

Catalysis Deoxygenation for Renewable Fuel from Edible and Non-Edible Oil

Fouad Warid^{1,3}, Ismail Zainol¹, Nada M.abbass², Nurulsaidah Rahim¹ and Alhussen Arkan Majhool¹

1. Department of Chemistry, Faculty of Science and Mathematics, Sultan Idris Education University, Tanjong Malim 35900, Perak Darul Ridzuan, Malaysia

2. Department of Chemistry, Faculty of Science, University of Baghdad, Iraq

3. Ministry of Education, Directorate of Education Thi-Qar, Iraq

Abstract: The critical problem arises from the fossil fuels which has stimulated recent interests in alternative sources for petroleum-based fuel. An alternative fuel should be technically feasible, readily available, environment acceptable and techno-economically competitive. The new generation of renewable fuel is known as green diesel. Green diesel is composed of long chain hydrocarbons that can be prepared from DO (deoxygenation) of palm oil. The feedstock used for the production of green diesel mainly comes from edible vegetable oil which is highly available in most of the countries around the world. However, the competition between food and fuel economies towards the same oil resources may bring global imbalance to the food supply and demand market. The focus on this research is to produce green diesel using edible feedstock via heterogeneous catalysed DO reaction.

Keywords: Sustainability, green-diesel, renewable energy, DO, heterogeneous catalyst.

1. Introduction

The increasing energy demand, depleting fossil fuels and environmental problem resulted in climate change by continues consumption of petroleum derived fuel, bringing challenges for the scientific community and the researchers worldwide today. The present energy situation has stimulated research focus on the production of renewable biofuels. Biofuel is considered a viable alternative to petroleum-derived fuel. Chemically, biofuels consist of a hydrocarbon with long chain from fatty acids derived from thermal cracking of lipid feedstocks such as vegetable oils or animal fats [1, 2]. Biofuels are renewable, biodegradable, less toxic, and have an environmentally friendly emission profile, a higher combustion efficiency, higher certain number, higher

flash point and better lubrication than petroleum derived fuel [3, 4]. Moreover, biofuels and diesel share similar physicochemical properties, so biofuels can be used on its own or mixed with diesel in conventional compression ignition engines with some engine modifications. Although biofuels gain a lot of attention from industrialists, however the high production cost of biofuels as compared to petro-fuel had becomes major obstacle for industrial commercialization. Thus, recent strategy for lowering the production cost of biofuels under industrial scale is implementing low-cost feedstock such as WCO (waste cooking oil) and palm oil. It was reported that WCO is able to decrease the production costs with approximately of 60% to 90% [5]. Furthermore, the raise of environmental concerns associated with the safe handling and disposal of WCO has encouraged the development of safer waste management and non-waste producing biodiesel. Thus, utilization of WCO as transportation biofuel can solve waste disposal problems and additional waste treatment[6].

Corresponding author: I. Zainol, professor, Department of Chemistry, Faculty of Science and Mathematics, Sultan Idris Education University, Tanjong Malim 35900, Perak Darul Ridzuan, Malaysia.

Finally, the evaluates the recent processes of the DO (deoxygenation) of the realistic oil.

2. Catalyst DO for Producing Green Fuels

The research work conducted by Knothe, G. identified the process by which olefins and paraffins were converted into green fuels through the catalyst DO of the triglycerides. The authors investigated the processes of DO of the triglycerides and the methyl ester that were used in the production of diesel components [7]. They examined the reaction processes to determine the effects of reaction temperature in the biodiesel production process and supportive components used in the reactive distillation fashion. Fernando et al. [8] indicated that natural fats and oils were recognized as the most effective feedstocks used in the production process of biodiesel production through the transesterification of triglycerides by which methanol is specifically used for the conversion process to convert the triglycerides into green fuels that were based on FAMEs (methyl esters and triglycerides). In the process of converting natural fats and oils into biodiesel fuel, homogeneous catalysts of DO were applied to convert the natural fats into desirable fuel properties. The research also described that the conversion of non-petroleum feedstocks resulted in the production of fungible diesel fuel into straight chain hydrocarbons. The authors indicated that alpha olefins process was recognized as valuable for the production of biodiesel fuels through the application of specialty chemicals. The research conducted an extensive research on the production of hydrocarbons through the utilization of different types of renewable feedstocks received either from animal fats or natural oils. Various catalysts of DO were used in the process of converting vegetable oils into hydrocarbons.

Hydrocarbons were produced in the gasoline rather than in the diesel range through the process of cracking thermal or catalytic vegetable oils in the batch reactors. Thus, most of the production processes

were preferred by chemists to convert the natural oils and fats into green fuels through the catalytic conversions by showing better control of the hydrogenation of the vegetable oil and animal stocks. In the process of producing green fuels, the catalyst DO was used to hydrogenate the vegetable oils over the Ni containing catalyst by adopting the linear chains of hydrocarbons from the DO reactions. Most of the researches conducted in the past showed the production of unacceptable amounts of aromatic and cyclic products with extremely high ratio of H₂ and TG along with long-term sulfidation processes to achieve better results. Knothe, G.. focused in their research work to produce long chains of hydrocarbons by specifically utilizing the methyl esters or triglycerides through the DO of the Pt catalysts. The authors focused on determining the production of long chain hydrocarbons by adopting catalyst DO for methyl esters and triglycerides supported with Pt catalysts to produce biodiesel fuel to get cost-efficiency for energy purposes. Alpha olefins were specifically used to get the higher level of reactive distillation with higher vapor pressure in comparison to solvent and reactants to reduce the isomerization or oligomerization reactions. In conducting the research work, the authors used platinum catalysts in the DO process of producing biodiesel fuel along with bimetallic catalysts. These catalysts were specifically used in the research methodology along with wetness impregnation to get aqueous solutions in acid hexahydrate to get 1 wt. % of the Pt loading. A complex research method was applied before adding active components in dissolving the tin precursors and platinum in the hydrochloric solution to form bimetallic complex indicated by red purple color [9].

The research work conducted by Thanh et al., examined catalytic DO technologies that were employed for the biodiesel fuel production through the utilization of glycerol. The authors described the term biofuel that has arisen from solid, liquid, or gaseous

fuels for which biomass was used in conducting the production processes of biofuel production. Most popular and useful biofuel and biodiesel production processes are identified in the research with natural oils received from sugar cane, corn, cassava or wheat and from sunflower, canola, and soybean oil that are produced from the food crops on seasonal basis. On the other hand, the production of ethanol is associated with inexpensive cellulosic biomass resources that are often received from woody plants grown in the areas of forestry residues and agricultural centers. The authors indicated that the production of biodiesel fuel through catalytic DO is produced from the biomass which is regarded as an excellent way of reducing the raw material costs in the production of biodiesel fuel. Furthermore, the production of biodiesel fuel has become inexpensive because it is associated with fast, simple and excellent processes in comparison to methane and ethanol production. Abdulkareem-Alsultan et al. [10] indicated that the production of biodiesel fuel through WCO and animal fats has increased because they are cheap raw materials to be used for the production of biodiesel fuel. The authors pointed out the potential benefits of biofuels because they are widely adapted with excellent filling properties to be used at the filling fuel stations. The biodiesel fuels can be successfully transferred to the vehicles as the substitute of diesel oil. The research indicated that the production of biodiesel fuel has increased over the years because they are available from the common biomass sources and can be easily biodegradable. Carbon-cycle in combustion is present in the production process of biodiesel fuels and they are preferred in various countries and societies due to their environmentally friendly characteristics in economic consumption.

The researchers indicated that the production of biodiesel fuels has increased dramatically in the past few years especially in the last two decades. The production of biodiesel fuel through the catalytic DO

has shown considerable increase from 2000 to 2010 with Brazil as the leading country where ethanol and biodiesel production has increased substantially in 2010. In contrast, the production of biodiesel fuel in Germany is recorded as highest in the world with 30 percent production of biodiesel out of the total world biodiesel production. In the production process of biodiesel production, natural feedstocks, food crops and raw materials are used including sugar cane, cereals, and oil seeds for the biofuel production. In the near future, there will be an increase of biodiesel production by finding out abundant inedible biomass resources such as agricultural residue, industrial waste and wood chip. The research indicated that biodiesel fuel production through the catalytic DO is associated with several potential benefits as it contains high cetane number up to 50, contains built-in oxygen, has burning capacity, contains no surplus content, no aromatics and contains complete CO₂ cycle. In the production of biodiesel fuel, methanol can be added to the catalytic DO process to WCO by using small amount of NaOH and KOH as the catalysts. Some questions still remain unanswerable as what could be the best raw materials to be used in the production of biodiesel fuel to ensure the stability of prices with no increase of food prices. It also examines what should be the ideal production process by which biodiesel fuel is produced in the catalytic DO by using fatty acid methyl ester obtained from the minimal waste emissions and low energy consumption. An ideal solution of producing the biodiesel fuel is that soap formation with alkaline with catalyst application is proposed but reaction rate is observed to be slower in comparison to other production methods. The producers of biodiesel can also produce it by using the mixture of oil as the solvent reaction along with methanol to produce it effectively in the homogeneous production phase [11].

The global biodiesel fuel production is shown in Fig. 1 given below.

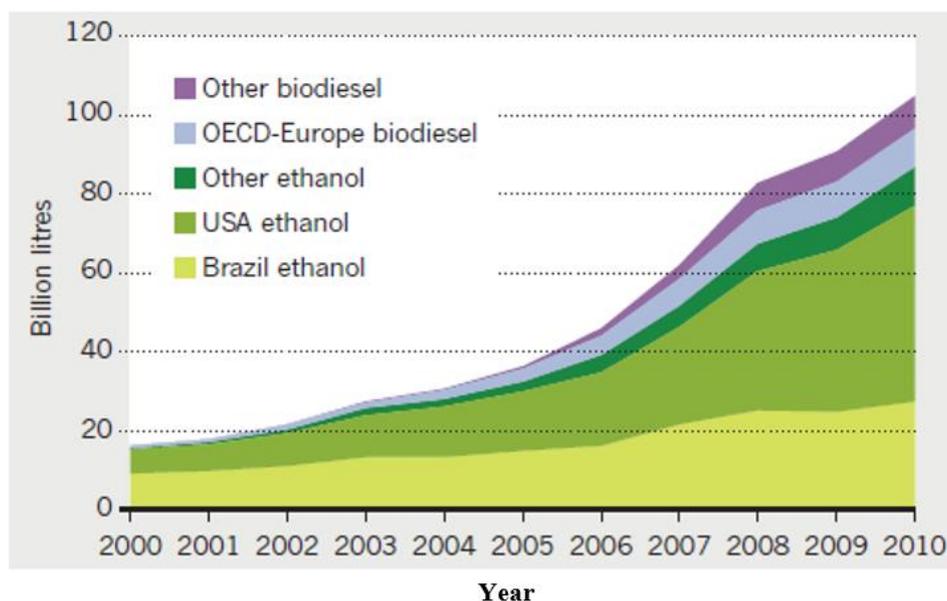


Fig. 1 Global biofuel production (OCED/IEA, 2011,[13]).

3. Catalyst HDO (Hydrodeoxygenation) for Producing Green Fuels

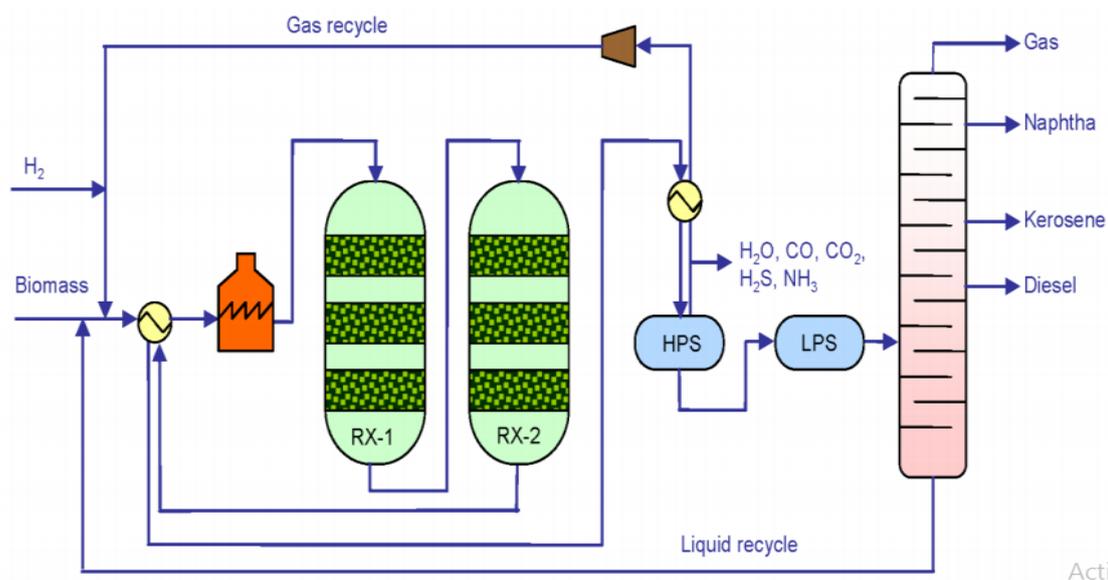
Razak, Yunus, Hashim & Mansor described catalysts HDO or hydro-treating of triglycerides-based biomass including vegetable oil and algae oil by which green diesel or biofuel is produced addressing environmental concerns. A mixture of carbon chains is used with alkanes to produce green diesel by using natural oils as the main ingredients that are derived from lignocellulosic biomass and considered to be naturally similar to petrodiesel. In the process of producing green diesel through the triglyceride biomass including vegetable oil and algae oil, double bond is used along with oxygen moieties containing decarboxylation or dehydration in the feedstocks that are broken and removed through the treatment of feedstocks with hydrogen in the elevated temperature with the presence of catalyst in a refinery [10]. According to the zeolite catalyst pyrolysis is another important approach that could be used in the process of biodiesel production where bio-oil is directly produced through the utilization of pyrolysis and upgraded as petrodiesel fuel by using zeolite catalyst which is present in the pyrolysis reactor [12]. In the areas of green diesel, there

are different types of green diesel as shown in the given table showing comparison of green diesel to FAME (fatty acid methyl ester) and ULSD (ultra low sulphur diesel). The results regarding the cetane value of green diesel indicated that they showed higher cetane value with excellent storage stability in association with excellent cold flow properties. The calorific value is the most important factor that determines the usefulness of biomass in the process of HDO of the vegetable oil and algae oil. Biodiesel fuel is considered to be highly efficient diesel oil in comparison to other fuels because it has higher calorific value. Biodiesel contains approximately 11 wt. % of oxygen because it is associated with lower level of mass energy content in comparison to petroleum and petrochemical diesel. Meanwhile, green diesel is based on zero oxygen level with mass energy content of approximately 44 MJ/kg which is quite similar to petrodiesel that had 43 MJ/kg properties.

The research conducted by Zuo et al., investigated the catalysts that could be used in diesel-like fuel production process through the HDO of the methyl palmitate over the supported Ni catalysts. Table 1 shows the comparison of green diesel with petro-diesel and biodiesel.

Table 1 Comparison of green diesel with petro-diesel and biodiesel.

Fuel Properties	Petrodiesel (ULSD)	Biodiesel (FAME)	Green diesel
Oxygen (wt%)	0	11	0
Carbon (wt%)	86.8	76.2	84.9
Hydrogen (wt%)	13.2	12.6	15.1
CN (Cetane number)	40	50-65	70-90
Kinematic viscosity (mm ² /s) at 40 °C	2-3	4-5	3-4
Specific gravity	0.84	0.88	0.78
Sulphur (ppm)	< 10	< 1	< 1
Cloud point (°C)	-5	-5	-5 to +15
Distillation (°C)	200-350	340-355	265-320
Stability	Good	Marginal	Good
Energy Content—LHV (Low Heating Value)			
Mass basis (MJ/kg)	43	39	44
Mass basis (BTU/lb.)	18,500	16,600	18,900
Vol. basis (1000 BTU/gal.)	130	121	122



Acti

Fig. 2 Schematic diagram of the catalytic HDO converting biomass into green diesel [13].

the schematic diagram of the catalytic HDO converting biomass into green diesel was shown by Fig. 2. HDO as the main process in producing biodiesel fuel by using vegetable oils as the raw materials to produce alkaline type biofuels. The authors were mainly focused on utilizing two main types of catalysts including sulfide CoMo and NiMo that inevitably resulted in contaminating the sulfur in the process of producing final biofuel products. Therefore, the exploration of the non-sulfured catalysts is considered to be highly important, but regarded an open challenge in the process of producing biodiesel fuel addressing

environmental challenges. The authors adopted specifically research methodology by preparing sulfur free Ni in support with SiO₂, HY, HZSM-5 and SAPO-11 through wetness impregnation by testing the performance of HDO catalysts of methyl palmitate in the production of biodiesel fuel. Long carbon chains are used with alkanes by adopting two parallel approaches such as hydrogenation of the hexadecanal to hexadecanol by following the processing of dehydration or hydrogenation to C16 alkane and the decarboxylation of the hexadecanoic acid to the C15 alkane. The acidity of catalysts used in the HDO of the

vegetable oils makes considerable influence on the catalytic performance because the catalysts Ni/SAPO-11 are associated with weak and medium acidity and show superior properties to other catalysts used in the production process of biodiesel fuel. The catalysts used in the process of HDO of the natural oils yielded 93% for C15+ alkanes and observed the wt% of over 7 for the catalysts Ni/SAPO-11 under the mild reaction conditions.

In the catalysis of HDO, there are several methods that are preferred in the green diesel production through the conversion of biomass including mechanical method, chemical, biochemical and thermochemical processes. The chemical process is conducted to experience change in the chemical structure of molecules by ensuring reactivity with other substances. A wide range of chemical reactions are used in the process of ensuring change in the molecular formulation. HDO is regarded as the most promising route which is used in the production of green diesel through the utilization of vegetable oils and animal fats. HDO is basically known as the thermochemical process by which biomass is converted into green diesel. The HDO is specifically used in the process of converting liquid biomass containing triglycerides into hydrocarbons at the temperature level which is recorded higher over the catalytic materials in excessive hydrogen atmosphere. In the areas of describing catalytic hydrodegeneration for the production of biodiesel fuel, the catalytic hydrothermal liquefaction is described as thermochemical process for which biomass materials can be transferred into green diesel. The HDO is the process by which liquid biomass can be specifically used for ensuring the conversion of triglycerides or lipids into hydrocarbons by using high temperatures and pressures using catalytic materials under excessive hydrogen atmosphere. HDO is regarded as thermochemical process by which biodiesel fuel is produced by removing the oxygenated compounds from the water molecules through the effective utilization of two

specific catalyst materials including nickel and zeolite. HDO, as investigated by Stella, is based on liquid biomass process very similar to the processes used in the development of petrochemical products. It describes the higher level of vegetable oil content containing 50 percent weight and it could make substantial influence on the low heating value, thermal and chemical instabilities and immiscibility of the fossil fuels that could increase the tendency of polymerization [14]. The process of HDO is regarded as highly effective and useful process by which the content of oxygen can be successfully removed from the fuel which aids in the production of biofuels. Consequently, the production of green diesel by utilizing biomass-derived carbohydrates is specifically based on the oxygen removal operations [14].

4. Types of Catalysts in DO&HDO of Biodiesel Production

Wang, Bai and Thapaliya described different types of catalysts that could be used for the DO of vegetable oil derived from fatty acids. The production of biodiesel fuel through the catalytic DO is regarded as highly important for renewable transportation purposes. The authors critically investigated the influence of this catalyst DO on the production processes of biofuel. Biomass is used as the major component as the hydrocarbon-based biofuel that can be effectively used for the production of biodiesel or bioethanol as the alternate to diesel or petroleum products. Among different types of catalysts, most promising feedstocks are used as vegetable oils and animal fats that can be used as excellent resources for the triglyceride-based biofuel production. The increased oxygen content is the greater disadvantage of these production processes by which triglyceride-based biofuels are produced. Low heating value, polymerize tendency, thermal instability, fossil fuel immiscibility and high level of viscosity are associated with greater challenges for these oils. Hydroprocessing technology has been specifically used in the thermos-catalytic processes to provide

better solutions in the triglyceride-based biodiesel production by using different types of catalysts.

The research conducted by Zhao et al. presented detailed review of the heterogeneous catalysts that could be effectively used for the catalytic upgradation of vegetable oils into biodiesel or biofuels of hydrocarbon hydro-processing. The authors specifically described the catalytic cracking as well as hydroprocessing of the vegetable oils derived from the oilseeds. They presented these two promising pathways by which the natural oils or vegetable oils can be successfully converted into hydrocarbon biofuels. The authors described heterogeneous catalysts as the most influential catalysts in the hydroprocessing of vegetable oils into biodiesel fuels. The review presented by authors in this research work examined current developments that were associated with the upgradation of vegetable oils into biofuels along with potential challenges. The properties, application, deactivation as well as regeneration processes were also identified in the research to determine the potential influence of heterogeneous catalysts in the hydrocarbon biofuel production. The authors adopted the comparative analysis of the catalysts that played an important role in upgrading the vegetable oil into biodiesel. They provided some important suggestions by which these catalysts can be applied to the process of upgrading vegetable oils into biodiesel by improving the quality of hydrocarbon biofuels. The authors indicated that the reduction of GHG (greenhouse gas) emissions is only possible if renewable energy resources are utilized to produce biofuels generated from biomass as the great alternative for the fossil fuels that are responsible for environment pollution. The conversion of biomass into biofuels through the heterogeneous catalysts has become a challenge for the chemists due to the higher oxygen content of the bio-oils along with their lower heating value, their corrosiveness to common metals, acidic nature of the catalysts and their thermal unstable condition [15,16].

Catalytic cracking has been presented as the most

influential method by which the raw materials (vegetable oil) can be transferred into biodiesel successfully. In the process of catalytic cracking, 380-525 °C reaction temperature was used to ensure the smooth processing of the chemical reaction to convert vegetable oils into biofuels. The described that lower temperature could never be capable to crack down the preliminary catalysts. Therefore, there was a need to increase the formation of reaction gases temperature to ensure successful cracking of the catalysts and 450 °C was regarded as the most suitable reaction temperature to enhance the biofuel production by reducing the char/coke yields. Furthermore, in the process of catalytic cracking of the vegetable oil, different ranges of the pressure were used starting from 1 atm to 99 atm to enhance the performance of the reaction process. The operating conditions are regarded as highly important in association with composition of the feedstocks to affect the catalyst deactivation to transfer the vegetable oil at the mass level to the biofuels. The authors described several reactions during the catalytic cracking process of decarboxylation and deoxidation to ensure the removal of oxygen atoms from the triglyceride molecules. The catalytic cracking of the vegetable oil has been regarded as highly influential method for the hydrocarbon of biofuels that was based on the biogasoline, liquid product based on organic materials and diesel-oil similar to hydrocarbons. The research indicated that in the bio-oil upgradation process, the coke yields of vegetable oil were largely dependent on the species of catalyst and their operational conditions. The catalytic cracking to be conducted for the vegetable oils produced higher results with more total hydrocarbon liquid products when they were compared to the catalytic cracking of the bio-oil.

The research work conducted by Chiappero et al., described the conversion of paraffins and olefins through triglyceride of catalysts in the DO of the methyl esters. The authors indicated that the interests of producing green diesel have been increased in the

past few years through the constant utilization of natural fats and vegetable oils as the potential feedstocks to produce surfactants and other chemicals. The authors described the transesterification of the triglycerides through the utilization of methanol to ensure the successful conversion of triglycerides into so-called biodiesel that contains fatty acid methyl esters. A selective path conversion process was used to convert the alpha-olefins into biodiesel from various types of renewable feedstocks. The authors indicated that hydrotreating has been regarded as highly effective and useful in the process of HDO to convert vegetable oils to hydrocarbons in flow and batch modes. The direct hydrogenolysis and hydrogenation activity was directly observed in the process of converting vegetable oils or animal fats into biodiesel. Two important processes were identified by the authors including thermal or catalytic cracking process by which animal fats or vegetable oils were cracked through batch reactors to produce hydrocarbons in the gasoline rather than producing diesel range products. Therefore, hydrogenation of the vegetable oils needed more control to ensure the successful conversion of vegetable oils into biodiesel over Ni containing catalyst that was extensively studied in the research work. The linear chains of hydrocarbons were produced through the hydrogenation or DO reactions but some unacceptable and aromatics products were formed in the process of producing biodiesel from the vegetable oils to hydrocarbons. In the catalyst preparation, the authors described platinum catalysts including Pt/Al₂O₃ along with Pt/SiO₂ as well as bimetallic catalysts including PtSn/SiO₂ and PtSnK/SiO₂. These catalysts were prepared through the incipient wetness impregnation but they adopted highly complex methods for the production of biodiesel through the DO of the catalysts. In the platinum catalysts, tin including 99.99 percent of chloride, anhydrous and power and chloroplatinic acid hexahydrate was based on the quantity of 99.9 percent, respectively. The tin and platinum compounds were dissolved into the

hydrochloric solutions before the successful addition of active components or promoters to the complex methodology of the biodiesel production. In the characterization of the catalysts, 100 milligrams of the catalysts were used in different TPR (temperature programmed reduction) with 1 percent Pt/SiO₂ to 1 percent Sn/SiO₂ and 1 percent Pt to 1.3 percent Sn/SiO₂ combinations with molar ratio of 1:2 and 1 percent Pt to 1.3 percent Sn and then 1.5 percent K/SiO₂ with molar ratio of 1:2:7 where TPR experimentation was carried out in the heating ramp of 10K/min to 973K. In the catalyst activity, the experiment was carried out with the pressure of 300 mL in the liquid phase by using the stirred reactor. A reactor was used for the placement of catalyst at the initial stage and it was reduced to 2 h at 623 K under the H₂ flow. The liquid feed was used in the experimentation process containing methyl octanoate in the *n*-dodecane along with methyl laurate in the *n*-hexadecane and it was added to the reactor by using an external reactor to prevent the air from entering. The semibatch mode took place in the early reaction of the experiment for the continuous removal of the product by flowing He. In the first trap, ice water was arranged while the second trap was based on ice and acetone. The reactions were conducted by using the 6h with liquid samples that were controlled in both the traps. The results of the research indicated that the catalyst Pt/SiO₂ had showed single reduction peak at just 400K and above and it corresponded to the reduction of platinum oxides to the metallic platinum. The peak temperature was also observed in the experiment and it corresponded to the dehydroxylation activity of the silica support. The catalyst Sn/SiO₂ showed considerable reduction peak at the 773K that corresponded to the tin reduction while PtSn/SiO₂ catalyst showed three times hydrogen consumption region. The results indicated that the peaks in all cases were related to different alloys of the PtSn containing PtSn, Pt₂Sn and PtSn₄ and the results proposed EXAFS (extended X-ray absorption fine structure), X-ray

diffraction, and TEM (transmission electron microscope) and no peaks were observed around 773 K. Finally, when the addition of potassium was increased, two broader peaks were also observed in the experimentation process where first peak was recorded at around 550K while the second peak was recorded at around 750 K that matched the tin reduction temperatures and suggested that there was some unalloyed tin found in the catalyst [17].

Baldauf, Sievers and Willner pointed out different types of catalysts including CoMo/Al₂O₃ and Pt/C catalysts that could be used in the HDO process of cracking vegetable oil and producing biodiesel fuels. The authors described the continuous processes of catalytic HDO to ensure the cracking of vegetable oils by which CO₂ and CO were observed in the reaction of gases and in addition to these hydrocarbon gases CH₄ and C₂H₆ were also observed. The catalysts that were preferred by the authors included CoMo as the cobalt-molybdenum and Al₂O₃ as supporting platinum Pt on the active carbon. The decomposition of the continuous thermal cracking of vegetable oils (CVO) was experienced and results were observed through the batch experimentation. The results indicated that GPRs (ground penetrating radar) or gas phase reactions at 50 bar H₂ temperature showed similar catalysts (CoMo and Pt) which indicated that CO and CH₄ can be formed by the decomposition process. The average water gas reaction process produced CO while CH₄ was produced from the CO and CO₂ methanation process [35]. The research work conducted by Baldauf, Sievers and Willner was focused on answering three important questions in the areas of using catalysts for HDO process of producing biodiesel fuel from the vegetable oil. The research was focused on determining the gaseous and liquid products that were produced in the HDO and CVO processes. It examined the gaseous and liquid phase composition interrelationship in the HDO of the natural oils. It examined the type of GPRs that was observed in the parallel processes of HDO and CVO. The authors examined the influence of two

different types of catalysts including the CoMo/Al₂O₃ and Pt/C in the HDO of the natural oils into biodiesel production through continuous experimentation of HDO and CVO [35].

5. Types of Feedstocks Used in Biodiesel Production

Pasqualino et al. [18] indicated that the production process of biodiesel is based on highly complex process by which biomass and plant oil could be successfully converted into bio-oil through the conversion of fast pyrolysis and appropriate upgradation of animal feedstocks into liquids. It was regarded as an excellent alternate to the petroleum products [19,20]. The name biodiesel was derived from biomass and plant oil and generally it is used in the form of feedstocks that were obtained from the conversion of pyrolysis by upgrading it into liquids that could be substitute of crude oil. The biodiesel was also used for the triglyceride transesterification of vegetable oil and in properties it was similar to the crude oil. Commonly acceptable raw materials of biodiesel production are based on different types of seeds and natural oils such as soybean oil, canola, corn oil, rapeseed, palm oil, mustard seed, sunflower, peanut and cottonseed. In the areas of animal fats, the most commonly used fats include beef fats, poultry fats and pork fats. Biofuel is based on highly oxygenated mixtures containing large amount of macromolecules involving oxygenated organics of all species including esters, ketones, phenols, organic acids and aldehydes. The average composition of raw pyrolysis oil is based on 65 percent of organic components, 30 percent containing water and 20 percent of the lignin fraction by which more than 400 organic components could be detected and classified into groups such as aldehydes ketones, phenolic compounds and organic acids.

5.1 Pyrolysis-Derived Bio-Oil

Biomass pyrolysis process is used for the development of biomass pyrolysis oil that can also be

known as bio-oil, bio-crude or pyrolysis oil. In order to ensure the successful production of bio-oil, rapid cooling process is required and quenching pyrolysis temperature is needed. In the areas of bio-oil, the properties of this oil could be substantially improved through the process of esterifying carboxyl and hydrotreating under mild conditions. The carboxylic acid compounds also have the ability of conversion into alcohol that would esterify with the acids that could never be converted into the bio-oil to produce esters. also indicated that the conversion of vegetable oils into bio-oil is possible through the HDO of the pyrolysis oil with properties of 5 wt% by utilizing the Ru/C catalyst through the required conditions of 290 bar, 230-340 °C with the reaction timeframe of 4 h in total to produce the desired results. The authors indicated that despite different properties of hydrodeoxygenation process, the pyrolysis oils could be successfully dissolved into 20% of long residue along with co-processed of the FCC.

5.2 Vegetable Oil as the Main Ingredient of Biodiesel Production

Hydrogenations of vegetable oils are used in the DO process to produce vegetable oils into biofuels. The biodiesel produced from the vegetable oils is associated with reduced level of CO and hydrocarbon emissions of 69% and 63% respectively could be highly effective and useful for the diesel engine life. In the process of biodiesel production, the partial hydrogenation is regarded as highly influential to improve the functional behaviors of vegetable oil. Typically, the process of developing vegetable oil into biodiesel is known as HDO under mild reaction conditions that range from 100-180 °C with the pressure values of 0.15 to 0.3 MPa respectively, and the value of Ni noble metals is supported by silica support. The research work conducted by Sendzikiene et al. [21] indicated that HDO is based on hydrogen consumption process according to the type of vegetable oil used in the conversion process. The conversion of vegetable oil to the biodiesel is also related to the

mechanism of the HDO. Feedstocks are made to be highly saturated in terms of animal fats and palm oil to get necessary benefits of reducing hydrogen requirements in the conversion process of vegetable oil to the biodiesel fuels. Feedstocks of palm oil and animal fats are specifically used for producing the commercially renewable diesel based on saturated feedstocks. According to the authors, camelina oil in the categories of vegetable oil is associated with higher amounts of unsaturated fatty acid chains with an overall estimation of around 27% to 40% with 18 to 3 ratio and it could be used for the production of hydrocarbons of the aviation fuels to be suitable for lowtemperature needs of presenting more cleavage sites in the production process [22]. The authors also described some other types of oils that also contain higher amount of unsaturated fats and associated with feedstocks that could be used in the aviation industry. Linseed oil could be another suitable choice that contains approximately 47% of unsaturated fats with 18 to 3 ratio [23]. The authors indicated that in the process of producing biodiesel from the vegetable oil, it is directly converted into hydrocarbons by using the total hydrogenation as the most promising route to be used for the production of biodiesel. The process which is adopted in the production of biodiesel fuel is based on the components of total hydrogenation of the vegetable oils and it has been developed and commercialized by the Neste Oil Finnish Company. However, the processing of vegetable oil into the hydrocarbons and then into the renewable diesel oils is regarded as difficult in terms of metallurgy reaction because the process could produce higher acidity in the standard hydrotreating of the reactors because only non-standard bonds could be effectively used as the triglycerides of exclusive components of the vegetable oils that are hydrogenated successfully.

6. Catalytic DO Pathways for Biodiesel Production

The catalytic DO pathways by which biodiesels are

produced by adopting the model compounds of biodiesel production. In the objectives of the research, the author described the strategy for catalytic biomass pyrolysis along with hydrogen were described by Abdulkareem-Alsultan et al. [12] and Bezergianni and Dimitriadis [14] investigated how to enhance the activity of DO in the catalytic DO pathways. They examined the hydrogen utilization at the lower pressure and determined how effectively its utilization could be increased by maximizing the recovery of carbon in the liquid product. In the areas of strategic development for catalytic DO pathways, [12] examined the utilization of different models for testing the DO activity and evaluating the effects of various fluidizable supports. The strategic evaluation of the research also investigated the screen catalysts that could be used in the DO process with different range of reaction conditions by determining reaction pathways to drive the catalyst development. [14] described different types of catalysts in the research including SA1, SA1-A, SA1-B, SA2, SA2-A, SA2-B, MMO1, MMO1-A and MMO1-B with solid acid and mixed metal oxide as the support catalysts. These catalysts are shown in Fig. 3 and also elaborated the automated compound reactor model by which programming of the reaction pathway was used with reaction and oxidation sequences, rapid screening to evaluate the DO activity

with model compounds determined as various levels and conditions. In experimental conditions, described different conditions for hot box temperature, reactor temperature, pressure, multiple carrier/feed gases, multiple reduction and oxidation gases and the testing of model compounds with anisole and guaiacol. In analytical methods, reaction steps and oxidation steps are described. In the reaction steps, 96 percent of conversion was described by which complete DO was presented with the development of products in the early reaction along with less DO and oxygen removal as water in the reaction process of the DO to convert biomass into biodiesel. The reaction and oxidation steps are shown in Fig. 4.

The results received on biomass pyrolysis indicated that there was an increased carbon recovery in the liquid product from SA2 and was received with lower level of oxygen content yielding less weight. The guaiacol DO reaction pathways were found and observed in the research as shown in Fig. 5 given below.

The research work conducted by Ko et al., [36] indicated that catalytic DO of the biomass was regarded as the most influential method by which it could be upgraded to biofuel. Bio-oil and biodiesel are produced through the DO of the biomass by adopting vast range of methods. The quality of biofuels depends

Support Type	Catalyst Name	Description
Solid Acid	SA1	Alumina-based
	SA1 – A	Alumina, low Ni loading
	SA1 – B	Alumina, high Ni loading
	SA2	Transition metal oxide
	SA2 – A	Transition metal oxide, low Ni loading
	SA2 – B	Transition metal oxide, high Ni loading
Mixed Metal Oxide	MMO1	Fe-based
	MMO1 – A	Fe-based, low Ni loading
	MMO1 – B	Fe-based, high Ni loading

Fig. 3 Types of catalysts with their descriptions.

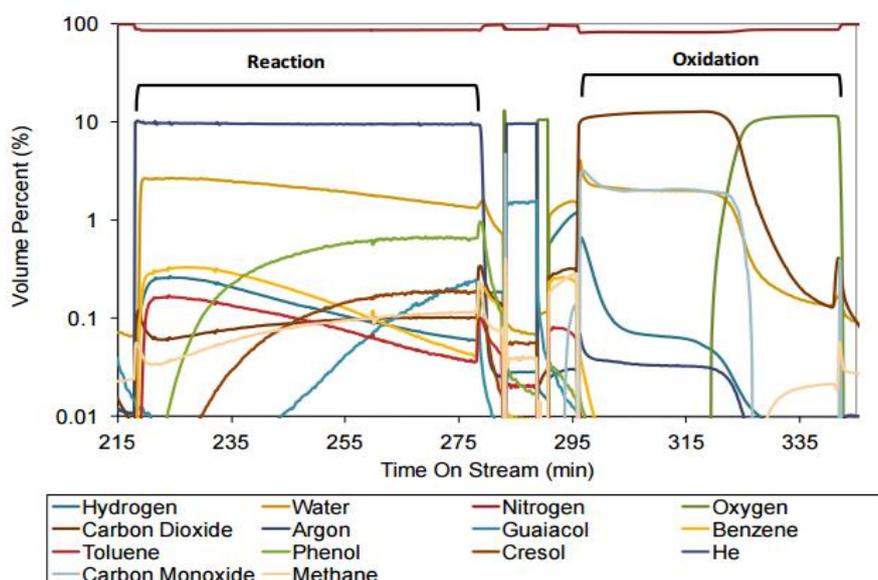


Fig. 4 Reaction and oxidation in the DO of biomass.

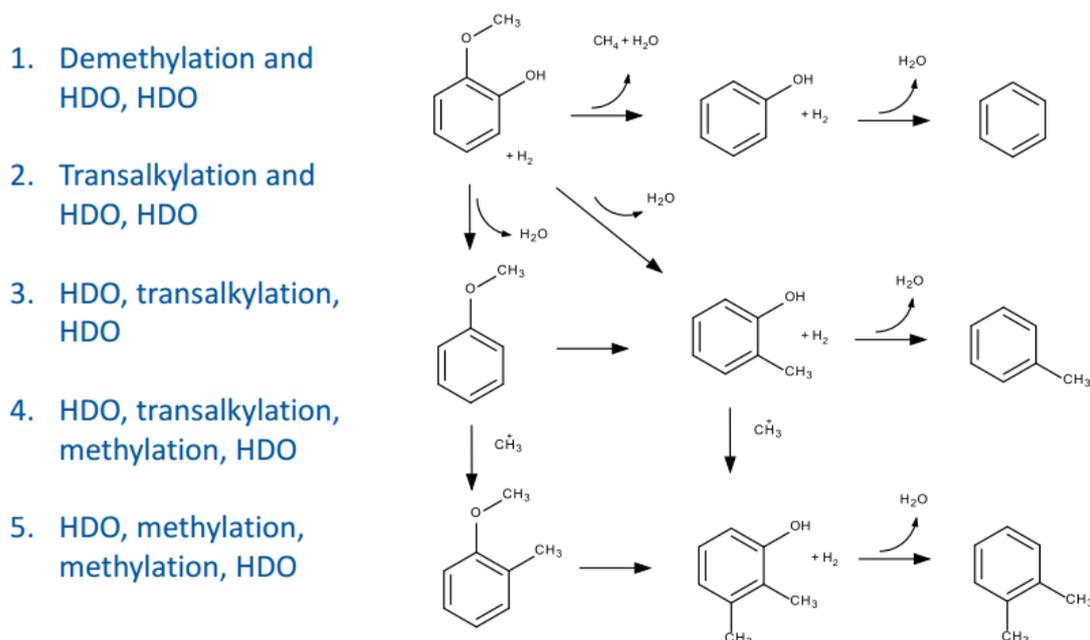


Fig. 5 Reaction pathways of DO process in the biodiesel production.

largely on the quantity of oxygen content and if the large content of oxygen is not removed from the biofuel, its quality could never be improved. In order to achieve desired results, the DO of the biomass is regarded as highly essential to upgrade the chemical properties of the biofuel. The authors have specifically reviewed the recent developments and pathways by

which catalytic DO of the biomass can be used including catalytic cracking of bio-oil as a promising method that could be used to enhance the bio-oil quality. The authors investigated different types of catalysts that were used to facilitate the DO of the biomass including mesoporous zeolites, microporous zeolites and the metal oxide for the catalytic cracking

of the biomass. Furthermore, various methods were also investigated and developed to eliminate the coking of catalysts and to make them capable of working with increased lifetime. In addition, the efforts regarding DO of the biomass with associated catalysts were also examined to determine the potential influence of process parameters for optimizing the composition of the final product. Two specific pathways were adopted by Hernando et al. [25] to ensure the catalytic upgradation of the triglycerides to the hydrocarbon-based fuels. Hydrodeoxygenation of the biomass was carried out for the elimination of the oxygen atoms from the H₂O hydrogenation triglycerides. The hydrogenated diesel was produced through the effective utilization of HDO to ensure the smooth operations of catalysts and the process by adopting well established technological solutions such as hydro-desulfurization. Most of the companies in the recent years have tried to establish commercialized HDO processes through the successful consumption of huge amount of hydrogen. In order to resolve the hydrogen problem associated with hindering the widespread use of HDO, minimum utilization of hydrogen is preferred in the DO of the biomass. Precious metal-based catalysts were preferred in the DO of the biomass because they showed reasonably better activity to deoxygenate the reagent-grade fatty acids through the batch-mode reaction method. Furthermore, the authors [25] indicated that the continuous hydrocarbon production in a fixed-bed was associated with reduction in the catalytic activity due to the coke deposition. The catalytic DO was largely based on maintaining to achieve the widespread production of the hydrocarbon-based fuels with their biological origin [20]

Hernando et al. [25] also described the DO pathways in the process of converting biomass into biofuels by assessing the biomass catalytic pyrolysis through efficient production of advanced biofuels. The authors identified the pathways by which catalytic pyrolysis of biomass could be performed to proceed it into bio-oil

by ensuring the effect of the operation conditions on bio-oil oxygenation composition and mass yield. The authors described the distribution of oxygen energy and chemical energy in the initial process of biomass by which different products related to bio-oil were produced. In the areas of biomass feedstock acid washed wheat straw was used to conduct the pyrolysis tests at the lab environment to determine the fixed-bed reactor working at the atmosphere pressure by employing the catalysts of nanocrystalline of H-ZSM-5 zeolite [25,45]. In order to examine the catalytic reactions, a systematic study was conducted to decouple both the thermal and catalytic reactions to examine the influence of three major variables on the DO of the biomass through thermal temperature zone, subsequent catalytic temperature and the ratio of catalyst to biomass used in the thermal and catalytic reactions. When the temperature of pyrolysis was increased in the thermal zone, it produced bio-oil on water-free basis by determining the char and water fractions. On the other hand, when the catalytic bed temperature was increased from 400 to 500 °C, the bio-oil production showed a significant decline due to the decarbonylation and decarboxylation of the biomass. also examined similar influence when the catalyst to biomass ratio was observed since it was associated with increased production of CO, CO₂ in the presence of coke and light olefins at the expense of reducing the bio-oil yield. Nevertheless, the results indicated that the bio-oil produced through the DO of biomass through this specific pathway contained oxygen as low as 10 wt% by retaining energy yield of 38% while coke, char and gaseous hydrocarbons were based on great part of the biomass chemical energy because their formation surpassed to further improvements in the bio-oil energy yields. The authors [25] observed the higher ratios of catalyst to biomass with bio-oil becoming rich in aromatic compounds showing hydrocarbon and oxygenation by showing considerable reductions in the oxygenated products of sugars, furans and carboxylic acids.

The research work conducted by Santillan-Jimenez and Crocker [37] critically investigated the catalytic DO of the fatty acids through the decarboxylation/decarbonylation of the biomass associated with their hydrocarbon derivatives. Fatty acids along with their derivatives could be successfully converted into the renewable energy sources such as hydrocarbons based on carbon-neutral fuel that were entirely fungible with the fossil fuels. The authors indicated that hydrotreating was associated with significant disadvantages when sulfided catalysts were used along with higher hydrogen pressure. In the areas of biodiesel fuel production, decarboxylation or decarbonylation has been proposed as the most significant method that could be used along with simpler catalysts and less quantity of hydrogen as required in the hydrotreating method. Therefore, decarboxylation was described as the most influential method in the process of DO to convert fatty acids and their derivatives into biofuels. The authors critically investigated the potential influence of feed, catalysts, reaction conditions and the reactor system on the decarboxylation or decarbonylation reaction in association with reaction mechanism and the deactivation of the catalysts in the biodiesel production process. In the areas of renewable energy sources, biofuel has been encouraged as an effective alternate to diesel and diesel-related products. The renewable energy sources are efficient because they are associated with decreased environmental concerns in comparison to other petroleum sources. Biofuels are usually derived from the biomass and the authors described them as the most effective sources of biodiesel production derived from biomass as renewable, carbon-neutral alternatives of the fossil fuels. The authors indicated that there had been large numbers of biofuel production sources over the years. Decarboxylation/decarbonylation reaction process was preferred in the current research because it needed less quantity of hydrogen along with simple catalysts. The transesterification of the triglycerides was also

proposed as the sources of converting vegetable oils and animal fats into fatty acid methyl esters in the process of biodiesel production. Saturated and high oxygen content are the greater disadvantages of the biodiesel or biofuel and they needed the method that could reduce higher oxygen content. Therefore, this pathway has been recognized as most effective and influential to convert the biomass into biodiesel or biofuel addressing environmental concerns and providing highly efficient energy resources to their customers.

7. Factor Influencing the DO Process

In this section of the literature review, different factors influencing the DO process are evaluated such as feedstocks, reaction atmosphere, reaction temperature, catalyst amount and the use of solvent. These factors are described in detail below to evaluate their potential influence on the DO process in the production of green fuel from the biomass.

7.1 Feedstocks

Abdulkarem-Alsultan et al. [12] evaluated biomass-derived feedstocks in the process of DO by describing hurdles and opportunities in the energy generation process. Dutta [38] explored that feedstocks have received increasing attention in the recent years because they can be effectively used for the production of renewable energy for transportation of fuels and chemicals. The research evaluated that the carbohydrates of the biomass-derived substrates are based on largest portions of biomass feedstocks [26]. These feedstocks are successfully converted into renewable energy with the set of platform molecules into tailored products and services. They investigated the conversion of cellulosic biomass molecules into the renewable energy oils and chemicals. The researcher pointed out that these feedstocks have gained huge importance in the recent years because they are associated with sustainable sources of energy production. But, Dutta [38] inspected fundamental challenges that the biomass feedstocks conversion process is facing due to high oxygen

content of the saccharides. The research evaluated that polyols are considered to be highly suitable feedstocks for the selective transformation of the biomass into the renewable fuel and chemicals. The researcher evaluated that in the hydrogenation of the sugar and cellulose into platform chemicals have exhibited poor solubility in the organic solvents and their manipulation is also difficult. The research conducted by Dutta [38] indicated that efficient DO reactions are essential to derivate sugar and cellulose in the presence of high temperature and acid catalyzed dehydration.

Popov and Kumar [27] also investigated the catalytic HDO process of the lipid-based feedstocks in converting the bio-fuels into renewable fuels for transportation purposes. Popov and Kumar [27] identified that biomass with higher content of lipid has become the highly attractive feedstock to be used for the successful production of renewable fuels. The researchers explored that biomass-derived fats as well as bio-oils have the chemical characteristics that can be used to convert them into biodiesel through the well-organized transesterification process. Therefore, the lipid-based feedstocks as explored in the research are proven to be more attractive as well as fungible options in processing the bio-fuels into the petroleum derived products through chemical composition of the indistinguishable materials [27].

7.2 Reaction Atmosphere

The research work conducted by Pattanaik and Misra [28] investigated the influence of reaction atmosphere in the DO process. Pattanaik and Misra [28] evaluated the effects of the reaction atmosphere as well as operating parameters on the DO of the bio-oils into diesel range hydrocarbon fuels. The researchers pointed out that fossil fuels have achieved increasing demand in the recent years because they are useful for environmental protection. The research also indicated that biodiesels have been synthesized from the animal fats and the vegetable oils because they showed the potential of alternative diesel fuels containing

comparable combustion and properties characteristics. The researchers pointed out that biodiesels have higher level of oxygen contents and raised concerns for their utilization in the diesel engines. It increased the attention of researchers and renewable energy developers on the second generation liquid hydrocarbon fuels that can be developed through catalytic DO of the vegetable oils and fatty acids. Pattanaik and Misra [28] mainly focused on the reaction atmosphere or pathways for the catalytic DO or HDO. Therefore, the researchers explored that reaction temperature, reaction atmosphere, feed type and type of solvency can make considerable influence on the operating parameters of the catalysts used in the production processes of catalytic DO.

7.3 Reaction Temperature

The research conducted by Griffin et al. [29] identified the influence of reaction temperature or conditions on the DO of the *m*-cresol over chosen catalysts known as Pt/C and Pt/TiO₂. The researchers indicated that catalytic DO has become the most effective method of converting the biomass into liquid transportation fuels that are environmentally friendly in comparison to fossil fuels that cause increased level of GHG into the environment [29]. Due to their environmentally friendly nature, the conversion of biomass into renewable energy sources has gained huge importance by the mechanistic in determining the role of catalyst supporting the influence of reaction temperature. The researchers investigated the conversion of biomass into renewable fuels through the DO of the *m*-cresol over the Pt/C and the Pt/TiO₂. By adopting experimental and computational techniques, Griffin et al. [29] pointed out that reaction temperature is influential in the process of direct DO and ring hydrogenation. The results collected by the researchers indicated that reaction temperature could be influential in the presence of synergic effects between the hydrogenation catalysts and metal oxides that provide considerable support into the reaction pathways for the

enhanced DO performance in the given period of time.

8. Recent Progress of DO of Realistic Oil

Chen [30], identified the recent progress of the DO of the realistic oil to be used for the transportation purposes in an environmental manner [30,31]. They indicated that fossil fuels resources are recognized to be dangerous for the environments and not sustainable for the long-term socio-economic development in different parts of the world. The GHG emissions associated with fossil fuels have increased the attention of governments and their policymakers to enhance the production of renewable energy sources through the catalysis DO of the biomass into realistic oil by ensuring their promises to the associated environments. The shift of the people from the fossil fuels to biofuels and bio-products is encouraged in different countries developed through alternate industrial feedstocks and green processes to live in environmentally friendly environment. The research articles presented by Chen [30] indicated that bio-oils and the gaseous fuels which are developed from the biomass materials, wastes, agricultural crops, feedstocks and forestry products have gained increased attention in the modern times. These green oil products have reduced the net carbon dioxide emissions by 78 percent in comparison to the dangerous elements of conventional diesel products and services produced from fossil fuels [30,31]. The alternative gaseous fuels have made considerable improvements on the environments by decreasing CO emissions by around 46.7 percent and unburned carbons by 45.2 percent. Therefore, biofuel products are very encouraging in the recent years and they have provided new prospects of energy for the transportation purposes in the absence of conventional diesel products. The growth of alternative fuels has made considerable influence on the petroleum refining companies.

9. Factors Responsible for Influencing DO Process in Green Oil Production

There are various important factors that were

responsible for the production of biodiesel through DO of the vegetable oils and animal fats. According to authors, biodiesel has become an excellent alternate of the diesel fuels produced through fossil fuels. The authors indicated that it was difficult to fully replace the petroleum diesel fuels with biodiesel fuel because the production of biodiesel has limits along with limited natural oils and animal fats and other available resources. The production of biodiesel was only possible through the transesterification reaction by which different types of animal fats and vegetable oils could be transferred into biodiesel fuel by using different types of catalysts [10,32]. The reaction was associated with alcohol molar ratio that was specifically used to reduce the content of water and other FFAs (free fatty acids) by utilizing specific reaction temperature, catalyst concentration and the agitation speed. The authors highlighted that biodiesel has now become a reality in the modern world because it is regarded as an excellent alternate to the petroleum diesel fuel and useful to reduce environment pollution cause by fossil fuels. The depletion of world petroleum resources also demand the governments of the world to increase their concentration on alternate energy and biodiesel fuel resources to reduce environment pollution, climate change and other important environmental related issues. The authors indicated that vegetable oils and animal fats are excellent source of converting biomass into biodiesel fuels. Vegetable oil is associated with higher viscosity that makes it impossible to the biodiesel production, but this viscosity of vegetable oil can be successfully reduced by applying different methods such as blending, micromulsification, pyrolysis and transesterification [33]. From all these effective methods of reducing viscosity of the vegetable oil, transesterification method has been widely accepted by the chemists at the commercial level to convert vegetable oils into biodiesel fuels through the transesterification method. The transesterification reaction is associated with several potential factors such as alcohol molar ratio,

catalytic triglycerides, water presence in the vegetable oils, FFAs, reaction temperature level, agitation speed and the reaction time that was needed to produce biodiesel from the vegetable oils. In the research work, Gnanaprakasam specifically described the effects of molar ratio of alcohol in the yield of biodiesel through the transesterification of vegetable oils. The normal level of transesterification reaction that needed 3 mol of alcohol to address the requirements of one mol of triglycerides to the fatty acid esters of three mol along with one mol of the glycerol. The research indicated that increased amount of alcohol would result in the increased level of fats conversion into esters within the shortest period of time. It indicated that the yielded biodiesel would be increased with an increase in the concentration of the alcohol up to certain level of concentration. However, further increase in the content of alcohol would not be essential to increase the biodiesel production but it would increase the costs of alcohol recovery. In conducting their research work, the authors also examined the influence of waters and FFAs on the transesterification reaction. The transesterification reaction based on base-catalysts would need water and FFAs at the lower level with approximately <1 as the raw materials to ensure good amount of transfer into biodiesel production. The authors also investigated several other factors that could be influential in the transesterification reaction to convert vegetable oils into biodiesel fuels such as catalyst concentration, agitation speed and reaction temperature that could be influential in the production of biodiesel fuels.

Liu et al. [40] examined different factors that were responsible for the production of bio-hydrogenated diesel through the process of hydrotreatment by using high-acid-value cooking oil. The authors described various catalysts that were used in the production of bio-diesel fuel such as ruthenium catalyst along with supporting catalysts of Al-polyoxocation-pillared montmorillonite. WCO was used in the research with acid value of 28.7 mg-KOH/g-oil to be used for

converting the cooking oil into bio-hydrogenated diesel through hydrotreating process over the Ru supported catalysts. The hydrotreatment process was associated with various important factors that were exercised in converting the WCO into bio-hydrogenated diesel containing H_2 pressure, standard reaction temperature, liquid hourly space velocity (LHSV), H_2 to oil ratio with 350 °C, 400 mL/mL, 2MPa and 15.2 h^{-1} respectively. The process of DO was conducted to reduce the quantity of FFAs and the triglycerides that was present in the WCO to form hydrocarbons in the hydrotreatment process. When Ru/SiO₂ catalyst was used in the hydrotreatment process along with hydrocarbon products including n-C₁₈H₃₈, n-C₁₇H₃₆, n-C₁₆H₃₄ and n-C₁₅H₃₂ containing longchain of normal hydrocarbons showing high melting points with liquid hydrocarbon products over the catalyst of Ru/SiO₂ along with high pour point of 20 °C. The authors indicated that the catalyst Ru/H-Y was not suitable for the current research to produce bio-hydrogenated diesel from the WCO because it was associated with large amount of C5 to C10 with gasoline-ranged paraffins on the strong acid sites of the HY. Through the utilization of Al₁₃-Mont along with support catalyst of Ru catalyst, the pour point of the liquid hydrocarbon showed a considerable decline to -15 °C by showing a significant conversion of C15 to C18 n-paraffins to iso-paraffins along with light paraffins by using the weak acid sites of the chosen catalyst. The characterization of the raw montmorillonite and its Al₁₃ pillared derivative has been shown in Table 2 given below [46].

10. Recent Progress of DO of Realistic Green Oil World

The research work conducted by Cardoso et al. [41] described recent progress made in the DO of green oil production through the esterification of oleic acid along with catalysts of SnCl₂. The authors indicated that biodiesel production has increased in the recent years due to their environmentally friendly

characteristics and they provided an excellent alternate of petroleum diesel fuels that were associated with higher content of carbon emissions into the air. The DO of the raw materials containing vegetable oils and animal fats contained high content of FFAs that made them more competitive in comparison to petroleum-derived fuel. The authors presented two specific approaches that were adopted recently in the production of biodiesel through the utilization of low-cost raw materials. These two approaches included the initial acid-catalyzed esterification of the FFAs that were followed by the process of triglycerides of the base-catalyzed transesterification. In the first step of the catalyzed transesterification process, H_2SO_4 was used along with tin(II) and chloride dehydrate ($SnCl_2 \cdot 2H_2O$) as the inexpensive Lewis acid and regarded as major component in the production of biodiesel fuel by using several fats and vegetable oil feedstocks. Tin chloride was used in the research work because it was found to be very useful in converting the oleic acid into ethyl oleate under mild reaction conditions where $SnCl_2$ catalyst was associated with mineral acid H_2SO_4 . The authors presented the potential environmentally friendly benefits of acid catalysts that were used for the production of biodiesel directly from the low-cost lipid feedstocks that were associated with high FFA concentrations. The conversion of these feedstocks into biodiesel through acid-catalyzed conversion process leads to the formation of significant water quantities along with making negative influence on the biodiesel production process because water can hydrolyze the ester products

by again producing FFAs.

Shi et al. [34] also described recent developments that have been made in the production of biodiesel fuel through the catalytic conversion of raw materials by using microalgae as experimentation and simulation processes. The authors identified non-renewable resources that have increased concerns about climate change and environmental complications in the recent years. The production of biodiesel fuel has increased because they are regarded as an effective alternate to fossil fuel-derived transportation fuels [34,44]. The production of biodiesel fuel has shown continuous increase in the recent years due to their potential of fast growth, high oil content and their ability to grow well during unconventional scenarios with inherent carbon neutrality. Furthermore, the utilization of microalgae has reduced the concerns that were associated with several biomass strategies because it provided no problems to the food crops associated with the food chains. The authors critically reviewed the progress made in the production and development of biodiesel fuel as the major source of transportation oil through the adoption of homogeneous and heterogeneous catalytic conversion of the microalgae. It described important tools and techniques that were associated with the production of biodiesel fuel by understanding the fundamental importance of catalysts, catalytic conversion reaction pathways and their conversion process by using computational modeling techniques. The authors investigated the catalytic conversion reaction pathways that were used in the production of biodiesel fuels through two specific approaches

Table 2 Characterization of raw montmorillonite along with its Al13-pillared derivatives.

Sample	$T_{\text{calination}}$ (°C)	d_{001} (Å)	BET (m^2/g)	Total V_p (cm^3/g)	Micro V_p (cm^3/g)
Na-Mont	25	12.4	82	0.079	0.004
	300	10.6	38	0.068	0.005
	400	10.5	29	0.065	0.004
	500	-	26	0.063	0.003
Al ₁₃ -Mont	25	19.2	156	0.150	0.078
	300	18.5	237	0.170	0.111
	400	18.5	270	0.180	0.122
	500	17.9	189	0.152	0.103

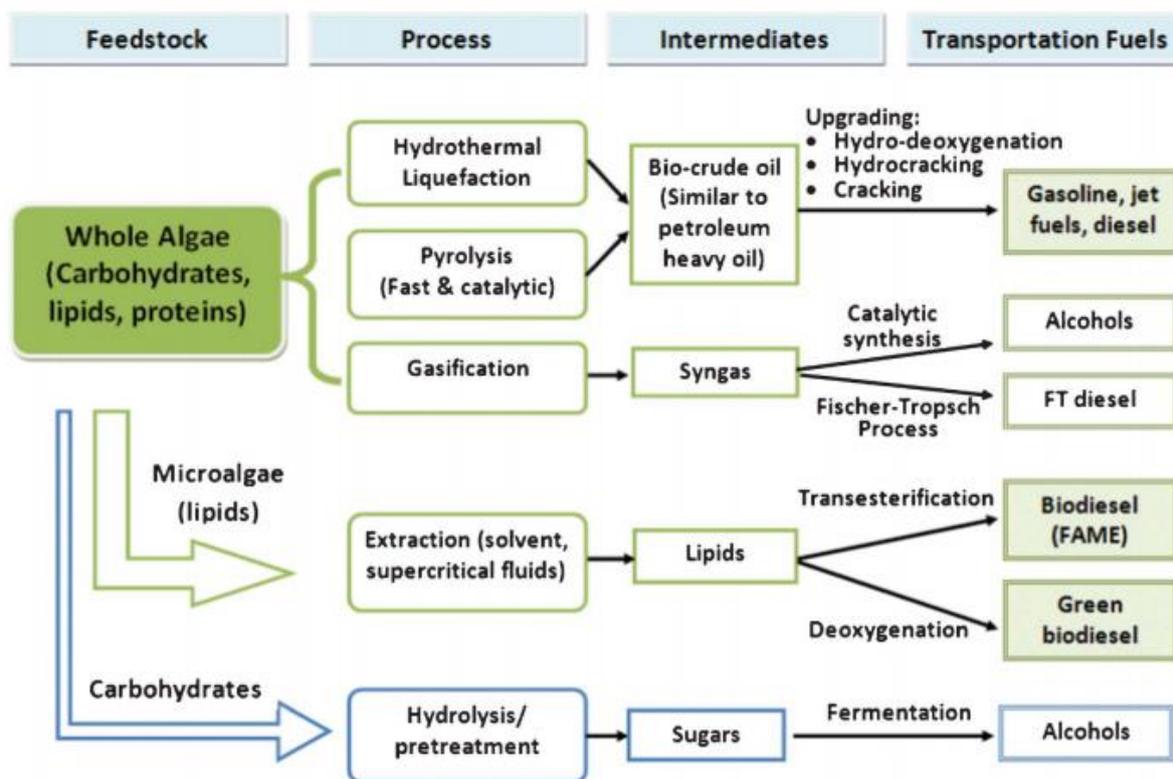


Fig. 6 Microalgae to biofuel conversion pathways.

containing experimental approach and theoretical approach. Finally, the authors described the potential of various thermocatalytic pathways that could be effectively used in the production process of producing biodiesel fuels through computational modeling techniques that were directed to elucidate the major information associated with the optimization of the conversion process [42, 43]. The authors described the pathways that were used for the production of biodiesel fuels through the utilization of microalgae in association with carbohydrates, lipids and proteins as shown in Fig. 6 given above.

11. Conclusion

The current research critically investigated to produce renewable diesel with high CN and without oxygen content from non-edible vegetable oil. The research reviewed and investigated different types of catalysts present in the DO process used for the production of renewable energy products that are energy efficient and reduce the chances of

GHG emissions caused by conventional diesel items. Moreover, the renewable diesel produced can ideally be directly used in diesel engine without any modification to engines, and blending with other fossil fuels is also not required.

References

- [1] Soares Dias, A. P., Puna, J., Neiva Correia, M. J., Nogueira, I., Gomes, J., and Bordado, J. 2013. "Effect of the Oil Acidity on the Methanolysis Performances of Lime Catalyst Biodiesel from Waste Frying Oils (WFO)." *Fuel Process Technol* 116:94-100. <https://doi.org/10.1016/j.fuproc.2013.05.002>.
- [2] Gu, L., Huang, W., Tang, S., Tian, S., and Zhang, X. 2015. "A Novel Deep Eutectic Solvent for Biodiesel Preparation Using a Homogeneous Base Catalyst." *Chem Eng J* 259:647-52. <https://doi.org/http://dx.doi.org/10.1016/j.cej.2014.08.026>.
- [3] Shuit, S. H., Ng, E. P., Tan, S. H., Hoong, S., Poh, E., and Huat, S. 2015. "A Facile and Acid-Free Approach towards the Preparation of Sulphonated Multi-walled Carbon Nanotubes as a Strong Protonic Acid Catalyst for Biodiesel Production." *J Taiwan Inst Chem Eng* 52:100-8. <https://doi.org/10.1016/j.jtice.2015.02.018>.

- [4] Dai, Y.-M. M., Wu, J.-S. S., Chen, C.-C. C., and Chen, K.-T. T. 2015. "Evaluating the Optimum Operating Parameters on Transesterification Reaction for Biodiesel Production over a LiAlO_2 Catalyst." *Chem Eng J* 280:370-6. <https://doi.org/10.1016/j.cej.2015.06.045>.
- [5] Correia, L. M., de Sousa Campelo, N., Novaes, D. S., Cavalcante, C. L., Cecilia, J. A., Rodríguez-Castellón, E., et al. 2015. "Characterization and Application of Dolomite as Catalytic Precursor for Canola and Sunflower Oils for Biodiesel Production." *Chem Eng J* 269:35-43. <https://doi.org/10.1016/j.cej.2015.01.097>.
- [6] Abdullah, N. H., Hasan, S. H., and Yusoff, N. R. M. 2013. "Biodiesel Production Based on Waste Cooking Oil (WCO)." *Int J Mater Sci Eng* 1:94-9. <https://doi.org/10.12720/ijmse.1.2.94-99>.
- [7] Knothe, G. 2010. "Biodiesel and Renewable Diesel: A Comparison." *Prog Energy Combust Sci* 36:364-73. <https://doi.org/10.1016/j.pecs.2009.11.004>.
- [8] Fernando, S., Hall, C., and Jha, S. 2006. "NO Reduction from Biodiesel Fuels NO_x Reduction from Biodiesel Fuels." *World Oil* 20:376-82. <https://doi.org/10.1021/ef050202m>.
- [9] Pimprikar, P. S., Joshi, S. S., Kumar, A. R., Zinjarde, S. S., and Kulkarni, S. K. 2009. "Influence of Biomass and Gold Salt Concentration on Nanoparticle Synthesis by the Tropical Marine Yeast *Yarrowia lipolytica* NCIM 3589." *Colloids Surfaces B Biointerfaces* 74:309-16. <https://doi.org/10.1016/j.colsurfb.2009.07.040>.
- [10] Abdulkareem-Alsultan, G., Asikin-Mijan, N., Lee, H. V., and Taufiq-Yap, Y. H. 2016. "A New Route for the Synthesis of La-Ca Oxide Supported on Nano-activated Carbon via Vacuum Impregnation Method for One Pot Esterification-Transesterification Reaction." *Chemical Engineering Journal* 304: 61-71. <https://doi.org/10.1016/j.cej.2016.05.116>.
- [11] Duan, P., Jin, B., Xu, Y., and Wang, F. 2015. "Co-pyrolysis of Microalgae and Waste Rubber Tire in Supercritical Ethanol." *Chem Eng J* 269:262-71. <https://doi.org/10.1016/j.cej.2015.01.108>.
- [12] Abdulkareem-Alsultan, G. N., Asikin-Mijan, H. V., Lee, U. R., Islam, A., Taufiq-Yap, Y. H., Alsultan, G. A., Mijan, N. A., Lee, H. V., Rashid, U., et al. 2019. "A Review on Thermal Conversion of Plant Oil (Edible and Inedible) into Green Fuel Using Carbon-Based Nanocatalyst." *Catalysts* 9:1-25. <https://doi.org/10.3390/catal9040350>.
- [13] Bezergianni, S., Dimitriadis, A., Kalogianni, A., and Pilavachi, P. A. 2010. "Bioresource Technology Hydrotreating of Waste Cooking Oil for Biodiesel Production. Part I: Effect of Temperature on Product Yields and Heteroatom Removal." *Bioresour Technol* 101:6651-6. <https://doi.org/10.1016/j.biortech.2010.03.081>.
- [14] Bezergianni, S., and Dimitriadis, A. 2013. "Comparison between Different Types of Renewable Diesel." *Renew Sustain Energy Rev* 21:110-6. <https://doi.org/10.1016/j.rser.2012.12.042>.
- [15] Tang, Q., Zheng, Y. Y., Wang, T., Wang, J., Alcalá, A., Bridgwater, A. V., et al. 2017. "Biorefineries for Biofuel Upgrading: A Critical Review." *Renew Sustain Energy Rev* 58:520-94. <https://doi.org/10.1016/j.fueleneab.2017.10.002>.
- [16] Hu, J., Yu, F., and Lu, Y. 2012. "Application of Fischer-Tropsch Synthesis in Biomass to Liquid Conversion." *Mississippi: Catalysts* 2012:303-26. <https://doi.org/10.3390/catal2020303>.
- [17] Loe, R., Santillan-Jimenez, E., Morgan, T., Sewell, L., Ji, Y., Jones, S., et al. 2016. "Effect of Cu and Sn Promotion on the Catalytic Deoxygenation of Model and Algal Lipids to Fuel-Like Hydrocarbons over Supported Ni Catalysts." *Appl Catal B Environ* 191:147-56. <https://doi.org/10.1016/j.apcatb.2016.03.025>.
- [18] Pasqualino, J. C., Montané, D., and Salvadó, J. 2006. "Synergic Effects of Biodiesel in the Biodegradability of Fossil-Derived Fuels." *Biomass and Bioenergy* 30:874-9. <https://doi.org/10.1016/j.biombioe.2006.03.002>.
- [19] Abdulkareem-Alsultan, G., Asikin-Mijan, N., Mansir, N., Lee, H. V., Zainal, Z., Islam, A., et al. 2018. "Pyro-Lytic De-oxygenation of Waste Cooking Oil for Green Diesel Production over $\text{Ag}_2\text{O}_3\text{-La}_2\text{O}_3/\text{AC}$ Nano-catalyst." *J Anal Appl Pyrolysis* 137:171-84. <https://doi.org/10.1016/j.jaap.2018.11.023>.
- [20] Abdulkareem-Alsultan, G., Asikin-Mijan, N., Taufiq-Yap, Y. H., Science, C., Abdulkareem-Alsultan, G., Asikin-Mijan, N., et al. 2016. "Effective Catalytic Deoxygenation of Waste Cooking Oil over Nanorods Activated Carbon Supported CaO ." *Key Eng Mater* 707:175-81. <https://doi.org/10.4028/www.scientific.net/KEM.707.175>.
- [21] Sendzikiene, E., Makarewiciene, V., Janulis, P., and Makareviciute, D. 2007. "Biodegradability of Biodiesel Fuel of Animal and Vegetable Origin." *Eur J Lipid Sci Technol* 109:493-7. <https://doi.org/10.1002/ejlt.200600243>.
- [22] Al-jaberi, S. H. H., Rashid, U., Al-Doghachi, F. A. J., and Abdulkareem-Alsultan, G. 2017. "Synthesis of $\text{MnO-NiO-SO}_4/\text{ZrO}_2$ Solid Acid Catalyst for Methyl Ester Production from Palm Fatty Acid Distillate." *Energy Conversion and Management* 139:166-74. <https://doi.org/10.1016/j.enconman.2017.02.056>.
- [23] Conversion, E., Asikin-mijan, N., Lee, H. V., Taufiq-Yap, Y. H., Abdulkrem-Alsultan, G., Mastuli, M. S., et al. 2016. "Optimization Study of $\text{SiO}_2\text{-Al}_2\text{O}_3$ Supported Bifunctional Acid-Base NiO-CaO for Renewable Fuel

- Production Using Response Surface Methodology.” *Energy Convers Manag* 141: 325-38. <https://doi.org/10.1016/j.enconman.2016.09.041>.
- [24] Asikin-Mijan, N., Ooi, J. M., Abdulkareem-Alsultan, G., Lee, H. V., Mastuli, M. S., Mansir, N., et al. 2019. “Free-H₂Deoxygenation of *Jatropha curcas* Oil into Cleaner Diesel-Grade Biofuel over Coconut Residue-Derived Activated Carbon Catalyst.” *J Clean Prod* 2019:119381. <https://doi.org/10.1016/j.jclepro.2019.119381>.
- [25] Hernando, H., Feroso, J., Ochoa-Hernández, C., Opanasenko, M., Pizarro, P., Coronado, J. M., et al. 2018. “Performance of MCM-22 Zeolite for the Catalytic Fast-Pyrolysis of Acid-Washed Wheat Straw.” *Catal Today* 304:30-8. <https://doi.org/10.1016/j.cattod.2017.09.043>.
- [26] Abdulkareem-Alsultan, G., Asikin-Mijan, N., & Taufiq-Yap, Y. H. (2016). Effective catalytic deoxygenation of waste cooking oil over nanorods activated carbon supported CaO. In *Key Engineering Materials* (Vol. 707, pp. 175-181). Trans Tech Publications Ltd.
- [27] Popov, S., and Kumar, S. 2015. “Rapid Hydrothermal Deoxygenation of Oleic Acid over Activated Carbon in a Continuous Flow Process.” *Energy and Fuels* 29:3377-84. <https://doi.org/10.1021/acs.energyfuels.5b00308>.
- [28] Pattanaik, B. P., and Misra, R. D. 2017. “Effect of Reaction Pathway and Operating Parameters on the Deoxygenation of Vegetable Oils to Produce Diesel Range Hydrocarbon Fuels: A Review.” *Renew Sustain Energy Rev* 73:545-57. <https://doi.org/10.1016/j.rser.2017.01.018>.
- [29] Griffin, M. B., Ferguson, G. A., Ruddy, D. A., Bidy, M. J., Beckham, G. T., and Schaidle, J. A. 2016. “Role of the Support and Reaction Conditions on the Vapor-Phase Deoxygenation of *m*-Cresol over Pt/C and Pt/TiO₂ Catalysts.” *ACS Catal* 6:2715-27. <https://doi.org/10.1021/acscatal.5b02868>.
- [30] Chen, S. 2012. “Green Oil Production by Hydroprocessing.” *Int J Clean Coal Energy* 1:43-55. <https://doi.org/10.4236/ijcce.2012.14005>.
- [31] Chojnacki, T. P., and Schmidt, L. D. 1991. “Microstructures of Pt-Sn and Rh-Sn Particles on SiO₂.” *J Catal* 129:473-85. [https://doi.org/10.1016/0021-9517\(91\)90050-E](https://doi.org/10.1016/0021-9517(91)90050-E).
- [32] Asikin-Mijan, N., Lee, H. V. V., Juan, J. C. C., Noorsaadah, A. R. R., Abdulkareem-Alsultan, G., Arumugam, M., et al. 2016. “Waste Clamshell-Derived CaO Supported Co and W Catalysts for Renewable Fuels Production via Cracking-Deoxygenation of Triolein.” *J Anal Appl Pyrolysis* 120: 110-20. <https://doi.org/10.1016/j.jaap.2016.04.015>.
- [33] Mäki-Arvela, P., Rozmysłowicz, B., Lestari, S., Simakova, O., Eränen, K., Salmi, T., et al. 2011. “Catalytic Deoxygenation of Tall Oil Fatty Acid over Palladium Supported on Mesoporous Carbon.” *Energy and Fuels* 25:2815-25. <https://doi.org/10.1021/ef200380w>.
- [34] Shi, F., Wang, P., Duan, Y., Link, D., and Morreale, B. 2012. “Recent Developments in the Production of Liquid Fuels via Catalytic Conversion of Microalgae: Experiments and Simulations.” *RSC Adv* 2:9727. <https://doi.org/10.1039/c2ra21594b>.
- [35] Baldauf, E., Sievers, A., & Willner, T. (2016). Hydrodeoxygenation of cracked vegetable oil using CoMo/Al₂O₃ and Pt/C catalysts. *International Journal of Energy and Environmental Engineering*, 7(3), 273-287.
- [36] Ko, C. H., Park, S. H., Jeon, J. K., Suh, D. J., Jeong, K. E., & Park, Y. K. (2013). Upgrading of biofuel by the catalytic deoxygenation of biomass. *News & Information for Chemical Engineers*, 31(1), 135.
- [37] Santillan-Jimenez, E., & Crocker, M. (2012). Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. *Journal of Chemical Technology & Biotechnology*, 87(8), 1041-1050.
- [38] De, S., Dutta, S., & Saha, B. (2016). Critical design of heterogeneous catalysts for biomass valorization: current thrust and emerging prospects. *Catalysis Science & Technology*, 6(20), 7364-7385.
- [39] Gnanaprakasam, A., Sivakumar, V. M., Surendhar, A., Thirumarimurugan, M., & Kannadasan, T. (2013). Recent strategy of biodiesel production from waste cooking oil and process influencing parameters: a review. *Journal of Energy*, 2013.
- [40] Liu, Y., Sotelo-Boyás, R., Murata, K., Minowa, T., & Sakanishi, K. (2012). Production of bio-hydrogenated diesel by hydrotreatment of high-acid-value waste cooking oil over ruthenium catalyst supported on Al-polyoxocation-pillared montmorillonite. *Catalysts*, 2(1), 171-190.
- [41] Cardoso, A. L., Neves, S. C. G., & Da Silva, M. J. (2008). Esterification of oleic acid for biodiesel production catalyzed by SnCl₂: a kinetic investigation. *Energies*, 1(2), 79-92.
- [42] Abdulkareem-Alsultan, G., Asikin-Mijan, N., Mustafa-Alsultan, G., Lee, H. V., Wilson, K., & Taufiq-Yap, Y. H. (2020). Efficient deoxygenation of waste cooking oil over Co₃O₄-La₂O₃-doped activated carbon for the production of diesel-like fuel. *RSC Advances*, 10(9), 4996-5009.
- [43] Albazzaz, A. S., GhassanAlsultan, A., Ali, S., Taufiq-Yaq, Y. H., Salleh, M. A. M., & Ghani, W. A. W. A. K. (2018). Carbon Monoxide Hydrogenation on Activated Carbon Supported Co-Ni Bimetallic Catalysts Via Fischer-Tropsch Reaction to Produce Gasoline. *Journal of*

- Energy, Environmental & Chemical Engineering, 3(3), 40.
- [44] Kamil, F. H., Salmiaton, A., Shahruzzaman, R. M. H. R., Omar, R., & Alsultsan, A. G. (2017). Characterization and application of aluminum dross as catalyst in pyrolysis of waste cooking oil. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12(1), 81-88.
- [45] Ghassan, A. A., Mijan, N. A., & Taufiq-Yap, Y. H. (2019). Nanomaterials: An Overview of Nanorods Synthesis and Optimization. In *Nanorods-An Overview from Synthesis to Emerging Device Applications*. IntechOpen.
- [46] Lim, S. T., Sethupathi, S., Alsultan, A. G., Leong, L. K., & Taufiq-Yap, Y. H. (2020). Hydrogen Gas Production Using Aluminum Waste Cans Powder Produced by Disintegration Method. In *Key Engineering Materials* (Vol. 853, pp. 228-234). Trans Tech Publications Ltd.