable oils, providing a vast source of raw material for biofuel conversion. Animal fats mainly constitute chicken oil, fish oil, lard, and so forth. Animal fats are characterized by a high saturated fatty acid content and cannot be directly used in engines as fuels. Vegetable oils have been studied for many years as a significant source of triglycerides. Furthermore, important sources of triglycerides are non-edible and waste oils as they are good fuel production candidates. Triglycerides are the easiest feedstocks to be converted into liquid transportation fuels due to their high energy density.[12]

The selection of feedstock that is cheaper, easily available, and economically feasible is important for biofuel production as this will reduce production costs.[12] Figure 1 depicts the feedstock production yield globally for 2018. In 2018, solid waste was the most suitable feedstock to be utilized for biofuel production because it was the most abundantly produced feedstock compared to the other feedstocks. Biofuels can be liquid, solid, or gaseous and are produced by converting renewable resources. The method of production depends on the desired product and used feedstock.[2]

2.1 | Solid waste

Solid waste can be regarded as garbage obtained from industrial, mining, domestic (unsorted residual/municipal waste), and agricultural activities.[13] It is considered to be a potential feedstock for liquid transportation biofuels and chemicals production since it is readily available or free and can be a sustainable solution for energy needs while environmental landfill impacts are minimized.[14] Hydrocracking has been utilized in municipal solid waste conversion. Solid waste is a heterogeneous matter that contains materials of all sorts of different shapes and sizes as well as compositions, of which most come from food leftovers and plastic.[15,16] It is expected that its size is reduced to 1 mm and sorted for it to be a suitable feedstock. It was suggested that solid municipal waste be converted into useful products like crude oil via pyrolysis, due to environmental concerns related to landfills or combustion of such waste.[17] Since the produced crude oil cannot be refined directly to petroleum fuels which can be used in combustion engines, further processing or upgrading will be required and hydrocracking is the supported method to refine the oil into lighter biofuels.[18]

2.2 | Liquid waste

According to Morais and co-workers,[19] fats, oils, or grease (FOG), gases, and sludges are considered to be liquid waste. Used oil from cooking oil has an outstanding

perspective as sustainable residual biomass that does not take part in the food chain, while its recycling can prevent environmental problems caused by their disposal.[20] Waste cooking oil (WCO) is the most economical choice of feedstock to produce biodiesel,[21] and its utilization lowers biodiesel production costs by 60%–90%.[21] The oil can be collected from restaurants, cafeterias, and other large commercial kitchens, and it is 2–3 times cheaper compared to vegetable oils.[12,22,23] WCO contains a high level of free fatty acids (FFA) which reduces its application for biodiesel generation.[24] The liquid waste oils are converted into transportation fuels by the use of different catalyst technologies,[25] and the WCO can undergo hydrocracking after the remaining impurities from cooking are removed through filtration to produce biogasoline,[26] and bio-jet since the FFA content does not interfere with the process.[27] FOG, with its high lipid content, can be regarded as a blend component feedstock used to boost other feedstock's conversion efficiency.[28] At the household level, waste fat is usually discarded down the drain, resulting in a sludge consisting of about 30% (by weight) lipid fraction. The sludge can also be used as a cheap and readily available feedstock for the production of biodiesel.[29]

2.3 | Vegetable oil

Vegetable oils are produced mainly from parts of the plants containing oil, which can be kernel or seeds from oil palms, jatropha, and sunflower as well as fruits or seeds from olives.[25] Vegetable oils are the most familiar ideal feedstock candidate to be transformed into liquid fuel as a result of their high energy density, liquid nature, and accessibility as a sustainable feedstock.[1] The vegetable oil's liquid nature makes it easily processable and transportable. Hydrocracking of vegetable oils produces paraffin in the C_{12} and C_{18} ranges. Various oil types have been studied in the context of hydrocracking based on the countries in which the oil is mainly produced (Table 1).

Sunflower and rapeseed oils have been widely studied as edible biofuel potential sources, while palm oil is stated to be easily processable due to its low content of linolenic acid. Furthermore, palm oil is preferred for biofuel production due to its abundant oil content. The selection of these vegetable oils relies mostly on their accessibility, costs, and weather conditions in that country.[1] This might be the reason why most non-edible oils have not been intensively studied for hydrocracking technology. Utilization of non-edible plant oils like castor oil, microalgae, and jatropha oil as feedstocks can mostly be considered the best option since they do not participate as a food source.[30,34,35] The challenge with their use is that they might require additional costs for harvesting or extraction of oil when compared to edible oils. Also, it was observed that non-edible oil has a higher product yield than edible oil, so the production costs can be reduced.[3] Biofuels produced from non-edible oils give an environmental benefit since the feed stocks are renewable biomass resources.[30]

2.3.1 | Castor oil

Castor is regarded to be among the most favourable non-edible oil crops and is mostly cultivated for its seed to produce castor oil, and it makes up only 0.15% of the vegetable oil produced.[36] Castor oil is extracted from castor beans using different methods.[37] The produced oil can be characterized as a yellow-brown, non-volatile, and non-drying oil that possesses a bland odour.[38] Castor oil is nonedible due to its toxicity, has a high oil yield of about 44%–55%, and requires less water. Castor oils fatty acid methyl ester (FAME) is highly viscous, which makes it have technological challenges due to fatty acid composition. The oil contains up to 90% ricinoleic acid (RA) which is the main fatty acid.[39] The high content of RA makes castor oil a versatile or valuable feedstock as the acid possesses 3 functional groups. The presence of hydroxyl group in the oil makes the oil highly viscous, resulting in it being impossible to be directly used as engine fuel. This drawback can be resolved by deoxygenation and hydrogenation of the castor oil FAME under partial hydrogen pressure.[40]

TABLE 1 Different vegetable oils used in hydrocracking.

Vegetable oils	Edibility	Country	References
Canola	Yes	Canada	Al-Sabawi and Chen[30]
Coconut	Yes	Philippines	Al-Sabawi and Chen[30]
Cottonseed	No	Greece/Turkey	Molefe et al.[2]
Castor	No	Western India	Molefe et al.[2]
Soybean	Yes	U.S.	Atabani et al.[31]
Sunflower	Yes	Europe	Zheljazkov et al.[32]
Palm	Yes	Southeast Asia	Keera et al.[33]

2.3.2 | Microalgae

Microalgae have been regarded as the potential alternative feedstock for vegetable oils when it comes to biofuel production.[41] This is due to their high oil yields of up to 65% compared to the other crops,[42] and their ability to capture waste carbon dioxide (CO_2) which helps in the maintenance and improvement of air quality.[43] The use of microalgae for fuel production will not compete with terrestrial plants for any agricultural land due to their aquaticity and being non-edible.[44] Renewable liquid fuels produced from microalgae are a major focus in achieving independence from fossil fuels and reduction in costs. Microalgae biomass or extracted macromolecules constitute 80% triglycerides and hydrocarbons that can be transformed into biofuels such as bioethanol, biodiesel, bio-crude, bio-jet, and also as a source of many other valuable substances for pharmaceuticals and pigments.[45] Hydrocracking can be an effective method for microalgae conversion into biofuels but the biomass needs to be dried properly to reduce moisture content before hydrocracking. The hydrothermal liquefaction (HTL) process is known to be an effective technical approach to eliminate the pre-drying step; this suggests that the wet microalgae biomass slurry can be directly used to produce bio-crude oil.[45,46] The produced bio-crude is very similar to the petroleum crude oil concerning their carbon chain length,[44] but could also slightly vary based on the species oil content, features as well as the nature and type.[46] The crude forms due to dehydration, condensation, hydrolysis, and deamination. The coupling of HTL with the hydrocracking technique for subsequent hydrogenation and hydrodenitrogenation can upgrade the quality of the produced bio-crude oil.[46,47]

2.3.3 | Jatropha oil

Jatropha curcas is a shrub from which jatropha oil is extracted and it has distinctive features like higher oil content compared to other plants, tolerance to different climate conditions, rapid growth, and so forth.[48,49] Jatropha oil has emerged as one of the promising feedstocks for biofuel production. This is because the oil is non-edible and therefore is not accounted as a threat to food security.[50] Jatropha oil is widely available worldwide and its seeds contain 30%–60% of oil.[48,49,51,52]

The economic viability of jatropha oil as feedstock for biofuel production may be increased by the higher oil yield; therefore, it is suggested that the seeds be harvested when the oil content is at its maximum.[50] The oil contains both saturated fatty acids (palmitic and stearic acids) and unsaturated fatty acids (oleic and linoleic acids). The high percentage of unsaturated acids supports the use of the oil for biodiesel production. Therefore, biodiesel can be directly used in combustion engines without modification unless the viscosity is high.[53] Based on the oil's chemical composition, renewable fuels can be produced via single-step hydrodeoxygenation, while higher selectivity towards the desired products can be obtained via hydrocracking.[51,53]

3 | PRODUCTION PATHWAY

3.1 | General hydrocracking process

Hydrocracking is a catalytic process in which heavy feedstocks are converted to saturated lighter products,[54] and is occasionally referred to as hydroprocessing.[55] Hydrocracking is viewed as a severe form of hydrotreating and it involves hydrotreating first to make the cracking products lighter and contains a minimal amount of undesired impurities.[56] The hydrotreating process is preferred when the desired product is in the diesel range fuel and eliminates hetero atoms. The number of atoms remains intact after C—C saturation.[57] However, hydrocracking favours the C—C bond breakage while drastically reducing the molecular weight to give rise to gasoline-range fuel.[20] This implies that the biodiesel can be transformed into bio-gasoline along with bio-jet fuel (or bio-aviation fuel) via hydrocracking as Usomboon et al.[58] and Liu et al.[39] have demonstrated.

Different reactions which occur during hydrocracking and hydrodeoxygenation (HDO) are the focus in this review.[17,59]

3.1.1 | Hydrodeoxygenation

HDO is a chemical process used to remove oxygen from organic compounds, specifically from oxygenated organic molecules such as those found in bio-oils and vegetable oils. The goal of this process is to produce hydrocarbons, which can be used as fuels or as feedstocks for the production of chemicals.[60] There are other alternative upgrading methods, such as catalytic cracking, esterification, emulsion, and steam reforming. Cracking is unattractive due to high yields of light hydrocarbons (C_1–C_4) and short-chain alkanes (C_5–C_{15}) with lower energy densities. The HDO reaction rates, as well as the mechanism, are highly determined by the used feedstock and catalyst type.[24] As mentioned, hydrocracking is a severe form of hydrotreating as it can transform heavy feedstocks into more valuable products.

The triglycerides-based feedstock contains oxygen content that ranges from 8% to 22%,[12] which can be removed

by the deoxygenation reactions in the presence of hydrogen pressure and catalysts. The unsaturated triglyceride bonds are transformed into saturated hydrocarbons first through the addition of hydrogen (hydrogenation), this is then followed by C—O bond scission of the triglyceride molecule to result in FFA.[61] The FFA will then be subjugated to 3 major reactions reported to eliminate oxygen: decarbonylation, decarboxylation, and hydrodeoxygenation.[62]

Decarboxylation and decarbonylation both produce hydrocarbons with one carbon atom less than the initial fatty acid and also produce a mole of CO_2 and CO and water, respectively.[60] The decarboxylation major products are C_{15}–C_{17} hydrocarbons.[63,64] HDO produces alkanes with the same number of C-atoms and 2 moles of water. HDO produces C_{16} and C_{18} hydrocarbon products.[34] Liquid fuels produced after oxygen removal will have a high energy content as well as high thermal stability.[60] The produced alkanes will need to be subjected to isomerization and cracking reactions based on their ultimate composition. This will help improve combustion properties and obtain iso-alkanes and lighter hydrocarbons.[60] Figure 2 depicts the general deoxygenation process.

Four different mechanisms have been proposed for hydrocracking reactions these include the bi-functional mechanism, hydrogenolysis, thermal cracking, and the Haag–Dessau mechanism.[65] Out of all the mechanisms, the bi-functional hydrocracking mechanism is the focus, as sketched in Figure 3.

Paraffinic feed molecule dehydrogenation takes place on the metal site resulting in alkane formation. Then the alkanes desorb and migrate to a Brønsted acid site by

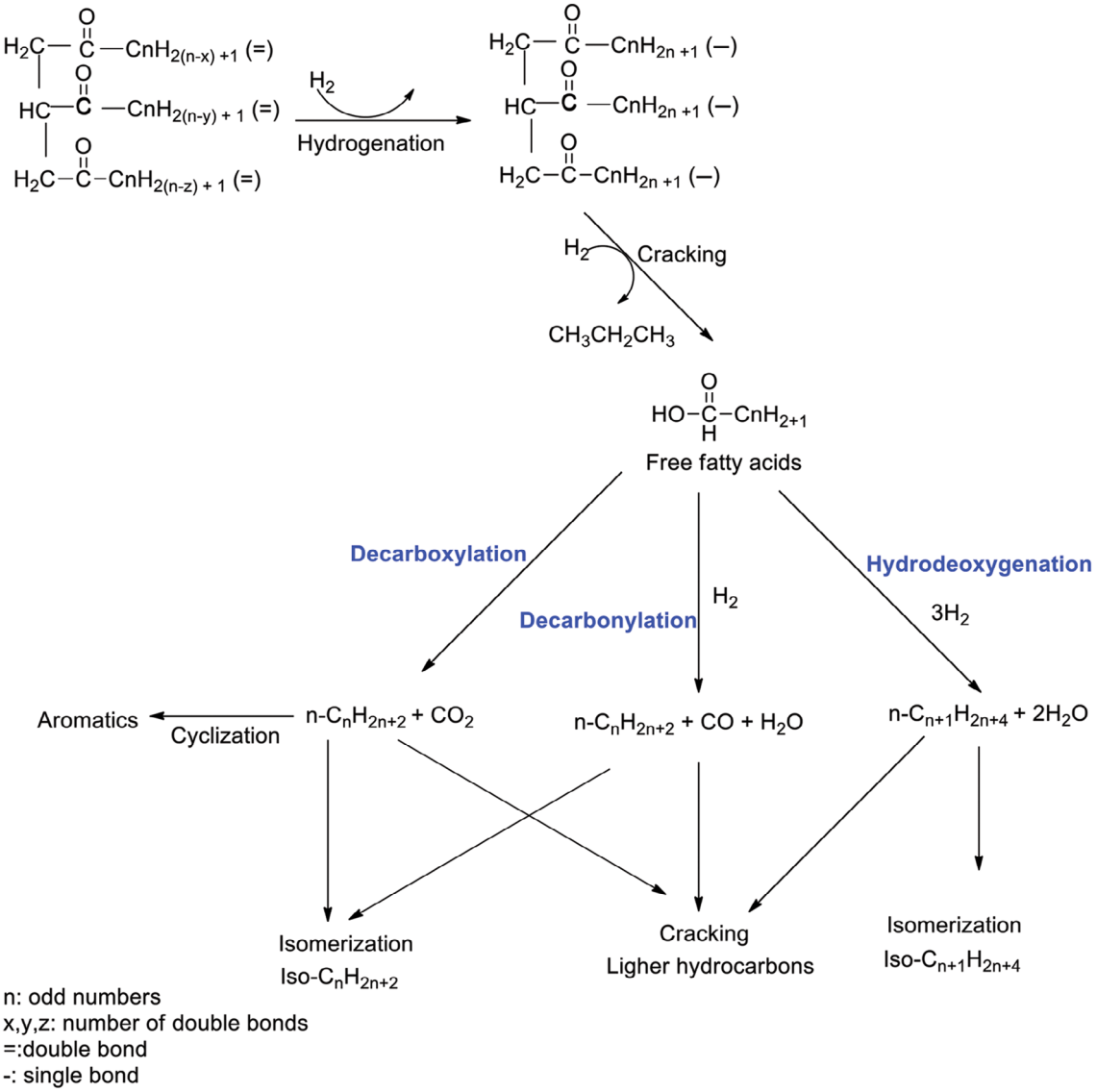

FIGURE 2 Triglyceride's deoxygenation process.[2]

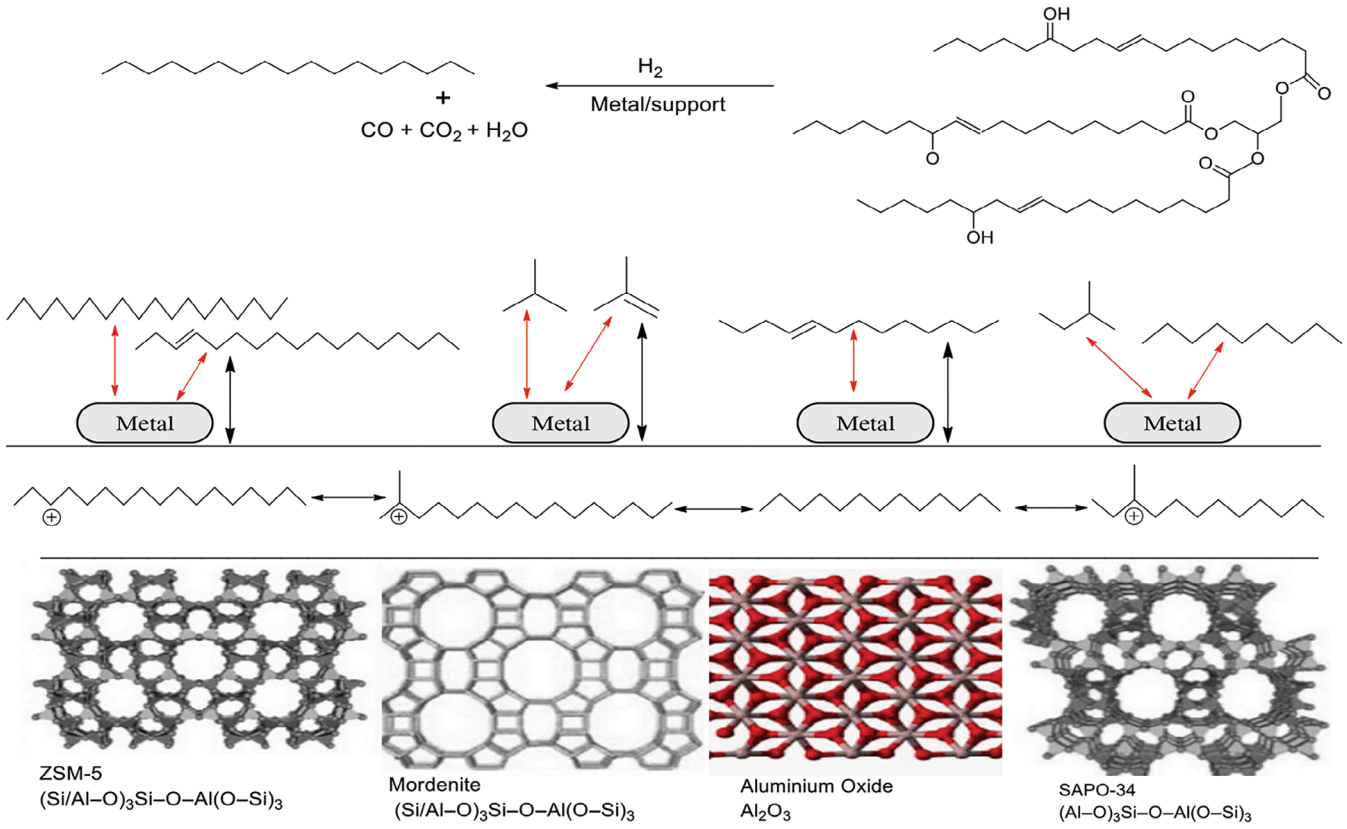

FIGURE 3 Bifunctional hydrocracking catalyst mechanism of paraffin.[12,17,67]

diffusion through the fluid phase, where it is protonated into a carbenium ion. Subsequently, the carbenium ion undergoes skeletal isomerization (such as alkyl shift or protonated cyclopropane) and cracking.[66] The carbenium ions β scission results in an olefin and shorter carbenium ions. The olefin can either be cracked to a greater extent on the acid site of the catalyst (secondary cracking),[66] or it can be subjected to a hydrogenation reaction over a metal particle. The produced shorter carbenium ions can be deprotonated to form an olefin, which migrates from the acid site by fluid-phase diffusion.[17]

3.1.2 | Hydrocracking via hydrolysis process

Hydrolysis is a chemical reaction in which a molecule is split into two parts by the addition of a water molecule. One part of the split molecule gains a hydrogen ion (H^+), and the other part gains a hydroxide ion (OH^-) from the splitting of water. The direct hydrogenation of triglycerides is proven to be expensive due to the hydrogen price at elevated pressure, thus hydrolysing triglycerides with high-pressure steam is usually favoured. Generally, the reaction is carried out using a 0.4–1.5 wt.% water-to-oil ratio at 100–260°C and 100–7000 kPa.[68,69] The esters hydrolysis takes place by the acyl–oxygen break with an excess of steam/water at elevated temperature or by the utilization of an acid catalyst that is appropriate to hydrolyse the glycerol pillar in the ester group of any triglyceride, di-glycerides, and mono-glycerides.[61] The hydrolysis reaction of triglycerides produces 3 mol of FFA and 1 mol of glycerol (Gly) (Figure 4). This reaction is a homogenous first-order reversible reaction.

The produced FFAs as main products have a high degree of purity and can be utilized in multiple industries such as the cosmetics and pharmaceutical industry. The saturated FFA can undergo deoxygenation via decarboxylation in the same hydrothermal medium as hydrolysis to produce *n*-alkanes chains.[72] The produced glycerol on the other hand plays an essential function when dealing with unsaturated fatty acids. The glycerol is catalytically gasified to produce hydrogen via APR (aqueous phase reforming) or hydrothermal catalytic reforming. The hydrogen will accelerate hydrolysis and facilitate the hydrogenation of the unsaturated fatty acids into saturated fatty acids.[73] Therefore, the saturated fatty acid will undergo hydrogenation, hydrodeoxygenation, decarbonylation, and decarboxylation reactions, which will rely on the catalyst used during the hydrothermal reaction.[73,74]

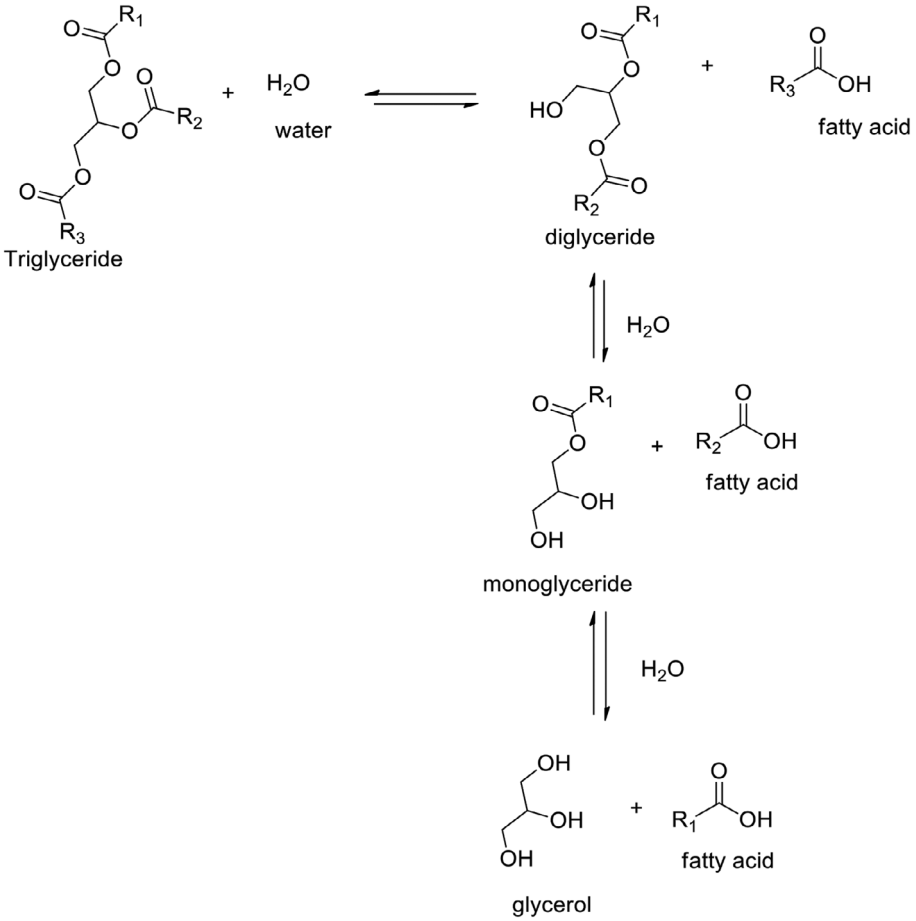

FIGURE 4 Triglyceride's hydrolysis reaction adapted.[70,71]

3.1.3 | Co-processing

Triglycerides-based feedstocks and petroleum fractions co-processing in existing refinery units to produce renewable fuels is considered to be a relatively low-cost method. Co-hydroprocessing has recently been explored due to its economic investments.[75] Recently, animal fats were researched as a possible feedstock for co-processing with gas oil, as well as light cycle oil (LCO), resulting in a high-quality product. Co-processing has significant advantages when compared to stand-alone biomass conversion techniques. Reduction of high investment costs and exploitation of existing refining infrastructure are some of the advantages that co-processing possesses.[76] Different studies have examined co-hydroprocessing blends of vegetable oil and fossil-based feeds including, for example, the co-hydroprocessing of mixtures of oil from WCO, straight-run gas oil (SRGO), and LCO, with a blending range of 0%–15%, 70%–85%, and 15% respectively.[77] Furthermore, Chen et al., under typical hydroprocessing conditions, investigated the low-grade canola oil co-hydroprocessing with heavy vacuum gas (HVGO), and from the results, it was discovered that more diesel was produced than gasoline in comparison to pure HVGO at the same operating conditions.[78] When Sági et al. investigated the co-hydroprocessing of FFA (0%–20%) with untreated gas oil and light gas oil, it was observed that the hydrocarbons in the diesel fuel range dominated the final product when the fat bio-content increased, these led to a decrease in the liquid product.[79] The bio-content played an important role in the production of the final product during the co-hydroprocessing of bio-based feedstock and petroleum fractions. Tóth et al. also experienced a decrease in liquid product yield when the vegetable oil content was increased during co-processing with SRGO.[77]

3.2 | Effect of hydrocracking catalysts and operating parameters

3.2.1 | Hydrocracking catalysts

A catalyst's typical features are to crack the reactant as well as to accelerate the reaction rate without undergoing any chemical change. Hydrocracking catalysts are bifunctional catalysts that consist of the hydrogenation/dehydrogenation function or acid function and the hydrogen activation function.[17] Bimetallic catalysts have

proven to have higher oxygen removal rates when compared to monometallic catalysts.[30] This was validated by Kubička and Kaluža in their hydrotreating of rapeseed oil study.[80] Deoxygenation rates of 3.5 were obtained using $NiMo/Al_2O_3$; this was 19 times greater than those obtained using single metals Mo/Al_2O_3 and Ni/Al_2O_3 catalysts, respectively. At a given reaction temperature, the Mo and Ni catalyst contact time had to be doubled and increased fourfold, respectively, for the same rates of deoxygenation to be obtained with $NiMo/Al_2O_3$. In their study, the presence of Ni increased the activity of the bimetallic catalyst $NiMo/Al_2O_3$ because it functioned as a Mo catalyst activity promoter in the deoxygenation of triglycerides.[80]

The balance between the metal and acid sites is a key element in designing the catalyst to improve the selectivity, durability, and activity of the catalyst.[65] Hydrcocraking's main objective is to provide high conversions of vegetable oils and produce high yields of middle distillates (kerosene, jet fuel, diesel, and heating oil) and not gasoline in petroleum refineries, though different catalysts can be used to modify it to produce biogasoline.[81] For example, the Pt-zeolite catalyst displayed a strong (effective) catalytic activity for cracking to yield gasoline due to its strong Brønsted acid side.[39] The hydrocracking process's final product composition differs as it is mostly influenced by different variables including the selected feedstock, the catalyst used, and reaction conditions, among others[63]; these can be observed in Table 2.

Metal catalysts

Noble metals and transition metals are mostly used in hydrocracking in their sulphided or reduced form. Sulphided/non-sulphided catalysts such as $Ni–Mo/\gamma\text{-}Al_2O_3$ and $Co–Mo/\gamma\text{-}Al_2O_3$ have a higher activity which makes them result in being the most widely used catalysts for HDO of oil for jet fuel production.[12] Sulphided catalysts are highly active and selective towards the transformation of triglycerides feedstock. However, they are associated with sulphur content contamination of the final product.[82]

Ni/Mo catalysts have been researched for both hydrotreating and hydrocracking studies. Current developments in using hydrotreating technologies for upgrading fractions of waste oil into usable transportation fuels were reported by De and Luque.[20] The focus was particularly fixed on the selection of the catalyst and the catalyst function in hydrotreating and hydrocracking processes. The following conclusions were made from their findings:

a. A combined sulphided $Ni–Mo/Al_2O_3$ catalyst has a high selectivity for the product in the diesel range($C_{15}–C_{18}$) from waste soya oil and gas oil mixture because of minimum cracking.
b. The sulphided $NiW/SiO_2–Al_2O_3$ catalyst produces a substantial product in the jet range as a result of cracking.
c. The catalyst NiMo is adequate for the removal of oxygen from triglycerides by hydrodeoxygenation.
d. Ni–W catalyst is highly adequate for both decarboxylation and decarbonylation due to its higher acidity.
e. The NiMo catalyst is examined for co-processing studies that can focus on both hydrotreating and hydrocracking.[20]

da Rocha Filho et al. carried out a hydrocracking experiment to investigate the effect of different degrees of saturation and chain length using sulphided $Ni–Mo/\gamma\text{-}Al_2O_3$ catalyst on the resulting products. The produced products were mostly in the diesel range in different quantities based on the used reaction temperature.[83]

Similarly, Sotelo-Boyás et al. conducted hydrocracking of rapeseed oil to inspect the effect of bi-functional catalysts: sulphided $NiMo/\gamma\text{-}Al_2O_3$ catalyst and non-sulphided (Pt/H-Y and Pt/H-ZSM-5). Both the non-sulphided catalysts resulted in more iso-paraffin than n-paraffin with $C_5–C_{22}$ range. The Pt/H-ZSM-5 acid sites had stronger 10-ring zeolites than Pt/H-Y and cracking products which were higher. However, the higher production of $C_{17}–C_{18}$ was due to the lower acidity of the Pt/H-Y catalyst. A higher diesel yield was observed with Pt/H-Y catalyst, while Pt/H-ZSM-5 was more relevant for green gasoline $C_5–C_{12}$ production. This was due to the fact that both zeolites experienced a cracking ability that was strong and favoured the higher formation of isoparaffin. The sulphided $NiMo/Al_2O_3$ catalyst has been reported to effectively promote triglycerides hydrocracking and carboxylic acid at 350°C and 8 MPa in 3 h.[84]

Catalyst supports

It is very important to choose the catalyst support carefully because it plays the main role in active phase dispersion and it is an important factor in HDO activity determination and selectivity of hydrocarbon.[17] Various supports such as zeolites (ZSM-5, H-Beta), mesoporous material (SAPO-11, Al-MCM 41, SBA-15), and metal oxides (TiO_2, AlO_3) are all potential supports that were studied.[12] However, zeolites are the most generally preferred support than other supports mainly because of the features they possess, which include higher catalytic activity, higher resistance to deactivation, good product selectivity, and higher regeneration capability.[96] Supports with average acidity are also favoured because of their high productivity and selectivity, while high-acidity supports were acknowledged to result in more cracking and decreased product selectivity.[104]

TABLE 2 An overview of different oil sources and product yields under different catalysts and operating conditions.

Material used	Operating conditions	Catalyst type and loading	Activity	References
Nyamplung oil	Hp = 30 bar, T = 200–350°C, Rt = 160 min	Non-sulphided CoMo/γ-Al_2O_3	Gasoil, gasoline	Rasyid et al.[85]
Waste cooking oil (WCO)	T = 250°C, Catalyst: Oil molar ratio = 1:75, Rt = 1 h	Ni-Mo/Alumina	Biogasoline = 59.5 wt.%	Mampuru et al.[86]
Coconut oil	T = 350°C, Rt = 2 h, Hp = 15 bar	5 wt.% Ni–Zn/HZSM-5	Hydrocarbons = 13.37 area%, carboxylic acid = 86.63 area%	Al Muttaqii et al. [87]
Waste palm cooking oil	T = 500°C, H_2 flow rate = 20 ML/min, Rt = 2 h, Weight ratio of catalyst: feed = 1:100	Mo/SBA-15, SBA-15 = 1 g	Gasoline = 42.46 wt.%, diesel =7.89 wt.%	Alisha et al.[88]
Coconut oil	T = 350, 375, and 400°C, Rt = 2 h	Ni–Fe/HZSM-5, Zeolite 0.05 wt.%, Ni & Fe 5 wt.%	*n*-Paraffin = 39.24%, gasoil = 18.4%, kerosene = 18.1%	Al-Muttaqii et al.[9]
Calophyllum inophyllum oil	T = 550°C, Rt = 2 h, H_2 flow rate = 30 ML/min	CoOMoO/γ-Al_2O_3, CoO =5 wt.%, MoO = 5 wt.%, CoO/γ-Al_2O_3, CoO = 10 wt.%	Liquid fraction = 65.56 wt.%, coke = 0.32 wt.%, gas fraction = 33.67 wt.% Liquid fraction = 55.48 wt.%, coke = 0.75 wt.%, gas fraction =44.20 wt.%	Trisunaryanti et al.[89]
Jatropha oil	Hp = 30 bar, T = 360°C, Rt = 5 h	Ni–W, Ni and W	Bio oil = 63.5 wt.%, bio oil = 19.3 and 12.5 wt.%	Yang et al.[90]
Palm oil	T = 340–420°C, Hp = 50 bar, LHSV = 0.5–1.5 h^{-1}, H_2/liquid ratio of 1000 N (cm^3/cm^3)	CoP/porous carbon, Co = 10 wt.%	Bio-jet fuel, green diesel	Kaewtrakulchai et al.[91]
Palm oil	Rt = 0.5–3 h, T = 280–320°C, Hp = 30 bar	Sulphided Ni–Mo	Green diesel alkanes = 75.3 wt.%	Burimsitthigul et al.[92]
Vacuum residue	T = 400°C, Rt = 4 h, Hp = 70 bar	Nano WC	Solid yield = 5.9 wt.%, liquid yield = 83.6 wt.%	Kim et al.[93]
WCO	T = 330–398°C, Hp = 83 bar, LHSV = 1.0 h^{-1}, H_2/Oil = 4071 scfb, liquid feed = 0.33 mi · min^{-1} and gas feed = 0.4 scfh	Commercial hydrocracking catalyst	Diesel = 90.1%, gasoline = 10.25, conversion = 90%	Bezergianni et al.[94]
Rapeseed oil	Liquid feed flow = 100 g · h^{-1}, H_2 flow = 0.1 Nm^3h^{-1}, WHSV = 1 h^{-1}, Gas/oil = 1 h^{-1}/920 NM^3, Hp = 70 and 1500 bar, T = 310 and 360°C (for results)	Ni–Mo/Al_2O_3 (commercial), NiO = 3.8 wt.%, MoO_3– = 17.3 wt.%, P_2O_5– = 6.7 wt.%	*n*-Alkane = 6.3 wt.%, *n*-heptadecane = 24.9, *n*-octadecane = 51.1, *n*-alkanes>n-C_{18} = 3.6, conversion, >99% @310°C, 100% @360°C	Šimáček et al.[55]
Castor oil	T = 325°C, Hp = 50 bar, (LHSV from 2 h^{-1})	CoMO/AL_2O_3, CoO = 4 wt.%, MoO_3 = 12 wt.%, Al = 84 wt.%, spiking agent dimethyl disulphide (DMDS, 2 wt.%)	Conversion = 87%	Zaher et al.[5]

TABLE 2 (Continued)

Material used	Operating conditions	Catalyst type and loading	Activity	References
Jatropha oil plus its mixtures with gas oil	T = 340–380°C, Hp = 50 bar, LHSV = 1, 2 h^{-1}, H_2 to feed ratio = 1500 mL, H_2 gas per mL liquid feed	Sulphided Ni–W/SiO_2, WO_3 = 26.7%, NiO = 26.9%, 3.3%, SiO_2 = 29.38%, Co–Mo/Al_2O_3, CoO = 3.0%, MoO_3 = 14.7% and 12.0%, Al_2O_3 = 27.09%, 81.97%, and 85.0%, NiMo/Al_2O_3	Diesel =80.8%, diesel = 49.2%, diesel = 97.9%	Kumar et al.[95]
Jatropha oil	T = 380°C, Hp = 30 bar, LHSV = 1.0 h^{-1}, H_2/Oil ratio of 1000 (v/v)	PTA-NiMO/ZSM-5, non-sulphide catalyst, Ni = 4.0 wt.%, Mo = 12 wt.%	BTX (benzene, toluene, and xylenes) =59 wt.%	Yang et al.[96]
Waste virgin coconut oils	T = 350–400°C, Rt = 1–3 h, Hp = 20–40 bar	Silica-alumina HZSM-5, mole ratio silica-alumina of the zeolite (80:1 wt.%)	Gasoline = 4, kerosene = 22.4%, diesel = 70%, Conversion = 80%	Yotsomnuk and Skolpap[97]
Soybean	T = 200–280°C, Rt = 2–4 h, interval of 0.5 h, Hp = 100 bar	Ni–W	Liquid yield 81.76% and *n*-alkanes 32.29%	Zhou et al.[98]
Jatropha oil	T = 280–400°C, Rt = 10–163 h, Hp = 3.5 MPa, LHSV = 0.9 h^{-1}, H_2 to feed ratio = 1000 mL H_2 gas/m liquid feed	NiMoCe/Al_2O_3, 10 g catalyst	Alkanes (C_{15}–C_{18}) = 80%, selectivity = 90%, conversion = 89%	Liu et al.[99]
Palm fatty acid distillate (PFAD) with light gas oil (LGO)	T = 280–350°C, Hp = 25 bar, H_2/feed ratio = 630 Nm^3/m^3 and 0.75 h^{-1}	CoMo/Al_2O_3, PFAD (5, 8, 12, and 25 wt.%) in LGO	Paraffin yield =30–40 wt.%	Boonyasuwat and Tscheikuna.[100]
Fatty acid by-product (BFA) and untreated gas oil (UGO) and light cycle oil (LCO)	LHSV = 2.0 h^{-1}, H_2/feed = 600 Nm^3/m^3, T = 320–380°C, Hp = 40–70 bar	NiMo/Al_2O_3, 10% LCO–90% UGO BFA = 0%–20%	Oil product = 94.1%–95.9%	Ságiet al.[79]
Vacuum gas (VGO) and hydrotreated pyrolysis liquid (PL) (pine wood)	T = 225°C and 120°C, Hp = 200 bar, Catalyst/oil ratio = 5–8	E-cat, Upgraded liquids (SPO-2)/VGO = 10/90, P = 200 bar	Total liquid = 6.4 wt.%, gasoline = 6.1 wt.%	Wang et al.[56]
Heavy vacuum gas (HVGO) and canola oil	T = 385°C, LHSV = 1.5 h^{-1}, Hp = 100 bar, T = 360°C, T = 395°C	HVGO/canola = 90/10, NiMo/Al_2O_3, HVGO/canola = 95/5, NiMo/Al_2O_3HVGO/canola = 80/20, NiMo/Al_2O_3	Diesel yield = 32.46 wt.%, diesel yield = 21.88 wt.%, diesel yield = 37.87 wt.%	Gieleciak et al.[101]
Straight-run gas oil (SRGO) and used cooking oil (UCO)	T = 350°C, LHSV = 2 h^{-1}, H_2/feed oil ratio = 340 NL/L, Hp = 100 bar, Hp = 55 bar	NiMo/Al_2O_3, SRGO/UCO = 80/20	Green diesel = 79–85 wt.%, light gases = 9.9–12.6 wt.%	De Paz Carmona et al.[102]
LCO and WCO	T = 340, 360, and 380°C, H_2/oil = 200 (scfh), LHSV = 1 h^{-1}, Hp = 83 bar	NiMo/Y-Al_2O_3, 90/10 LCO/WCO	Middle distillates between 90% and 98%	Dagonikou et al.[103]

Abbreviations: Hp, hydrogen pressure; LHSV, liquid hourly space velocity; Rt, reaction time; T, temperature.

The study by Kim et al. demonstrated an increase in selectivity towards bio-jet production with hydrocracking of palm oil over zeolites (Bulk-ZSM-5, Nano-ZSM-5, and nano beta) as acid supports for Pt catalyst at a temperature of 220–240°C.[105] The Pt/nano was the best hydrocracking catalyst producing the greatest yield of bio-jet in

both the single and the two-step process (hydrotreating and hydrocracking). The two-step process produced high yields of jet fuel range (C_8–C_{16}) with 71.5 wt.%, while the single-step produced high levels of light hydrocarbons (≤C7). In the single-step process, the lighter hydrocarbons remained the dominating cracking product, while the isomerized C_8–C_{16} selectivity continued to be low. The results show that the single-step direct conversion of triglycerides using a bifunctional catalyst is less effective in the production of bio-jet fuel compared to the two-step process concerning product selectivity and catalyst deactivation. However, the challenge will be to produce a bio-jet in one process.[105]

Tiwari et al. employed hydrocracking on waste soya oil mixture to investigate the mesoporous silica-alumina (SiO_2–Al_2O_3) and alumina oxide (Al_2O_3) effects as supports with sulphided Ni–W and Ni–Mo catalysts.[106] At a temperature of 140–250°C, sulphided Ni–W/SiO_2–Al_2O_3 was discovered to be selective via decarboxylation or decarbonylation for kerosene range hydrocarbons from C_8 to C_{18} formation which increased with the oil's degree of saturation and this alkane's selectivity increased with increasing temperature up to a specific point before dropping again past that point. At a temperature of 250–380°C, sulphided Ni–Mo/SiO_2–Al_2O_3 was discovered to be a less acidic catalyst and more selective for diesel range hydrocarbons from C_{15} to C_{18}; this catalyst is mostly preferred for the HDO pathway for the elimination of oxygen from triglycerides.[106]

When soybean was catalyzed with NiMo/Al_2O_3 and NiMo/25USY (14)60A, they both produced mostly diesel, while hydrocracking using NiMo/25HY (5.5) 60A slightly increased the gasoline yield. NiMo/25Beta (37) 60A resulted in the highest gasoline production of about 70% and research octane number (RON) value of more than 80%. The NiMo/25-ZSM (90) 60A caused hydrocarbon over-cracking to yield great amounts of gaseous products which resulted in decreased iso−/n-ratio. In contrast, the NiMo/25ZSM(1770)60A selectively produced an 80% yield of diesel with iso−/n-ratio of 0.13 between those of NiMo/25USY(14)60A and NiMo/Al_2O_3.[107]

Furthermore, an intensified increase in liquid biofuel production of gasoline, kerosene, and diesel fractions was observed in the hydrocracking of crude palm oil, which was to investigate the effect of bimetallic catalysts. The NiW-HY produced a greater yield of gasoline in contrast to the NiW-HZMS-5 zeolite catalyst and the NiW-HZMS-5 produced a higher yield of kerosene as compared to the NiW-HY. The results indicate that the catalyst doped with NiW had a better hydrocracking performance compared to the catalyst that was not metallically modified.[108] The NiW was again used for hydrocracking with NiMo in their sulphided form for a conversion comparative study on Jatropha oil at a temperature of 400 and 425°C. The sulphided NiMo and NiW were in combination with the hierarchical mesoporous SAPO-11 (MSP-1 and MSP-2). Higher temperatures alongside the supports and acidic character were more selective for the kerosene production, due to hydrocracking activity favoured for those conditions. NiMo (MSP-1 and MSP-2) and NiW (MSP-1 and MSP-2) catalysts resulted in a kerosene range of 25%–38% and 22%–38% respectively. The slightly higher acidic NiW/MSP-2 produced 30% more kerosene yield at 450°C than the lower acidic NiW/MSP-1.[109] The acid strength influenced the selectivity of HDO production.

3.2.2 | Hydrocracking operating parameters

Temperature

Temperature is the dominating parameter for catalyst effectiveness and has a dominating effect on the product yield. Temperatures below 200°C have been reported to show a significant effect on double bond hydrogenation and resulting in correlating saturated TG's.[12] The temperature increased from 230 to 280°C causing the degradation of hydrogenated triglycerides into multiple intermediates and FFA. Further temperature increases to roughly 300°C increased the hydrocarbon yield and temperatures of 350–375°C were said to be the optimal temperatures for the fatty acids C═O bond scission with the least formation of coke during the HDO.[110]

An increasing temperature from 300°C to 400°C in soybean oil exhibited an increase in diesel yield this was when Ni catalyst was used, at 400°C both the diesel yield and conversion were at their maximum values because the decarbonylation and decarboxylation reactions were the dominating reaction pathways for the triglyceride's deoxygenation reaction. At 350°C, the CoMosx catalyst produced a higher yield of diesel than what was obtained with the Ni catalyst this was observed after the effect of temperature was investigated.[111]

The kerosene yield from the waste virgin coconut oil was observed to increase with increasing temperature, while the diesel yield decreased. At 400°C, kerosene reached the highest product yield and the highest conversion of the coconut oil. At 350°C, diesel was the highest produced product. The biofuel conversion decreased with increasing temperature, this was attributed to that the HZMS-1 catalyst contained only an acidic site short of a metallic site.[97,112]

Hydrogen pressure

During hydrocracking, pure H_2 can be used in combination with other inert gases like argon (Ar), nitrogen (N_2), helium (He), and so forth. An increasing reaction H_2

pressure is known to be most favourable in increasing the conversion of the aromatic into by-products that are saturated, thus increasing the jet fuel and diesel quality with a higher/elevated viscosity index, which is exceptional.

From the investigation of the parameters conducted by Anand et al., it was discovered that with hydrocracking of vegetable oil at a temperature of 420°C and hydrogen pressure greater than 60 bar, the C—O bond scission was improved, which resulted in an elevated yield of naphtha and kerosene-like jet fuel hydrocarbons while hydrogen pressure lower than 60 bar displayed more C—C bond cleavage and dehydrogenation instead.[113] When the pressure was further increased to 90 bars, there was a slow increase in the formation of naphtha and kerosene (2%–10%). Furthermore, the hydrogen pressure increase also favoured cracking and lower-range hydrocarbon formation. From the investigation, it can be said that higher hydrogen pressure is more acceptable to reduce heavy product formation to improve the selectivity of the lower-range hydrocarbons in hydrocracking.[12]

Šimáček et al. hydrocracked rapeseed oil using Ni-Mo/Al_2O_3, under a hydrogen pressure of 7 Mpa and 15 Mpa and temperatures of 260–340°C.[55,81] It was found that a higher reaction temperature above 310°C and pressure of 7 MPa resulted in a drastic increase in n-alkanes n-C_{17} and n-$C1_8$. The high temperature increased the formation of i-alkanes formed from the *n*-alkanes and improved the low-temperature properties of the biodiesel (product) due to the increase of i-alkanes,[55,81] while an increase in pressure in the waste virgin slightly affected the biofuel yield increase.[97]

Reaction time

Reaction time is an important factor that plays a role in determining the extent of cracking, quality as well as yield of the gas and liquid products. Mampuru et al. investigated the effect of reaction time on WCO from 0.5 to 2.5 h using the Ni-Mo/alumina catalyst for the production of biogasoline.[86] It was discovered that an increase in reaction time from 0.5 to 1 h increased the biogasoline production yield from 36.10 to 59.50 wt.%. However, the reaction time increase above 1 h decreased the biogasoline yield and the oil started to polymerize. This was said to be due to the unsaturated cooking oil triglycerides as they caused more cracking and coking, which reduced the catalyst activity.[86] The catalyst coking was also observed by Vela et al. at a reaction time of less than 15 min when studying the effect of time on HDPE co-hydrocracking with vacuum gas (VGO) at different conditions (PtPd/HY, 15 and 120 min, 420°C, and 80 bars).[114] Naphtha yields increased with increasing time from 36.9 to 46.3 wt.% at 120 min, while the naphthene's and iso-paraffins concentration decreased to 27.6 and 13.9 wt.%. The effect of reaction time was also studied by Suwannasom et al.[115] from 30 to 180 min to determine the jet fuel optimum yield using palm oil over Ni–Mo/HY zeolite. It was observed that an increase in time from 30 to 120 min increased the jet fuel yield from 24.8% to 30.15%, while with a further increase above 120 min the jet fuel decreased to 19.3%.[115] Thus, an optimized yield of jet fuel and the desired selectivity of hydrocarbon product can be achieved when an optimum reaction time is known.

4 | HYDROCRACKING CHALLENGES AND PERSPECTIVES

Hydrocracking has demonstrated its effectiveness and promise for biofuel production, but it is also associated with different challenges such as:

a. High H_2 gas consumption
b. Catalyst deactivation and coke formation.

4.1 | H_2 gas consumption

Despite the fact that hydrocracking requires high hydrogen pressure to promote the reaction and reduce the formation of coke, the use of high hydrogen pressure is associated with additional production costs and safety issues.[116] The hydrogen demand may also increase due to unwanted cracking reactions formed from unsaturated hydrocarbons.[117] The hydrocracking process can be made slightly economical by recycling the unused hydrogen.

4.2 | Catalyst deactivation and coke formation

Catalyst deactivation is another challenge that hydrocracking is faced with. The deactivation of the catalysts can either be temporary or permanent based on the type of catalyst used or operating condition. The temporary deactivation is usually caused by heteroatom deposition and this deactivated catalyst can be regenerated. On the other hand, the permanently deactivated catalyst activity cannot be restored and thus the catalyst needs to be replaced. During hydrocracking, catalyst deactivation is induced by the formation of coke, while the polymerization reaction of reactants causes coke formation.[118] Blockage of

pores due to coking prevents/inhibits the active site's accessibility to reactant molecules. Increases in hydrogen pressure as well as both a decrease in reaction time and temperature were found to be advantageous in the inhibition of coke formation. These parameters will lower the adsorption rate of heavy compounds and saturate large amounts of unsaturated compounds.[117] In hydrocracking, catalyst selection plays a big role. Highly acidic catalysts are known as the most significant factor for the acceleration of coke formation. The use of activated carbon as a support at low hydrogen consumption has demonstrated strong resistance to coke formation, and strong selectivity for direct oxygen removal. Thus, future research on finding inexpensive and active catalysts with a long lifetime needs to be done through catalyst morphological manipulation.[119] This typically can involve the degree of mesoporosity and its relationship with acidity and active sites. Catalyst regeneration is another topic that needs further exploration, as this may amend the economics of the process.

5 | CONCLUSION

The hydrocracking technique is more advantageous than other biofuel production methods. Different feedstocks, hydrocracking reactions, the effect of catalysts, and parameters were discussed. Feedstock selection is a critical issue in achieving high biofuel yield and quality. From this aspect, easy accessibility, abundant availability, and chemical properties (degree of saturation and chemical properties) were identified as key factors for the reduction of production costs. Hydrocracking is a two-in-one method and involves hydrotreating first to make the cracking products lighter and contain fewer amounts of undesired impurities. HDO is the most preferred hydrocracking reaction due to its ability to form higher alkane as unsaturated feedstock is deoxygenated into saturated feedstock. In addition, deoxygenation rates of 3.5 were obtained using $NiMo/Al_2O_3$; this was 19 times greater than those obtained using single metals Mo/Al_2O_3 and Ni/Al_2O_3 catalysts, respectively. This has proven that bimetallic catalysts have higher oxygen removal rates when compared to monometallic catalysts. The presence of Ni increased the activity of the bimetallic catalyst $NiMo/Al_2O_3$ because it functioned as a Mo catalyst activity promoter in the deoxygenation of triglycerides. Zeolite (Al_2O_3) is the most preferred support for the conversion of vegetable oils to achieve good product selectivity.

The utilization of higher hydrogen pressure is more acceptable to reduce heavy product formation to improve the selectivity of the lower-range hydrocarbons in hydrocracking. An increased temperature favours the fatty acid C═O bond scissions, whereas an increase in resident time reduces the catalyst activity. Coke formation is one of the challenges faced with hydrocracking despite that it can be reduced by high hydrogen pressure; this will increase the cost of the entire process.

AUTHOR CONTRIBUTIONS

Sharron Ratshoshi: Writing – original draft. **Hembe Elie Mukaya:** Supervision; writing – review and editing. **Diakanua Nkazi:** Conceptualization.

CONFLICT OF INTEREST STATEMENT

The authors confirm that there is no conflict of interest with this submission.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

ORCID

Hembe Elie Mukaya https://orcid.org/0000-0002-8033-8161

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