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Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation

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ABSTRACT

One of the challenging issues faced by the modern world is the scarcity of fossil fuels, a result of the increasing use of fuel for transportation. Therefore, it is necessary to develop an alternative fuel source that can replace non-renewable fossil fuels. The use of biomass-derived fuels in place of conventional fuels is an emerging field of interest, and studies are on-going to find a solution to avoid a future energy crisis. Hydrodeoxygenation, which converts biofeed to hydrocarbon fuels that have all the qualities of conventional fossil fuels, is one of the most interesting and promising techniques in this field. The hydrodeoxygenation of vegetable oils to biofuel is an area in development. In the present paper, an overview of the catalysts used for hydrodeoxygenation of various vegetable oils is presented. In addition, the nature of the catalysts and reaction conditions necessary for the desired activity and selectivity of the catalysts are included. The current state of the field, trends in production processes and a brief description of commonly used feedstocks are presented as well.

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1. Introduction

Oil scarcity, non-renewable resources, unpredictable prices and increasing environmental issues involved with petroleum-based fuels lead to the need for alternative sources to fulfill fuel needs [1]. Industry and transportation, especially air transportation, play crucial roles in increasing the emission of greenhouse gases, which cause global warming [2–4]. One fifth of the total oil produced is consumed by the transportation sector, including both land and air transportation [5]. A demand of 106.6 million barrels of biofuel is expected by 2030 [6].

The aviation industry has recently begun investigating alternative fuel sources to replace the conventional fuel, paraffin (also known as kerosene) from crude-oil reserves that are near depletion. Because this fuel is also shared with land transportation, the reserves will deplete quickly. The Kyoto Protocol in 1997 aimed to reduce greenhouse gases, such as CO_2, NO_X, CH_4, and SO_X, but current technologies and fuel requirements are not sufficient to

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uphold the protocol and result in increased greenhouse gas emissions [7,8]. To overcome the fuel crisis, the European Union (EU) proposed the 2003/30/EC and 2009/28/EC directives. The directives call for the substitution of conventional non-renewable transportation fuels with high-quality renewable biofuels [9].

Paraffin-based biofuel is getting major interest especially in aviation industries compare to diesel-base biofuel due to it satisfies the properties of conventional jet fuels. Paraffin-based biofuel are characterized by good cold flow properties, proper ratio of hydrocarbons (*n*-alkanes, isoalkanes, cyclo paraffins and aromatics) and high energy density [10]. It improved ignition and extinction characteristics, low aromatic content and sulphur content and perfect blending with conventional fuels [11]. When blended with conventional fuel, paraffin-based biofuel can be used in the same aircrafts or engine without further modifications. Besides, the usage would save environment by reduce air pollution and GHG emissions [12].

Biomass conversion into hydrocarbon fuel, or biofuel, has become an attractive solution to overcome this problem, as well as the environmental concerns of renewability, nitrogen and sulfur content and gas emissions in comparison to fossil fuels [13,14]. Currently, research is mainly concentrated on finding high-performance, eco-friendly, alternative second-generation biofuels that can replace conventional fuel without greenhouse gas emissions or causing a food crop crisis [15]. The main opposition to the use of cultivated crops for the production of biofuel is that it would affect the food chain. Farming of non-edible crops for fuel purposes can also adversely affect the food chain by utilizing water, land and fertilizer [16]. Despite these effects, this production process is relevant because it is an effective alternative to the use of fossil fuels.

Vegetable oils are a promising resource in the production of biofuel. Currently, focus is concentrated on non-edible vegetable oils. However, these vegetable oils cannot exactly replicate conventional fuels due to their high oxygen content (up to 50%), which leads to low heating value, immiscibility with fossil fuels, a tendency for polymerization, thermal instability and high viscosity [17,18]. The viscosity of vegetable oils can be lowered by chemical and thermal processes; however, the best-known process for lowering oil viscosity is pyrolysis, which leads to low-value products [19].

Catalytic hydroprocessing is a promising technology for the conversion of liquid biomass to biofuel. The process of catalytic hydrotreating involves the saturation of olefinic bonds and the removal of heteroatoms such as sulfur, nitrogen and oxygen [20]. Hydrodeoxygenation is the process of removing oxygen from oxygenated feedstocks, such as water [21]. Catalytic hydrodeoxygenation of vegetable oils results in hydrocarbon fuels with improved ignition qualities. Many research reports and patents focus on the conversion of fats and oils into biofuel. Jakkula et al. made use of fats in milk and vegetable oils, including rapeseed, sunflower, and canola oils, among others [22]. Petri and Marker used grease and vegetable oils [23], whereas Herskowitz claimed the use of both animal and vegetable oils as feedstock [24].

The present paper is an overview of the various metal catalysts used to produce paraffin-based biofuels by hydrodeoxygenation of vegetable oils. It is observed that the type of catalyst and nature of the feedstock influence the extent of hydrodeoxygenation and the efficiency of the fuel produced. The review also provides a glance into the current status and trends in vegetable oil hydrodeoxygenation, focusing on paraffin-based biofuels.

2. The feedstock

Typical feedstocks for second-generation biofuels are vegetable oils with high energy contents. The intention is to use vegetable oils directly as fuel [25]; however, the use of unmodified vegetable oils as the fuel is not efficient because of their high viscosity [26]. Although there are a number of vegetable oils available as feedstock, only soybean, palm, sunflower, safflower, cottonseed, rapeseed and peanut oils have been proven to have the potential to produce alternative fuels [27,28]. In developing countries, especially those in the Asian sub-continent, the production of edible vegetable oils is not sufficient, and so it is essential to use non-edible oil sources [29]. Rapeseed and sunflower oils are the main feedstocks used in Europe for biofuel generation. Palm and coconut oils are mainly used in the tropics, and soybean oil is used in United States [30]. The advantages of these oil seeds are their abundant oil content, better adaptation to growing conditions, regular maturation periods, low maintenance and formation of eco-friendly waste during oil extraction [28,30].

Camelina plants require little water and nitrogen for growth and can be cultured as a rotation crop for wheat. The plant needs less maintenance, such as the use of fertilizers [31]. The camelina seed contains approximately 40% oil, with the major content in

Table 1
Characteristics of the potential feedstocks used for biofuel production.

Feedstocks	Advantages	Disadvantages
Sunflower	More tolerant to low temperatures Can grow in a wide range of soil types [55] Can be cultivated as a rotational crop [56]	Edible oil Quality of oil depends on weather conditions and agricultural practices [57]
Rapeseed	Less used for food purposes Can grow on most soil types Can be cultivated over a wide range of temperatures [58]	Requires good drainage Easily attacked by diseases
Palm	Large scale production Long life span Less affected by climate Harvest throughout the year [59]	Edible oil Limited regional range due to high rainfall need Grow mostly in rain forest regions [60]
Soybean	Need optimum temperature Minimum water supply for growth [61] Large scale production [62]	Edible oil Requires extensive land and uses of pesticides [62]
Camelina	Need less water and fertilizer to grow Short growing season Can be grown as rotation crop for wheat By-product can be fed to animals [63]	Edible oil Depresses the growth of nearby plants [64]
Jatropha	Wide range of climatic suitability Large land volumes in subtropical regions Land use change can be carbon positive [60] Non-edible oil Long lifetime and less water consume [64] Draught resistant	No compatible production [64]