



Review

Catalytic upgrading of vegetable oils into jet fuels range hydrocarbons using heterogeneous catalysts: A review

Ahmad Galadima^a, Oki Muraza^{a,b,*}^a Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia^b Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:

Received 11 February 2015
 Received in revised form 18 March 2015
 Accepted 30 March 2015
 Available online 4 April 2015

Keywords:

Vegetable oils
 Jet fuels
 Hydrotreatment
 Hydroisomerization
 Catalysis

ABSTRACT

The production of high grade jet fuels from vegetable oils is an issue of special interest to refineries. The conversion process involved hydrotreating (i.e. hydrodeoxygenation and hydrodecarboxylation) of the oils followed by subsequent hydroisomerization. The paper reviewed recent literature on the role of heterogeneous catalysts in the various processes. Catalysts based on Ni and Mo supported on oxides are considered very active for the hydrotreating process whereas Pd and Pt supported on zeolites as the main hydroisomerization catalysts. However, further studies are still required on the role of catalyst topology, reaction mechanisms and the strategies for mitigating catalyst deactivation.

© 2015 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Contents

Introduction	12
Objectives of the review	13
Hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) of vegetable oils	13
Reactions with noble metals	14
Reactions with other transition metals	15
Effect of catalyst support	15
Effect of catalyst composition and reaction conditions	16
Role of catalyst modification with metal or phosphorus	17
Recent HDO and HDC studies with other transition metals	17
Catalyst deactivation during HDO/HDC of vegetable oils	17
Hydroisomerization of the HDO and HDC products	18
Conclusions	21
Acknowledgements	21
References	22

Introduction

The production of vegetable oils is an important issue of global interest for decades before now. These oils are particularly attractive due to their renewable and environmental friendly nature and the possibility of conversion into energy fuels (i.e. fuels for energy generation). By the year 2000, the global productions of palm, soybean and rapeseed oils were 20, 25 and 15 million tons

* Corresponding author at: Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.
 Tel.: +966 13 860 7612.

E-mail addresses: omuraza@kfupm.edu.sa, oki.muraza@gmail.com (O. Muraza).

Table 1
Typical composition of a jet fuel (JP-4) derived from either petroleum or shale.

Composition	Shale-based fuel (wt.%)	Petroleum-based fuel (wt.%)
n-Alkanes (n-C ₇ to n-C ₁₅)	68–70	40–44
i-Alkanes (straight chains)	6–10	27–32
Cycloalkanes (n- and i-)	5–7	2–4
Aromatics (benzene, toluene, xylenes, etc., n- and i-)	6–10	6–12

Source: Refs. [16,17].

but increased to 50, 41 and 25 million tons in 2012, with further increase projected for the current and future years [1]. Vegetable oils are primarily employed in the energy industry for conversion into biodiesel, mostly via the process of catalytic transesterification [2–7]. However, the current trend in the global energy crisis as related to fossil fuels production and consumption accounted for evaluating the prospects of the vegetable oils in the production of jet fuels (i.e. biojet fuels) [8–11]. The jet fuels, otherwise referred to as aviation fuels, are mainly produced from the refining of petroleum feedstock for the purpose of powering aircrafts. They are suitable for use in both internal combustion and turbine engines (i.e. in both low and high temperature and pressure engines). The quality and specification requirements for these fuels such as the ability to burn without danger and cleanly, high calorific efficiency, chemical stability and low viscosity in compliance with low temperature implied that, the fuels can suitably be derived from renewable resources. Jet fuels are composed primarily of hydrocarbon compounds that include saturated straight and cyclic alkanes (could be up to 85%), aromatics especially benzene and low concentrations of olefins (usually 1%) [12–15]. Table 1 reports a typical composition of jet fuel sourced from either petroleum or shale [16,17].

The straight paraffin components are characterized by a high ratio of hydrogen to carbon and therefore give rise to high production of heat per unit mass compared to the other hydrocarbons. They are similarly capable of burning cleanly and are therefore required in large quantities in the aviation fuels. The cyclic paraffins are important for ensuring suitable density and reduced-freezing points of the fuels. The respective rapid smoke production and reactivity of aromatics and olefins during combustions accounted for their low concentration requirements. These compositions and features desired of high quality aviation fuels indicated that vegetable oils, which are mainly triglyceride esters, must undergo appropriate conversion processes. For this reason, the biojet fuels are produced via catalytic hydrodeoxygenation (HDO)/hydrodecarboxylation (HDC) and catalytic isomerization (Scheme 1). Both HDO and HDC remove lighter hydrocarbon species like propane in addition to carbon dioxide and

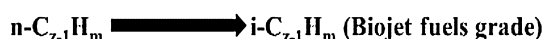
water. They proceed with the formation of even and odd-numbered chains of paraffins, respectively [18]. The isomerization process, on the other hand, converts the derived linear paraffins into corresponding isomers with enhanced biojet fuels properties. In all cases, the appropriate choice of reaction parameters such as catalyst, temperature, space velocity, feedstock and pressure is very critical in achieving optimal yields.

Objectives of the review

The paper presents a review on the role of heterogeneous catalyst systems for the conversion of vegetable oils into hydrocarbon compounds (i.e. paraffins) in the range suitable for jet fuels. Emphasis would be given to catalyst development and activity evaluation during conversion of the vegetable oils into n-paraffins through HDO/HDC and subsequent isomerization to high grade biojet fuels. To the best of our knowledge, no any critical review has been previously published on this specific subject. The paper will therefore provide a baseline for identifying the progress made and the ways forward. Heterogeneous catalysts are the main catalyst systems so far identified for this process due to their cost-effective nature and environmental sustainability in related reactions. Therefore, the paper will mainly focus on these catalytic materials. Noble metals (i.e. platinum group metals like Pt, Pd, Ru, etc.) and composite transition metal catalysts based on NiMo, CoMo, NiCo and their supported analogs were reportedly studied for the HDO/HDC reactions whereas zeolitic materials as the candidates for isomerization due to their structure-acidity properties. The paper covers concise details on these materials, with emphasis to their activities and operation conditions. Factors responsible for catalyst deactivation and the regeneration methods would also be discussed. Homogeneous catalyst systems have not been captured because they are not being employed for this process due to their associated recyclability, disposal/environmental, corrosion and costly problems.

Hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) of vegetable oils

Both hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) are simultaneous hydrotreatment processes that occur during the upgrading of petroleum feedstock, but the scope have recently be extended to include the upgrading of biomass-based feedstock like the vegetable oils. The HDO proceeds by the removal of oxygen from oxygenated compounds (i.e. oxygen containing compounds) in the feed following the incorporation of hydrogen and an appropriate catalyst. With vegetable oils, the long chain glyceride esters contain carbonyl oxygens that could be removed



Key: z, m are even numbers (m>z), x= moles of species, n = normal, i = isomer, TGE = Triglyceride ester, HTGE = Hydrogenated triglyceride ester.

Scheme 1. Schematic routes for the conversion of vegetable oil to biojet fuels via HDO/HDC and isomerization.

Download English Version:

<https://daneshyari.com/en/article/228354>

Download Persian Version:

<https://daneshyari.com/article/228354>

[Daneshyari.com](https://daneshyari.com)