



Review

Hydroprocessing challenges in biofuels production

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ARTICLE INFO

Article history:

Received 2 November 2012

Accepted 23 November 2012

Available online 12 February 2013

Keywords:

Biomass conversion

Biofeeds hydroprocessing

Biofuels production

Biodiesel properties

Hydroprocessing catalysts

Coproducting biofeeds with petroleum feeds

ABSTRACT

Biofuels production from biomass of lignocellulosic, vegetable oils and algae origins as well as from municipal solid waste via hydroprocessing (HPR) is in various stages of development. The conversion of biomass from these sources to biofeeds and chemical composition of the latter are presented. Differences between the mechanism and kinetics of HPR reactions occurring during the HPR of biofeeds and petroleum feeds are evaluated. Fundamental aspects of conventional and non-conventional HPR catalysts, with emphasis on their applications in biofuels production are discussed. Catalysts exhibiting high activity and stability under conditions encountered during the HPR of biofeeds are identified. They include catalysts consisting of conventional metals (Mo/W and Co/Ni) supported on various supports as well as novel catalytic phases containing noble metals as well as phosphides, carbides, nitrides and borides of transition metals in combination with supports varying widely in surface acidity. The studies on coprocessing biofeeds with the feeds of petroleum origin as well as those on blending biofuels with petroleum fuels were reviewed. Improvement in properties of petroleum diesel, particularly in terms of diesel number, can be achieved by blending with biodiesel from vegetable oil sources.

Developments in upgrading biofeeds in aqueous environment (subcritical water, supercritical water and supercritical alcohols) in the presence of various catalysts and hydrogen, are addressed.

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List of acronyms

CCR	Conradson carbon residue
CDL	coal derived liquids
CFPP	cold filter plugging point
CUS	coordinatively unsaturated sites
DBF	dibenzofuran
DBT	dibenzothiophene
DDO	direct deoxygenation
DDS	direct desulfurization
DMDBT	dimethyldibenzothiophene
DMDS	dimethyldisulfide
DMS	dimethyl sulfide
DFT	density functional theory
EN	European norm
FAME	fatty acids methyl esters
FBP	final boiling point
FCC	fluid catalytic cracking
FTS	Fischer–Tropsch synthesis
GC–MS	gas chromatography–mass spectroscopy
GTL	gas-to-liquids
HAAD-STEM	high angle annular dark-field scanning transmission electron microscopy
HCR	hydrocracking
HDI	hydroisomerization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HPR	hydroprocessing
HRTEM	high resolution transmission electron microscopy
HYD	hydrogenation
LC	liquid chromatography
LCO	light cycle oil
LH	Langmuir–Hinshelwood
LHSV	liquid hourly space velocity
NMR	nuclear magnetic resonance

SCW	supercritical water
STM	scanning tunneling microscopy
THF	tetrahydrofuran
TPD	temperature programmed desorption
TPS	temperature programmed sulfiding
ULSD	ultra low sulfur diesel
USDA	US department of agriculture
VGO	vacuum gas oil
WCO	waste cooking oil
WGS	water gas shift
WHSV	weight hourly space velocity
XPS	X-ray photoelectron spectroscopy

1. Introduction

In the comprehensive reviews on different aspects of biofuels published by Corma et al. [1,2], Naik et al. [3] and Demirbas [4], current methods and future opportunities for the production of transportation fuels from various sources of biomass, were presented. This included the chemistry and catalysis of processes, biorefinery concepts, engineering challenges and solutions. In the case of economic analyses, a life cycle which begins with biomass planting, growing, harvesting and biomass preparation for the production of biofeeds, was not always considered. The authors [1–4] pointed out that economic analyses are very site specific and may vary considerably depending on the current and future regional economic and market situations.

There has been a tendency to classify biofuels into three generations to reflect the level of development and commercialization [5,6]. The first generation biofuels such as ethanol and biodiesel have already been commercially available. The latter is represented by fatty acids methyl esters (FAME). Detailed accounts of the FAME production and properties were given in the comprehensive review published by Van Gerpen [7]. The first generation biofuels are of the food-based biomass origin. In this regard, corn, potatoes, beet, sugarcane, etc. are primary sources of commercial ethanol, while vegetable oils derived from rapeseed, olive, sunflower, soya, palm,

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