



Catalyst evaluation for waste cooking oil hydroprocessing

Stella Bezergianni*, Aggeliki Kalogianni, Athanasios Dimitriadis

Centre for Research & Technology Hellas – CERTH, Chemical Process Engineering Research Institute – CPERI, Thessaloniki, Greece

ARTICLE INFO

Article history:

Received 9 February 2011

Received in revised form 16 July 2011

Accepted 24 August 2011

Available online 10 September 2011

Keywords:

Hydrotreating

Hydroprocessing

Waste cooking oil

Biofuels

Catalyst evaluation

ABSTRACT

Catalytic hydroprocessing is an effective technology with various applications in the petrochemical industry that are lately expanding in the area of biofuels production. The selection of a hydroprocessing catalyst is a critical step defining the hydrotreating products' yields and their corresponding quality as well as the expected run-length of the process. This work involves the process of selecting a suitable hydroprocessing catalyst for the conversion of waste cooking oil into biofuels. In particular three commercial catalysts are evaluated: a hydrotreating catalyst, a mild-hydrocracking catalyst and a severe hydrocracking catalyst. The catalyst effectiveness was assessed over a temperature range suggested by the catalyst manufacturers, covering a temperature range of 330–390 °C, under constant LHSV (1 h⁻¹) and a range of pressure 8.27–13.79 MPa. Several parameters were considered for evaluating the effect of temperature including product yields, conversion, selectivity (diesel and gasoline), heteroatom removal (sulfur, nitrogen and oxygen) and saturation of double bonds.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative fuels, such as Fatty Acid Methyl Esters (FAME) biodiesel [1] which are produced from various vegetable oils via transesterification. The aim of the EU's biofuel directive is to raise the proportion of biofuels and other renewable fuels to 5.75% of total gasoline and diesel consumption (based on energy content) by 2010 [2]. However, compared to petroleum-based diesel, the high cost of FAME biodiesel is a major problem for its commercial applications. It is reported that approximately 70–85% of the total biodiesel production cost arises from the cost of raw material [3]. However, the use of low-cost bio-based feedstocks such as waste cooking oil (WCO) can potentially make biodiesel competitive with petroleum diesel, but lowers the quality of the produced biodiesel [4].

Catalytic hydroprocessing is an alternative conversion technology of liquid biomass to biofuels which is lately raising a lot of interest in both the academic and industrial world. Catalytic hydroprocessing has first appeared in petrochemical industry a key process which enables heteroatom (sulfur, nitrogen, oxygen, metals) removal, saturation of olefins and aromatics and cracking [5]. These hydroprocessing reactions render catalytic hydroprocessing as an advantageous process for biomass conversion to biofuels.

For example, the deoxygenation reactions lead to biofuels products with increased cetane number, heating value and oxidation stability [6,7]. The effectiveness of the hydroprocessing reactions depends on specially manufactured catalysts which characterize the process and products, which usually consist of active metals (Co, Mo, Ni, Pt, Pd) dispersed on high surface area alumina.

Many research efforts have been made for the evaluation of hydroprocessing process for different biomass types. The investigation of the hydrogenolysis of various vegetable oils such as maracuja, buritima tucha and babassu oils over a Ni–Mo/γ–Al₂O₃ catalyst was studied as well as the effect of temperature and pressure on its effectiveness was first studied by Da Rocha et al. [8]. The same group studied extensively the transformation of vegetable oils on sulfide catalysts under hydrogen pressure [9]. Rapeseed oil hydroprocessing was also studied in lab-scale reactor for temperatures 310 °C and 360 °C and hydrogen pressure of 7 and 15 MPa using three different Ni–Mo/alumina catalysts by Simacek et al. [10]. These products contained mostly n-heptadecane and n-octadecane accompanied by low concentrations of other n-alkanes and i-alkanes [11]. Sebos et al. [12] studied a commercial CoMo catalyst for hydroprocessing of cotton-seed oil in a trickle bed reactor. The effectiveness of catalytic hydroprocessing was also explored for co-processing of vegetable oil – petroleum fractions by Huber et al. [13] and Bezergianni et al. [14] utilizing commercial hydrocracking catalysts. Finally, waste cooking oil (WCO) was also investigated as an alternate bio-based feedstock for hydroprocessing for the production of diesel over commercial NiMo/Al₂O₃ catalyst [6,7]. In all cases the catalytic hydroprocessing was proven an effective and promising technology for converting liquid biomass to biofuels. However the issue of catalyst choice was not systematically addressed.

* Corresponding author. Address: Chemical Process Engineering Research Institute – CPERI, Centre for Research & Technology Hellas – CERTH, 6th km Harilaou-Thermi Rd, Thessaloniki 57001, Greece. Tel.: +30 2310 498315; fax: +30 2310 498380.

E-mail address: sbezerg@cpери.certh.gr (S. Bezergianni).

The selection of a hydrotreating catalyst is a critical step defining the hydrotreating product yield and quality as well as the operating cycle time of the process in petroleum industry [15]. Specifically however the hydrotreating catalyst selection for biomass applications is a crucial and challenging for two reasons: (a) Catalyst activity varies significantly, as commercial catalysts are designed for different feedstocks, i.e. feedstocks with high sulfur concentration, heavy feedstocks (containing large molecules), feedstocks with high oxygen concentration etc. (b) Currently there are no commercial hydroprocessing catalysts available for processes using waste cooking oil as feedstock.

This paper involves the process of selecting a suitable hydroprocessing catalyst which will be employed for the hydroprocessing of 100% WCO for biofuels production. Three commercial hydroprocessing catalysts were employed (a hydrotreating, a mild-hydrocracking and a severe-hydrocracking catalyst) and their activity was investigated for a range of temperatures.

2. Methodology

For the catalyst evaluation, the small-scale pilot plant unit VB01 of the Laboratory of Environmental Fuels and Hydrocarbons (LEFH) of CERTH has been utilized. This small-scale pilot plant is a continuous flow unit which consists of a feed system, a fixed-bed reactor system and a product separation system, as schematically depicted in Fig. 1. From the range of operating parameters (Fig. 1) it is evident that this unit enables the study of all typical industrial scale conditions.

A typical experimental run for evaluating the activity of a hydrotreating catalyst consists of four parts: (a) catalyst loading, (b) catalyst presulfiding, (c) main catalyst assessment protocol and (d) catalyst unloading and cleaning. The catalyst loading design procedure and implementation is performed according to the reactor and catalyst geometries and desired liquid hourly space velocity (LHSV) and normally lasts 1–2 days. The catalyst presulfiding procedure is defined by the catalyst manufacturer and is performed between 1–3 days. The catalyst assessment protocol, which is employed for each catalyst, consists of several temperatures (Table 1) suggested by the catalyst manufacturer. Each temperature/condition lasted between 4–6 days. Finally the catalyst unloading and cleaning lasts usually 1–2 days.

In order to evaluate and compare the three different commercial catalysts, three different experimental runs had to be conducted, one for each catalyst (Table 1). Catalyst A or HDT is a conventional NiMo hydrotreating catalyst (manufactured for hydrodesulfurization and denitrogenation of heavy petroleum streams), catalyst B or MID-HDC is a medium severity CoMo hydrocracking catalyst (directed for saturation and mild cracking) and catalyst C or HDC is a NiMo hydrocracking catalyst (designed for maximizing the middle distillate yields of heavy petroleum fractions). For the three experimental runs a total of 45 lit (0.045 m³) of waste cooking oil (WCO) was required as feedstock and approximately 30 m³ of hydrogen. The WCO consists of a mixture of used cooking oil coming from local restaurants and homes. The triglycerides content of the WCO employed in the three experimental runs is given in Table

Liquid Flow	0–60ml/h
Gas Flow	0–70 lit/h
H ₂ /oil	0–1600ml/l
Pressure	0–150 atm
Reactor Temperatures	25–450°C
Reactor Volume	114ml
Catalyst Volume	6.5–50ml

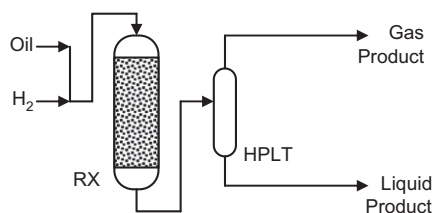


Fig. 1. Simplified schematic diagram of LEFH/CERTH hydroprocessing pilot plant.

Table 1
Operating conditions for catalysts A, B and C.

	Catalyst A: HDT	Catalyst B: MID-HDC	Catalyst C: HDC
T (°C)	330–370	370–385	350–390
P (MPa)	8.27	8.27	13.79
LHSV (h ⁻¹)	1.0	1.0	1.5
H ₂ /oil (N m ³ /m ³)	506	506	1013

Table 2
Triglycerides analysis of WCO.

Triglyceride type	Wt.%
C8:0	0.07
C14:0	0.05
C16:0	7.46
C16:1	0.10
C17:1	0.03
C18:0	2.97
C18:1	33.52
C18:2	54.79
C18:3	0.31
C20:0	0.21
C22:0	0.49
Total	100.00

2, while its basic properties are given in Table 3. It should be noted that the increased sulfur content is attributed in the Di-Methy Di-Sulfide (DMDS), which is added in the WCO feedstock to regulate the catalyst activity.

The main catalyst assessment protocol follows the catalyst loading and presulfiding steps. The catalyst assessment protocol consists of three different operating conditions where three different temperatures are examined (covering the operating range of each catalyst). In order to determine the catalyst activity in each condition, the process dynamics and associated hydroprocessing reactions have to reach steady-state. In order to determine whether steady-state has been reached, a daily liquid product sample is collected and the product density is measured. The system is considered to have reached steady-state only when the product density is stable between two consecutive days (to the 3rd decimal point in kg/l basis), which usually happens after 4–6 days. The product collected during the day that steady-state is reached represents the actual representative product characterizing this operating condition and is analyzed in detail.

A significant part of the overall methodology is the analysis of the products obtained at each operating condition. The total liquid product is analyzed exclusively in the analytical laboratory of LEFH/CERTH. The simulated distillation curve is determined via an Agilent 6890 N-GC according to the ASTM D-7213 procedure. The density of the total liquid product is measured via an Anton-Paar density/concentration meter DMA 4500 according to ASTM D-1052. The concentration of sulfur and nitrogen is measured via an Antek 5000 system, according to ASTM D5453-93 and ASTM D4629 procedures respectively. Total carbon concentration is

Download English Version:

<https://daneshyari.com/en/article/6645185>

Download Persian Version:

<https://daneshyari.com/article/6645185>

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