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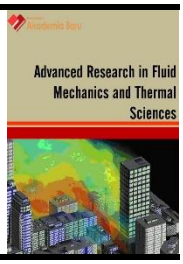

Catalysis Deoxygenation and Hydrodeoxygenation of Edible and Inedible Oil to Green Fuel

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ABSTRACT

Green diesel or known as the hydrocarbons (alkane and alkene) is a renewable and globally friendly biofuel which generally was derived from the triglycerides or fatty acids. The sustainability of the green diesel always concerned the cost of the production, energy supply and demand (net energy balance), the sustainability of more significant crops production or feedstock supply, acceptance of the country and economic stability. Above all, the lack of the petroleum products, the increase in fuel efficiency and affordable by the public are significant reasons for the green diesel to become one of the most important energy supplies for our future The review found important research areas to be reduction in cost of production and maintenance, improvement in fuel quality and improvement in the environmental benefit from using green diesel. With regard to cost reduction, experiments have been conducted on use of low cost catalysts, waste products as feedstocks and H_2-free reaction atmosphere. Fuel quality improvement studies have proposed new catalysts, reaction pathways and conditions to improve hydrocarbon selectivity and fuel stability. Future studies must specifically focus on commercial feasibility of the use of waste materials as feedstocks, heterogeneous catalysts, improvement in reaction pathways to production green diesel and similar other concerns. This article covers the catalysis for deoxygenation, the factor influencing the deoxygenation process and the recent progress of deoxygenation.

Keywords:
Sustainability; green-diesel; renewable energy; deoxygenation; heterogeneous catalyst

1. Introduction

The current study in the literature review section critically investigates the catalysis deoxygenation and hydrodeoxygenation as the chosen methods of converting edible and inedible oil

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to green fuel [1]. The research evaluates that catalytic deoxygenation is typically based on fatty acids decarboxylation and their esters are investigated over Pd supporting the active carbons that are used to make the edible oil into the green fuels. The catalysis deoxygenation is successfully used for the transformation of fatty acids of the oil leads to hydrogenated products, which are further reacted into the hydrocarbons [2]. The research distinguishes between the deoxygenation and hydrodeoxygenation that are used to convert the edible and inedible oil into green fuel. It also evaluates the differences between the green diesel and the biodiesel and alternative pathways by which green diesel is produced through the processes of deoxygenation, HDO and the pyrolysis [3]. The research conducted on determining the catalysis deoxygenation and hydrodeoxygenation of edible and inedible oil and their conversion into green fuel also evaluate different types of catalyst in the DO. It also explores how to DO can be used over carbon-based catalyst by determining the development of carbon-based catalyst in the DO, the selectivity of decarboxylation over the carbon-based catalyst and coke affinity of DO over the carbon-based catalyst. The literature review section of the current research also investigates factors that could influence DO processes such as feedstocks, reaction atmosphere, reaction temperature, catalyst amount and the use of solvent affecting DO process [4]. Finally, the literature review evaluates the recent operations of the deoxygenation of realistic oil.

Although research on green diesel is only a few decades old, extensive work has already been done in this area, which therefore requires review in order to develop an understanding of the new technological solutions available for better production of hydrocarbons from natural sources. This paper offers an overview of current research on production of green diesel from natural feedstocks in order to highlight the research progress in this area as well as to examine several important issues pertaining to it. The review summarizes the multiple reactions proposed in studies for the production of green diesel, including examining the roles of catalysts, feedstocks, reaction atmosphere, and reaction temperatures. A separate section is dedicated to discussion of carbon-based catalysts, as this has appeared as an important advancement in terms of technology for the production of green diesel with at lower cost and with higher reuse stability. The paper ends with an overview of the related topics researched in last five years in an attempt to highlight promising future research direction [5].

2. Green Diesel vs Biodiesel

Green diesel has been defined as the oil which is environment-friendly and economical to use than traditional diesel oil. The green diesel is the by-product of the petroleum products and it is considered to be safer in comparison to conventional oil because it doesn't contain carbon emissions. Green diesel is created from the animal facts and plants and it is based on refined technology that is more chemically similar to the traditionally refined oil. The research work conducted by Lamsal and Tyagi indicated that green diesel is also known as second-generation diesel because it is derived from thermal, hydrotreating and biomass production [6]. Green diesel is developed by using the same terminology as they are used in biodiesel and it is chemically the same as the petro-diesel. On the other hand, Lane describes biodiesel as the oil which is produced through a chemical process by joining ester and alcohol to form another ester and alcohol. The triglyceride oils are used in the creation of biodiesel with methanol to produce the biodiesel described through fatty acid alkyl esters. As shown in the diagram below, the triglyceride is based on three methyl esters and glyceride. Sodium hydroxide is used as the reaction catalyst in the formation of biodiesel and it is effectively used to develop methanol for disassociating and producing the methoxide ion which is known as the

actual catalyst to be used for creating the reaction towards the development of biodiesel [6,7] (See Figure 1).

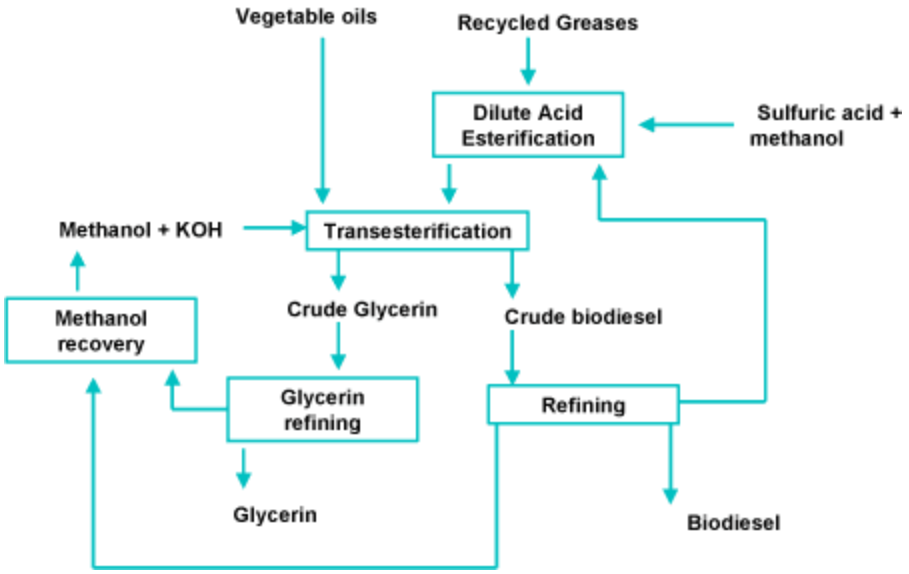

Fig. 1. Production process of biodiesel [6]

3. Alternative Pathways for the Production of Green Diesel

3.1 Deoxygenation

Deoxygenation is one of the methods that are used for the production of biofuels through chemical reactions. But, the high content of oxygen in the biofuels could affect the quality of biodiesel negatively. Catalytic deoxygenation is a chemical process which is specifically used for the production of biofuels by upgrading its quality. Catalytic cracking is used in the process of deoxygenation to improve the chemical properties of bio-oil. Ko *et al.,* in their research work indicated that catalytic deoxygenation can be specifically used to optimize the composition of the biofuel product. In the catalytic deoxygenation, hydrodeoxygenation or HDO is used so successfully eliminate the oxygen atoms from the triglycerides [8]. HDO is specifically adopted in the chemical process to overcome hydrogen problems with deoxygenation of the minimum utilization of hydrogen. Precious metal catalysts have shown that deoxygenation can be consistently used for the production of hydrocarbon in the initial catalytic activity to reduce the coke deposition. The catalytic deoxygenation is based on a chemical activity which is specifically used to achieve increased production of hydrocarbon-based fuels in the biological format by improving the quality of the biofuels [8,9].

The research work conducted by Mijan *et al.,* investigated the production of green fuel by adopting the catalytic deoxygenation process of the curcas oil [10]. According to Mijan *et al.,* biomass is used for the production of green diesel for industries and transportation purposes and it could significantly reduce the dependency of petroleum products associated with greenhouse gas emissions. The utilization of green diesel in industries and transports has dramatically reduced the dependency of these sectors on traditional oil associated with greenhouse gas emissions. The research indicated that catalytic deoxygenation is the process which is specifically used to derive green diesel from the Jatropha oil. The multi-walled carbon nanotube is used along with supporting catalysts to improve the quality of oil for industrial and transportation usage. The research article indicated that effective use of Ni-Co described higher catalytic activity in the routes of

decarboxylation with an overall 80 % saturated and unsaturated hydrocarbon to be produced in the range of C_8 - C_{17} [10].

3.2 HDO (Hydrodeoxygenation)

Hydrodeoxygenation or HDO is used in the production of green diesel or renewable diesel from the biomass. In the hydroprocessing and decarboxylation of the triglycerides, hydrodeoxygenation is used for the elimination of oxygen by creating the chemical creation of triglycerides & FFAs with the hydrogen to form the n-paraffins and water by eliminating the oxygen from the carbon dioxide or carbon monoxide. Hydrodeoxygenation (HDO) is the process by which pyrolysis bio-oils are upgraded through the most promising route to produce liquid transportation fuels [11]. For the success of this process, catalysts used and the quality of bio-oils are considered to be highly crucial for the smooth transition of bio-oils into liquid transportation fuels. He and Wang investigated hydrodeoxygenation as the most critical process that can be used for the generation of transportation fuels by upgrading pyrolysis bio-oils. He and Wang studied the up-gradation process of bio-oil into transportation fuels by utilizing different types of catalysts and recent advancements in HDO by concentrating on reasons that are associated with poor stability of current catalysts and hindered pyrolysis found in oil HDO processes at the industrial level. The researchers discussed the composition of pyrolysis bio-oils and their upgradation processes through Hydrodeoxygenation (HDO) based on different chemical elements such as carboxylic, aldehydes, guaiacols, alcohols, carbohydrates and ketones. The researchers, He and Wang, also discussed different routes that the chemistry of model compounds can adopt over different catalysts with the development of different products. They elaborated the reaction of different catalysts through HDO process by discussing classical sulfided hydrotreating catalysts, phosphides, nitrides, non-precious metals and other metals like bio-metallic catalysts of amorphous and the reduced bronzes of metal oxide. The researchers also reviewed the processes by which different supports to HDO are observed. They also described the deactivation of the catalyst mechanism in the formation of coke because it deactivates the polymerization and the polycondensation reactions [12].

Asphaug investigated the catalytic hydrodeoxygenation of the bio-oils and how effectively HDO can be used with the supporting catalysts MoP to covert bio-oils into transportation oils. Asphaug indicated that the process of HDO has become highly relevant in recent years because the demand for renewable energy has increased worldwide [13]. The interest of people is increased regarding the conversion of bio-oils into green oils by adopting the chemical process of HDO. Biomass from the energy crops and agricultural residues is used for energy development from non-food-competing feedstocks, including the wastes at the urban level and the forest residues. The researcher indicated that biomass is firstly converted into bio-oils by adopting the process of pyrolysis treatment without giving importance to the presence of oxygen. In the upgrading of bio-oils, water and oxygen are used to remove the wastes and poor chemical properties of the bio-oils to convert them into renewable energy oil successfully. The results regarding the conversion of bio-oils into renewable energy oils indicated that surface areas of the supports reduced during the process of impregnation. Furthermore, the process of TPR analysis also confirmed that three stages were reduced based on MoO_3 and MoP. The results indicated that the activity of the catalysts decreased by which MoP was divided by TiO_2 over the period because the catalyst deactivation and the activity showed variations that were not associated with significantly different pressures and the H_2/oil ratio [14].

3.3 Pyrolysis

Pyrolysis is specifically used for heating the organic materials when the oxygen is not available for heating purposes like the biomass material. The presence of oxygen is essential for the combustion of materials, but the chemical composition of these materials can thermally be decomposed into combustible charcoal and gases. When these combustible gases are further condensed into a combustible liquid, it could facilitate in the heating process and known as pyrolysis oil or bio-oil through which some permanent gases are produced such as CO_2, CO and H_2 and the light hydrocarbons. Therefore, pyrolysis of the biomass can be effectively used for the production of three types of products, including bio-oil as a liquid, bio-char as solid and syngas as the gaseous. When the pyrolysis temperature reaches at 500 °C, all these things become equal and the production of bio-oil is optimized, and the heating rate reaches at the point of 1000C/s which describes the fast pyrolysis condition. Under this process, a large quantity of bio-oil is produced through the heating process of typical biomass feedstock with 65% of bio-oil and 25% of biochar and the remaining 10% of syngas. Thus, the processes that are associated with a slower heating rate describe slow pyrolysis where bio-char is greatly produced in comparison to bio-oil. The pyrolysis processes in conducting the heating of biomass material are often found to be self-sustained because they are achieved based on syngas combustion with a portion of bio-oil or bio-char that provides the required energy to drive the reaction as shown in Figure 2 below

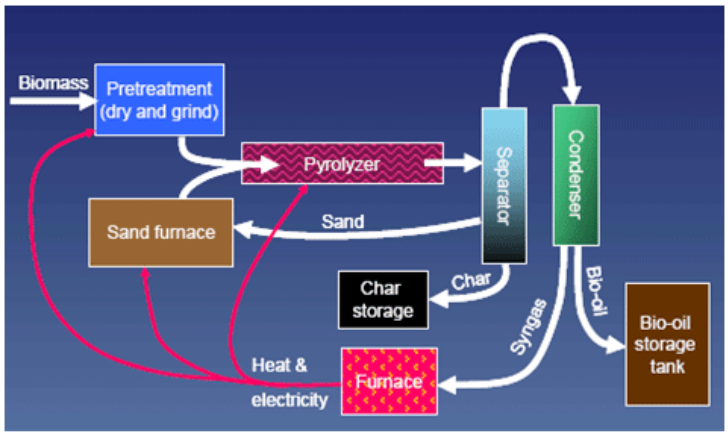

Fig. 1. Pyrolysis heating process to produce bio-oil, bio-char and syngas [15]

4. Requirements of Feedstock for Pyrolysis

In the pyrolysis process, a wide range of feedstock containing biomass is used for the production of bio-oil, bio-char and syngas. The moisture content is essential in the process of pyrolysis, and it should be approximately 10 % to make sure consistency in the pyrolysis process. When the moisture content is higher, it could result in higher production of water and a lower level of moisture content increases the risks of producing dust instead of oil. In high moisture content, waste streams like meat and sludge are produced as the processing waste and it needs drying of the content for the effective pyrolysis process. Therefore, the research work conducted by Zafar indicates that the efficient processing of the pyrolysis is mainly dependent on the size of particles containing in the feedstocks. In most of the pyrolysis processes, the small particles should be around 2mm to make sure the continuity and rapid heating process to produce oil. The demand for small particle size indicates that

the feedstock should contain the size which is reduced according to the requirements of the pyrolysis process [9,15] (See Figure 3).

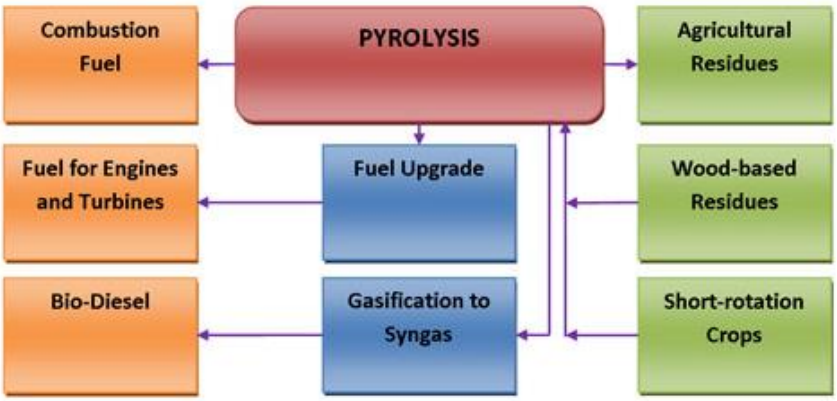

Fig. 2. Feedstock availability and energy products from biomass pyrolysis [15]

5. Type of Catalyst in DO

The use of various metal-based catalysts for deoxygenation process is indeed numerous as discussed in the preceding section (Table 1). The research work conducted by Dawes *et al.,* described the essential kinds of DO by which biomass are used for the production of green oil for transportation purposes.

Table 1
Deoxygenation processes over heterogeneous catalysts

Metal catalyst	Preparation method	SBET (m^2/g)	Major reaction pathways	Reaction temperature (K)	Yield (%)	Selectivity (%)	References
Pd/Fe_2O_3 (5.0 wt% Pd)	Dry impregnation	40	Hydrodeoxygenation	573	56	92	[16]
Cu/SiO_2 (10.3 wt% Cu)	Dry impregnation	110	Hydrodeoxygenation	563	70	14.2	[17]
MoS/Al_2O_3 (9.9 wt% Mo)	Dry impregnation	251	Hydrodeoxygenation	613	70	7.9	[18]
Co/Al-MCM-41 (10 wt% Co)	Wet impregnation	583.0	Hydrodeoxygenation/ Transalkylation	673	100	20	[19]
Ru/CsPW-I (5 wt% Ru)	Wet impregnation	103	Dehydrogenation/ Dehydration	373	96	100	[20]

Decarboxylation and decarbonylation are the two primary types that are described by Dawes *et al.,* in the production of green oil from the biomass. The researcher indicates that biomass if more essential and functional in comparison to feedstocks and defunctionalisation of biomass makes it suitable for use. Thermal deoxygenation is possible for producing bio-oils, but catalytic deoxygenation (DO) has proved to be a highly efficient method because it is associated with lowering the activation energy of the reaction. The correct designing of the catalytic deoxygenation makes it more suitable for energy production in various ways. Decarboxylation and decarbonylation are the

two critical types of catalytic deoxygenation associated with several classes of catalysts such as homogenous, heterogeneous, organocatalysts and biofuels. The researchers, Dawes *et al.,* indicated that these classes are also associated with some limitations that needed to be addressed properly [21]. In homogenous catalyst, the selectivity and the specificity of the catalyst are superior but are challenging to separate from the reaction process. On the other hand, heterogeneous catalysts are comparatively easier to isolate in the reaction and can be used in the higher temperature level. Heterogeneous catalysts are associated with lower selectivity is highly complicated reaction mixtures. Bio-catalyst is another type of catalyst which is ideally suited to ambient temperatures when the volumetric productivity is more moderate. The researchers indicated that it remains difficult to judge which catalyst will be most suitable in terms of selectivity and conversion in the presence of optimum processing conditions. Therefore, Dawes *et al.,* investigated the classes of catalysts that can be adopted for the decarbonylation and decarboxylation of the bio-based molecules with their associated limitation and advantages. They were mainly focused on the activity of catalysts where they perform exceptionally well in terms of specific activity and temperature level concerning metal-based catalysts such as homogenous or heterogeneous catalysts.

6. DO Over Carbon-Based Catalyst

6.1 Development of Carbon-Based Catalyst in DO

Sun, Wang and Su conducted their research on the carbon-based catalyst in Do by investigating their metal-free characteristics that are most effectively used in the areas of nanomaterials and catalysis. They described the advantages of nanocarbon catalysts over metal catalysts and indicated that nanocarbon catalysts are more effective and efficient in carbon-based catalysts in Do because they are environmentally compatible, consume a lower level of energy and show corrosion resistance in comparison to metal catalysis. Nanocarbon is also efficient because they can be catalyzed in the conversion of alkane, energy catalysis, chemical-based synthesis and other processes of heterogeneous catalytic. The research article written by Sun, Wang and Su reviewed the recent progress achieved by the researchers in the areas of carbon-based catalysts in DO by understanding their surface properties, their performance at the catalytic level and macroscopic architecture and reaction mechanism of the catalysts. They have discussed the state of the art in the carbon-based catalysts and future challenges associated with metal-free heterogeneous catalysis [22].

Ampelli *et al.,* [23] also investigated the development of carbon-based catalysts by indicating that these catalysts have opened up new scenarios by which next-generation nano-engineered catalytic materials are developed in chemical processes used for the conversion of bio-oils into renewable energy oils. They defined the dimensions and functional properties of carbon materials that largely depend on the nano-scale architecture and features and preferably used as advanced catalytic materials. The indicated that carbon-based catalysts are considered to be highly supportive to the electrocatalytic applications and nanocarbon because they have offered unconventional ways of addressing new challenges of converting bio-oils to green energy sources to more sustainable future [23]. The research elaborated the importance of nanocarbon that are proven to be catalytic materials of the next generation. Some aspects of new directions of the carbon-based catalysts are adopted in the research by elaborating the need for R&D to progress in the desired direction [2].

Zhou *et al.,* also investigated recent developed that were achieved through the hydrogen-evolution based reaction of the carbon-based catalysts. The researchers highlighted the need for developing effective technologies to deliver clean and sustainable future goals of hydrogen energy. They described an effective and promising approach by which the hydrogen production process is used on the electrolysis of water. These electro-catalysts are considered to be highly effective

because they are Pt-group metal and associated with lower potentials in generating the large catholic densities. But they also show higher costs and scarcity which reduces their broader utilization in the process of sustainable hydrogen energy. Transition metal compounds are adversely used to counter costs and scarcity issues. The researchers, Zhou *et al.,* 2016 explored that recent developments of carbon-based catalysts are considered to be highly effective because they have low over-potential regarding HER. The carbon-based catalysts in DO can be perfectly used to enhance the transition process through nanoparticles as the core and non-metal doping materials presented in carbon skeleton [24].

6.2 Decarboxylation/Decarbonylation Selectivity Over Carbon-Based Catalyst

Dawes *et al.,* Identified the selectivity of decarboxylation/ decarbonylation over the carbon-based catalyst in the process of sustainable energy production for future generations. The researchers described that decarboxylation/decarbonylation is associated with several catalysts classes such as heterogeneous, homogeneous, bio and organocatalysts. They distinguished between these classes by indicating that homogenous catalysts are more effective in selectivity and specificity their reaction from the separation is more complex. On the other hand, heterogeneous catalysts in the categories of decarboxylation/decarbonylation can be easily isolated at the higher temperatures, but in selectivity and specificity, they are not superior. Bio-catalysts are considered to be highly useful and can be operated at ambient temperatures. The researchers, Dawes *et al.,* highlighted various categories of decarboxylation/decarbonylation based on biodiesel molecules and explored their benefits and limitations in comparison to other deoxygenation processes [10].

6.3 Coke Affinity Over the Carbon-Based Catalyst

The research work conducted by Robinson, Hensley and Medlin described coke affinity over carbon catalysts as the biomass material which is used for the conversion of bio-oils into renewable energy oils. Robinson, Hensley and Medlin indicated that deoxygenation is considered to be highly important reaction process in which biomass materials are oxygenated into fuels and chemical like coke affinity. In the refining of biomass, the pyrolysis oil is produced through increased heating of the raw biomass feedstock. The pyrolysis oil produced in this way is used proved to be highly oxygenated and feasible in determining the ability of the biomass to selectivity deoxygenates pyrolysis oil showing the components that create a stream of producing high-value finished items. Robinson, Hensley and Medlin evaluated different catalyst materials that could be used as active and selective materials to deoxygenate the pyrolysis oil. One of these components is rarely capable of producing various types of elementary reactions needed to have deoxygenated biomass-derived components. The researchers, Robinson, Hensley and Medlin paid considerable attention to the bifunctional catalysts in which two active materials are used to provide catalytic sites several reaction steps. The research evaluated a different range of materials, including metal and bimetallic catalysts, sulfides, nitrides, and phosphides that are used in the process of oxygenation of fuels and chemicals [25].

The research work conducted by Fau *et al.,* [26] evaluated the process of hydrocarbon pyrolysis by using a methane focus on the catalytic effect of the coke production. The researchers, identified that hydrocarbon pyrolysis process has been widely recognized as a coolant or used for fuel cells as well as the production of hydrogen used with a catalyst. The research article evaluated that heterogeneous and homogenous chemical phases were found to be unclear although they were the heart of Physicochemical phenomenon. The researchers, Fau *et al.,* [26] also evaluated the processes

of thermal formation by which solid carbon particles are used like coke depositing on the structure and impacting the reactions of various phase chemistry. The research reviewed the literature based on the processes of hydrocarbon pyrolysis that are based on solid surfaces and the particles of coke. Furthermore, the research article also described influent parameters evaluating the nature of the fluids, their level of temperature up to 2000 K, their level of pressure up to 100 bars, their residence time, the reactor type and the catalysts used such as inert, metallic and more complex material like zeolites are evaluated and critically discussed. The researchers also assessed the relationship between the coke production and the catalysts by focusing on the particular of the methane because they were proved to be the growing interests of the hypersonic applications in the hydrocarbon pyrolysis process [26].

7. Factor Influencing the DO Process

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

7.1 Feedstocks

The research conducted by Dutta evaluated Biomass-derived feedstocks in the process of deoxygenation by describing hurdles and opportunities in the energy generation process. Dutta explored that feedstock have received increasing attention in 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 the largest portions of biomass feedstocks. These feedstocks are successfully converted into renewable energy with the set of platform molecules into tailored products and services. The researcher, Dutta, investigated the conversion of cellulosic biomass molecules into renewable energy oils and chemicals. The researcher pointed out that these feedstocks have gained huge importance in recent years because they are associated with sustainable sources of energy production. But Dutta inspected fundamental challenges that the biomass feedstocks conversion process is facing due to the 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 renewable fuel and chemicals. The researcher assessed that in the hydrogenation of the sugar and cellulose have exhibited poor solubility in the organic solvents and their manipulation is also tricky. The research conducted by Dutta indicated that efficient deoxygenation reactions are essential to derivate sugar and cellulose in the presence of high temperature and acid-catalyzed dehydration [27].

Popov and Kumar also investigated the catalytic hydrodeoxygenation process of the lipid-based feedstocks in converting the bio-fuels into renewable fuels for transportation purposes. Popov and Kumar identified that biomass with a higher content of lipid have 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 [28]. 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 the chemical composition of the same materials.

7.2 Reaction Atmosphere

The research work conducted by Pattanaik and Misra [29] investigated the influence of the reaction atmosphere in the deoxygenation (DO) process. Pattanaik and Misra [29] evaluated the effects of the reaction atmosphere as well as operating parameters on the deoxygenation of the bio-oils into diesel range hydrocarbon fuels. The researchers pointed out that fossil fuels have achieved increasing demand in recent years because they are useful for environmental protection. The research also indicated that biodiesel has 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 biodiesel has a 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 deoxygenation of the vegetable oils and fatty acids. Pattanaik and Misra [29] were mainly focused on the reaction atmosphere or pathways for the catalytic deoxygenation or hydrodeoxygenation. Therefore, the researchers explored that reaction temperature, reaction atmosphere, feed type and type of solvency can make a considerable influence on the operating parameters of the catalysts used in the production processes of catalytic deoxygenation.

7.3 Reaction Temperature

The research conducted by Griffin *et al.,* identified the influence of reaction temperature or conditions on the deoxygenation of the m-Cresol over chosen catalysts known as Pt/C and Pt/TiO_2. The researchers indicated that catalytic deoxygenation had become the most effective method of converting the biomass into liquid transportation fuels that are environmentally friendly in comparison to fossil fuels that cause an increased level of greenhouse gases into the environment. Due to their environmentally friendly nature, the conversion of biomass into renewable energy sources has gained massive importance by the mechanical in determining the role of the catalyst supporting the influence of reaction temperature. The researchers investigated the conversion of biomass into renewable fuels through the deoxygenation of the m-cresol over the Pt/C and the Pt/TiO_2. By adopting experimental and computational techniques, Griffin *et al.,* pointed out that reaction temperature is influential in the process of direct deoxygenation and ring hydrogenation [30]. The results collected by the researchers indicated that reaction temperature could be prominent in the presence of synergic effects between the hydrogenation catalysts and metal oxides that provide considerable support into the reaction pathways for the enhanced deoxygenation performance in the given time [21].

7.4 Effect of Catalyst

Catalysts are commonly used in development industries and research works to optimize the product distribution and to increase the product selectivity. Catalyst pore structure, pore volume, surface area and acidity are precisely the essential properties which have significant effects on deoxygenation reaction property and product selectivity. The catalyst has a significant impact on deoxygenation reaction, two types of catalyst have been used to produce the biofuel from palm oil which is based catalyst and acidic catalyst. Asikin-Mijan *et al.,* used CaO as a supported catalyst. The liquid product over Co-CaO and W-CaO yielded 32% and 22% of C8-C17 hydrocarbon fractions with gasoline selectivity of 75% and 65%, respectively [10]. On the other hand, Santillan-Jimenez *et al.,*

studied the effect of catalyst amount over 20 wt.% Ni/C and 5 wt.% Pd/C catalysts. The 20% of Ni/C gives a lighter hydrocarbon which suggests that the increase on the number of the active sites let to increase on the cracking process and lead to shorter hydrocarbon compare to the Pt/C. The differences in the performance of these two catalysts may be attributed to the higher acidity of the Ni-based formulation, which favours the adsorption of carbonaceous species and the occurrence of cracking reactions [31].

8. Recent Progress of Deoxygenation of Realistic Oil

The researchers Chen [32], Choudhary and Phillips [33] and Jahirul *et al.,* [34] identified the recent progress of the deoxygenation of the realistic oil to be used for the transportation purposes environmentally. They indicated that fossil fuels resources are recognized to be dangerous for the environments and not sustainable for long-term socio-economic development in different parts of the world. The greenhouse gas 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 deoxygenation of the biomass into realistic oil by ensuring their promises to the associated environments. The shift of the people from fossil fuels to biofuels and bioproducts are encouraged in different countries developed through alternate industrial feedstocks and green processes to live in an environmentally friendly environment. The indicated that bio-oils and the gaseous fuels which are developed from the biomass materials, wastes, agricultural corps, feedstocks and forestry products had gained increased attention in modern times. These green oil products have reduced the net carbon dioxide emissions by 78 % in comparison to the dangerous elements of conventional diesel products and services produced from fossil fuels. The alternative gaseous fuels have made considerable improvements in the environments by decreasing carbon monoxide (CO) emissions by around 46.7 % and unburned carbons by 45.2 %. Therefore, biofuel products are very encouraging in recent years and they have provided new prospects of energy for transportation purposes in the absence of conventional diesel products. The growth of alternative fuels has made a considerable influence on petroleum refining companies [32-34].

9. Conclusion

The current research critically investigated the catalysis deoxygenation and hydrodeoxygenation processes that are used for the conversion of biomass into efficient renewable fuels for transportation purposes. It evaluated deoxygenation, hydrodeoxygenation and pyrolysis as the unique and distinguished processes that could be used for the further production of renewable fuels from feedstocks and other biomass resources. The research reviewed and investigated different types of catalysts present in the deoxygenation process used for the production of renewable energy products that are energy efficient and reduces the chances of greenhouse gas emissions caused by conventional diesel items. It also evaluated deoxygenation (DO) over the carbon-based catalysts such as the development of the carbon-based catalyst, decarboxylation/decarbonylation and coke affinity over the carbon-based catalysts. It also evaluated the influence of different factors on the deoxygenation (DO) processes including feedstocks, reaction atmosphere and reaction temperature. Finally, the literature review on catalysts deoxygenation and hydrodeoxygenation with the recent progress of the deoxygenation in the realistic oil products that are environmentally friendly and reduced the possibilities of increased greenhouse emissions into the air.

Production costs of green diesel is one key areas of research, driven by the critical need to make such alternative diesels commercially feasible. These costs are highly dependent on the production

process used, and it has been noted that there are important differences in the feedstock, catalysts, and thermodynamics used in DO, HDO, and Pyrolysis, the three key reaction pathways for the production of hydrocarbons in the fuel range. Vegetable oils such as palm oil have been used most commonly as feedstocks, but they come with a variety of issues that include increased deforestation, higher use in the edible oil market, and high base costs. Several studies have thus suggested the use of waste cooking oil as well as looking for non-edible natural sources for the production of green diesel. Further improvements in the economic viability of green diesel are also possible through the utilisation of better catalysts that can effectively yield the desired hydrocarbons without the involvement of hydrogen and which can be reused multiple times. Unsaturated fatty acids, however, lack efficiency in the DO process due to catalytic deactivation.

Studies have also focused on the reduction of maintenance costs through the use of carefully selected catalysts. New catalysts have been introduced in recent research that offer better catalytic activity and reduced costs, and carbon based catalysts in particular are emerging as offering good potential in experiments with the decarboxylation and decarbonylation of vegetable oils. Carbon based catalysts are preferred over other catalysts for their reduced coke affinity, higher selectivity of decarboxylation/decarbonylation processes, and solid form, which enables their easy removal from the reaction solution.

This review confirms the effects of reaction atmosphere and reaction temperature, and taken together, these drive the recommendation that DO in an H_2+Ar environment should be used with fatty acids and esters as feedstocks. The use of triglycerides has also found much support from the literature, as they show higher conversion rates in H_2 free environments. With regard to reaction temperature, a balance must be maintained with respect to selectivity of fuel-range hydrocarbons and the conversion rate of the feedstock.

The research conducted so far supports the potential of green diesel as a commercial fuel supply. Further studies are needed, however, in order address the various technical hurdles inherent in transforming the lab procedures into production facilities. Future studies must thus specifically focus on the commercial feasibility of the use of waste materials as feedstocks, the use of carbon-based catalysts, making improvements in reaction pathways for the production of green diesel, and similar commercial concerns.

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