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Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel range hydrocarbon fuels: A review

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ABSTRACT

Growing demand for fossil fuels and related environmental issues have directed global attention towards development of alternative fuels from renewable sources. In this regard, biodiesel synthesized from vegetable oils and animal fats has shown potential as alternative to diesel fuel owing to its comparable fuel properties and combustion characteristics. However, higher oxygen content in biodiesel has raised some technical issues for its long term utilization in engines. Subsequently, the second generation liquid hydrocarbon fuels are being developed via catalytic deoxygenation of fatty acids present in vegetable oils. Presently, the research focus is on the pathways for catalytic deoxygenation like hydrodeoxygenation, decarboxylation, and decarbonylation. In hydrodeoxygenation, use of hydrogen gas and sulfided metal catalysts ensure higher conversion of vegetable oil into hydrocarbon fuel compared to the other two pathways. On the contrary, decarboxylation and decarbonylation are mostly hydrogen-free processes ensuring economical production of hydrocarbon fuel from vegetable oils. Hence, the techno-economical issues related to deoxygenation process need to be addressed for its commercial viability. Further, key operating parameters like nature of catalysts and supports, catalyst amount, reaction temperature, reaction atmosphere, hydrogen partial pressure, feed type, feed rate, type of solvent, H_2/fatty acid molar ratio etc. are reported to have substantial influence on the hydrocarbon yield and selectivity. This review paper expounds a comparative assessment on the various deoxygenation pathways with their reaction mechanisms to opt for the suitable pathway for conversion of vegetable oils into hydrocarbon fuels based on yield and selectivity of the desired product, ease of use, economy etc. It also explicates the influence of various operating parameters to obtain optimum hydrocarbon conversion and selectivity during catalytic deoxygenation of vegetable oils and related feedstock.

1. Introduction

Ever increasing growth of civilization leads to rapid industrialization, urbanization and increase in number of automobiles, which in turn has resulted rapid increase in world energy consumption over the last few decades. Due to increased demand of petroleum fuels for transportation and power generation in recent times, there is a rapid depletion in world's petroleum reserves along with increasing environmental concerns [1]. The present rate of increase in consumption of fossil fuels is supposed to continue in the coming years resulting in exhaustion of the world petroleum reserves [2]. The fossil fuels are not regarded as sustainable source of energy and their uses are not satisfactory from the economic, ecology and environmental point of views. Fossil fuel combustion largely contributes to increase in greenhouse gas (GHG) percentage in the atmosphere [3]. Industry and transportation sectors are providing greater contribution towards increasing the emission of GHGs, which are responsible for global warming [4–6]. Hence, the requirement for sustainable and environment friendly energy sources have become essential for fulfilling the energy scarcity in the field of industry and all modes of transportation in these years [7].

In this context, alternative and renewable energy technologies like solar energy, wind energy, hydrogen energy, fuel cells, and biomass seem to be promising for fulfilling the future global energy demand. Presently, a major part of renewable energy research is focused on harnessing energy from biomass. Biomass is the major renewable energy source which produces solid, gaseous and liquid fuels with highest potential to meet the future energy needs of a modern world [8]. Biofuels produced from renewable resources like biomass and vegetable oils could be suitable as alternative fuel, thereby reducing the fossil fuel consumption and subsequent GHG emissions. Biofuels are carbon neutral in nature as the CO_2 released by their combustion is neutralized by the CO_2 utilization for growing the plants producing crops for biofuel production, thereby not affecting the net CO_2 level in

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the atmosphere. Also, production and utilization of biofuels and other bioproducts promotes employment opportunities in the rural sectors and helps in saving foreign exchange, consequently strengthening the economy [3,9].

Extensive research on production of biofuels from various renewable feedstock and related technology has gained momentum across the globe in the last few years [2,10–12]. Fuels derived from lipid feedstock such as vegetable oils and animal fats have received enormous attention as alternative fuels. Biodiesel or fatty acid methyl ester (FAME) derived from lipid feedstock is treated as one of the most popular alternative fuel at present [13,14]. Biodiesel comprises mono alkyl esters of long chain fatty acids derived from vegetable oils and animal fats via transesterification of these lipids with methanol in presence of a base catalyst. It is renewable and biodegradable in nature, and possesses excellent fuel properties like low sulfur content, greater lubricity and higher flash point [15]. However, several drawbacks such as higher oxygen content, poor cold flow properties, poor storage stability, lower heating value, higher nitrogen oxides (NO_x) emissions, and engine compatibility issues make biodiesel unsuitable as complete replacement of diesel fuel [16].

In view of the shortcomings associated with biodiesel, efforts are on for development of next generation advanced biofuels, which are renewable in nature and fully compatible with diesel fuel. Presently, catalytic deoxygenation (DO) of fatty acids present in vegetable oils over various supported metal catalysts has emerged as a promising alternative for the production of diesel-like hydrocarbon fuels. The catalytic DO is carried out via hydrodeoxygenation (HDO), decarboxylation (DCX), and decarbonylation (DCN) reaction pathways, wherein oxygen is separated from the fatty acid structure of vegetable oils as H_2O, CO_2, and CO. Many researchers have come out with a number of significant findings related to DO of vegetable oils and related feedstock. Most of them have highlighted the importance of operating parameters, such as nature of supported metal catalyst, type of feed, feed rate (residence time), reaction temperature, reaction atmosphere, H_2 partial pressure, amount of catalyst, and type of solvent, in evaluating the yield and selectivity of the diesel-like hydrocarbon fuels produced by DO of vegetable oils and related feedstock via the above reaction pathways. Based on the findings of various researchers, these DO reaction pathways have their own merits and demerits in terms of yield and selectivity of the desired product, ease of use, economy etc. for their commercial use to produce deoxygenated hydrocarbon fuels from vegetable oils. It demands for techno-economical analysis of these reaction pathways along with critical evaluation of the influence of various process parameters for obtaining optimum hydrocarbon conversion and selectivity.

This review paper presents a brief overview on the evolution of advanced biofuels since its inception and a comparative assessment on DO reaction pathways with their reaction mechanisms to opt for the suitable pathway for conversion into hydrocarbon fuels based on economy and ease of use. It also explicates the influence of various process parameters to obtain optimum hydrocarbon conversion and selectivity during catalytic DO of vegetable oil based feeds. Finally, the recent trend in DO of vegetable oils and related feedstock is appended in this paper suggesting some scope for further research.

1.1. Biofuels

Biofuels are known as liquid or gaseous fuels derived from plant extracts such as agricultural crops, municipal wastes and agricultural and forestry byproducts which are capable of replacing either completely or partly the conventional petroleum-based fuels in automotive engines [17]. Biofuels are sustainable in nature, completely degradable and their combustion produce improved emissions compared to fossil fuels. Biofuels represent a CO_2 cycle and are environment friendly [18]. Biofuels, in the course of time have emerged as more attractive option as substitute of fossil fuel as they allow mitigation of GHGs, greatly contribute towards energy security and promote employment opportunities [19]. Biofuels are produced from biomass via biochemical or thermo-chemical conversion routes. Biochemical conversion of biomass via alcoholic fermentation produces liquid fuels and that via anaerobic digestion produces biogas [20]. The biofuels of present era are classified into first generation and second generation biofuels. The main features, production processes and application of these biofuels are presented in the following sections.

1.2. First generation biofuels

The commonly available first generation biofuels today are bioethanol produced by fermentation of sugars (sources like sugarcane, corn, sugar beet, wheat etc.), biodiesel produced via acid/base catalyzed transesterification of vegetable oils with alcohols and biogas produced by anaerobic digestion of biomass in a digester [21]. These biofuels have gained popularity as alternative fuels due to their inherent ability to get easily blended with fossil fuels, good combustion quality in the internal combustion engines and ability to get distributed within the existing infrastructure. The first generation biofuels are established as commercial fuels today with approximately 50 billion liters produced annually around the world. They are beneficial to be used in blended form with petroleum-based fuels, can provide CO_2 benefits and can help to promote the energy security [3]. However, the future of these biofuels seems uncertain due to limited feedstock availability, concerns about their environmental impacts and carbon balances, their impact on biodiversity and availability of land which tends to limit the increase in production of these biofuels. The major controversy associated with these biofuels being their competition with food production as the increase in production of these biofuels may raise the prices of food products [22]. It has also been found that biodiesel is not a successful technology as far as GHG emissions are concerned. Therefore, researchers have proposed for development of new and efficient alternatives from renewable feedstock for reduction in GHG emissions and abate the global warming [23].

1.3. Second generation biofuels

Due to serious concerns over the sustainability of the first generation biofuels from economic and environmental point of views, the alternative fuel research is gradually shifting towards the development of technologically more advanced and sustainable biofuels known as the second generation biofuels. The second generation biofuel technology has been developed to overcome the drawbacks related to the first generation biofuels. The prime objective behind the second generation biofuel technology is to expand the global biofuel production capability by incorporating residual biomass of food and non-food crops and municipal organic wastes, thereby increasing the sustainability without producing the undesirable byproducts [24,25]. Bioethanol derived from lignocellulosic biomass and fuels produced from biomass-derived synthesis gas ($CO+H_2$) are commonly known as second generation biofuels. However, the definition of second generation biofuels is not restricted to these fuels only; rather, the concept of the second generation biofuel refers to those advanced biofuels which are technologically superior, beneficial in terms environmental impacts and are sustainable in nature [21]. The second generation biofuel production can be achieved from waste biomass and plant residues, and making use of the abandoned land, thereby enabling these biofuel crops and production technologies to become more efficient. However, the second generation biofuels may become unsustainable if their production competes with the production of food crops on the available land. Therefore, it is very much desirable that the production of these biofuels must meet with the criteria of minimum lifecycle GHG reductions along with land use change and social standards to be regarded as sustainable fuels [26].

The second generation biofuels can be mainly produced via thermo-