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Review

Recent advancement and prospective of heterogeneous carbonaceous catalysts in chemical and enzymatic transformation of biodiesel

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ABSTRACT

Carbon derived from waste biomass has emerged as a promising candidate towards the synthesis of catalyst or catalyst support for chemical and enzymatic reactions. Excellent surface properties like large specific surface area and high porosity make carbon an exceptional contender for catalyst support. Moreover, appreciable electron conductivity and relative chemical inertness enrich its applicability in chemical processes. The biomass-derived carbon catalysts are environmentally benign for reducing carbon footprint and cost competitive to other heterogeneous catalysts available for biodiesel production. Carbons functionalized with different alkali metals, SO_3H group, alkoxides, enzymes and transition metals enhance the catalytic activity in the transesterification of triglycerides to alkyl esters. Biodiesel, a promising alternative to the conventional petro-diesel is studied globally in the modern era. The cost-effective process for the biodiesel synthesis involves heterogeneous catalysis employing various catalyst supports. The traditional process of biodiesel synthesis is expensive on the indus trial scale; hence, heterogeneous catalysis plays a vital role in minimizing the cost of the final product due to high stability, efficient activity, and noticeable reusability. For the success of biorefinery concept in the present day and sustainable development towards future, there is a need for the design of a new generation of multi-functional catalysts perhaps consisting of carbon as a support derived from waste biomass. This, in turn, will enhance the selective transformation of non-conventional sources into biodiesel as a sustainable source of energy. Henceforth, the present review offers a broad synopsis on the synthesis of evolving carbonaceous catalysts such as activated carbon, graphene, carbon nanotubes, carbon monoliths and carbon nanohorns for their use in biodiesel production.

1. Introduction

The sustainable development is commonly referred to the economic growth achieved by employing effective methodologies to meet the present demand without exploiting the natural resources by conserving for future generations. It has become a maxim to the entire scientific and modern community that industrial corporations and governmental bodies are encouraging the research programs in food security, sustainable energy, materials, buildings retrofit and even city planning. In the context of energy, though extensive research has been carried out towards the exploration of crude oil reserves using enhanced oil recovery techniques [1], yet there are significant uncertainties in the economics of its exploitation by existing exploration technologies. Furthermore, burning of such enriched carbon sources violates the United Nations Framework Convention on Climate Change (UNFCC) targets of maintaining the global mean temperature [2,3]. With the rapidly increasing world population, the energy demand is predicted to increase by 50% of its present by 2040. However, the tightrope between energy demand and supply needs to be reduced by introducing renewable sources of energy to mitigate the current CO_2 emission and climate change [4]. The biggest challenge of the present century is to meet the expedition for sustainable energy and production techniques. Despite of numerous renewable sources possessing the potential to curtail the growing energy demand, biomass serves itself as a low-cost and readily executable solution to replace the conventional diesel though biorefinery concept by lipid transesterification for the synthesis of biodiesel [5]. The first generation biodiesel was synthesised from edible oils and condemned tremendously over the food security and competition between uses of agricultural lands for the cultivation of crops for food or fuel preparation [6]. Henceforward, in order to maintain the sustainability, utilisation of biomass and non-edible sources have provoked the researchers for the production of second generation biodiesel.

Biodiesel, a renewable, biodegradable and eco-friendly fuel derived

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from non-edible plants, animal fats, waste oils and algal biomass, is viewed as a promising alternative or additive to the conventional diesel [7–10]. In the present scenario, biodiesel is produced by homogeneous transesterification of triglycerides with alcohol in the presence of acid or base catalyst along with notable by-product glycerol. The use of homogeneous acids or bases in the transesterification as a catalyst suffers from severe limitations like corrosion of reactor and engine manifolds. Moreover, their recovery from the reaction mixture is an energy demanding process, and neutralization step leads to saponification problem [11–13]. Therefore, the development of novel, effective and green heterogeneous catalyst through economic route is a greater challenge on industrial scale for biodiesel production. The solid acid and base catalyst are widely used in transesterification, as they offer a continuous mode of operation, enhanced process efficiency, improved glycerol purity, appreciable activity in reusability, and less wastewater generation in the purification step [14–17]. In the recent years, the emerging concept of green chemistry inspired the use of eco-friendly and bio-based catalyst especially developed from waste materials such as biomass [18]. However, the efficient conversion of waste biomass into the effective catalyst is still a challenge for the researchers. Since last few decades, biomass is the prominent precursor for the synthesis of porous carbonaceous material via pyrolysis. The activation of pyrolyzed char using a physical technique (steam) or chemical technique using strong acids/bases yields ordered porous activated carbon that can be directly used as an adsorbent and catalyst support [19]. The tuning of the surface properties and designing of well-ordered porous activated carbon using existing methodologies are the challenging issues. Although, few studies show that the macroporous structure of the precursor can be retained and controlled to the good extent to achieve the well-ordered porous carbon [20,21]. Preparation of the novel carbon materials from waste and renewable sources is an important and emerging area of research due to its wide application and cost-effectiveness. Furthermore, the use of these carbonaceous materials in advanced applications in future plays a vital role towards sustainable development.

The use of waste and inexpensive materials for the synthesis of porous carbons has attracted the considerable attention of researchers towards utilisation of carbon in a variety of processes. Porous carbon has been encouraged as a leading material for chemical and enzymatic conversion processes due to its excellent surface properties viz. high surface area and porosity, good electron conductivity and relative chemical inertness. To the present, several metal oxides have been used as a heterogeneous catalyst in biodiesel synthesis process. However, oxides like alumina, hydrotalcite, TiO_2, mesoporous silica, etc. gets deactivated in the harsh process conditions like high temperatures ($100\,^{\circ}C < T < 250\,^{\circ}C$) and pressurized water ($P*H_2O$ $(T) < P < 100$ bar) [22]. The structural consistency of these oxides diminishes when exposed to extreme temperatures in pressurised condition resulting in reduced catalytic activity by leaching of catalyst in reaction mixture causing product contamination and hindrance in catalyst separation which ultimately upsurges the operational cost. In comparison to silica and alumina, the stability of porous carbon at high temperature and pressure in extremely acidic and basic conditions, resistant to the structural deformation in hydrolytic conditions in aqueous environments, etc. make carbon a suitable catalyst support. The important characteristics of carbon like diverse porous structure, low cost, easy recoverability and functionality with various dopants by different activation methodologies encourage its utilisation in catalytic processes [23]. The use of carbon is advancing in the field of biotechnology for the immobilisation of enzymes and support to the microbial growth in the direction of production of sustainable energy sources. The overall aspect of carbon as a catalyst support in biodiesel synthesis and general chemical and enzymatic processes have been addressed [15,24]. However, the proper use of carbon as a catalyst and its utilisation for immobilisation of base functionalities and lipase towards application as an effective catalyst in biodiesel synthesis is still unexplored. Thus, carbon derived from waste biomass and advanced carbon forms (Nano carbons) have immensely attracted the scientists for establishing a sustainable economy.

This review is aimed at focusing on the recent advancements made in the development of carbon support from waste biomass and its use in chemical and enzymatic conversion of triglycerides into alkyl esters. This contribution also explores the use of carbon materials ranging from amorphous solids to nanoporous materials for impregnation and doping of the acid, base and enzyme functionalized catalyst. Special attention is being paid to the new carbon synthesis processes and its functionalization for the development of a low-cost heterogeneous catalyst for biodiesel synthesis. The catalytic activity of carbonaceous catalysts in biodiesel synthesis is also reviewed concerning diffusional resistance of the reactants, hydrogen spillover, catalyst leaching, and reusability. The distinct emphasis is also given to structural properties and morphologies of the different carbonaceous forms used extensively in the transesterification reaction. This paper elaborates the industrial application of carbon as a catalyst support in biodiesel synthesis process, recent developments and widely used forms of carbon as a catalyst support and its future prospect in the direction of sustainable progress in developing countries like India. A brief introduction to the general process of biodiesel synthesis, feedstocks, and its characteristics has been provided.

2. General background of carbon materials

Carbon, the fourth most abundant element in the universe by mass, is a common element as it can form polymers at the actual temperatures on the planet. Commonly, carbon materials are found in three forms i.e. charcoal, diamond, and graphite. By the virtue of chemistry, carbon is classified into different allotropes depending on the atomic arrangements and hybridization state. The detailed carbon allotropes are summarised in Fig. 1. The porous materials are categorized into three different classes based on the pore structure; microporous carbon has pore diameter less than 2 nm, mesoporous carbons possess pores of diameter in the range of 2–50 nm, and macroporous carbons have a diameter greater than 50 nm. Activated carbon (AC), the mostly derived form of charcoal possesses a wide range of micropore and macropore distributed uniformly [25]. Microporosity of the classical activated carbon and carbon black makes them specific candidates for their use in catalysis, electrochemistry, fuel cell, biomedical appliances, energy storage, etc. The low cost and abundant availability of the activated carbon precursors also encourage its application in chemical processes. The production techniques associated with classical AC yield microporous material. The AC is generally prepared by physical and chemical activation of the carbonised char. Initially, the precursor is pyrolyzed in an inert atmosphere at a higher temperature depending on the properties (moisture, volatile matter and ash content) of the material. The pyrolyzed char is subsequently exposed to the higher temperatures in the oxidising environment created by air or steam [26]. The physical activation of biomass derived char by steam or air gives surface area in the maximum range of 500–1500 m^2/g [27]. However, the chemical activation of biomass derived char using strong acids (H_2SO_4, HCl, H_3PO_4, etc.) or strong bases (KOH, NaOH) is reported to provide higher surface area up to 3000 m^2/g [28]. Although the surface area obtained through physical activation is lesser than the chemical activation, but the method is advantageous in terms of waste water generation. The wastewater generation in chemical activation for neutralization of the product is a great concern, which is eliminated in case of physical activation. The surface modification using chemicals by impregnating the precursor followed by carbonization may corrode the furnace at higher temperatures. This route is beneficial as desired properties can be achieved at lower temperatures and less time; however, corrosion of the furnace is the serious issue. This limitation can be overcome by impregnation of carbonised char at a lower temperature using strong acids or base. The applicability of the porous carbon can be elevated to the