Catalysis Today 156 (2010) 38–43

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydroprocessing of crude palm oil at pilot plant scale

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ARTICLE INFO

Article history:
Available online 4 February 2010

Keywords:
Hydrotreating catalyst
GC–MS
Crude palm oil
Renewable diesel
Deoxyhydrogenation

ABSTRACT

High cetane index renewable diesel can be obtained by hydroprocessing of palm oil using conventional hydrotreating catalyst (NiMo/γAl_2O_3). At 40–90 bar hydrogen pressure crude palm oil (CPO) can be deeply converted into paraffins in the diesel range. However, at lower pressures hydrodeoxygenation cannot be fully reached and the appearance of intermediates as C16–C18 alcohols, C16–C18 acids and esters were preliminary identified in the reaction product. Times of stream (TOS) experiments have shown that conventional hydrotreating catalyst suffers of slight deactivation as the reaction proceeds.

1. Introduction

The option of using vegetable oils as an alternative diesel fuel is restricted by their high viscosity. Several routes have been tried for reducing this viscosity, such as diluted vegetable oil with diesel fuel, microemulsification with alcohols, pyrolysis, and transesterification [1]. In recent years, hydroprocessing technology has been used to convert lipid feedstocks into distillate fuels [2–7]. The two main products consist of a liquid distillate fuel with very similar properties to petroleum diesel, and propane in the gas phase stream. This fuel is incorporated into EPAct05 biodiesel definition as non-ester renewable diesel (NERD) in "thermal depolymerization" technology that can become a most effective tool in reducing the carbon footprint [8]. The primary advantages of this fuel over first-generation biodiesel technology are: (1) the cold weather properties are superior; (2) the propane byproduct is preferable over glycerol byproduct; (3) the heating content is greater; (4) the cetane number is greater; and (5) capital costs and operating costs are lower [9].

Under high hydrogen pressure and relative high temperature vegetable oils can be converted into paraffins (from n-C15 up to n-C18) having water, propane and CO_x gases as by-products. Intermediates as monoglycerides, diglycerides, ketenes, aldehydes, acrolein and carboxylic acids have been proposed [2,10], these are formed in the initial step and subsequently hydrogenated or broken down via decarboxylation, decarbonylation or hydrodeoxygenation. In addition to the main reactions mentioned above, cyclization and aromatization reactions can take place especially when fatty acids that compose the triglycerides in the vegetable oil are polyunsaturated as linoleic and linolenic acids [11].

Although in principle common industrial hydrotreating catalyst can be used for this purpose their stability to the presence of by products as water and CO_x has not been established yet [12]. In this paper experiments at pilot plant scale combined with chromatographic methods has been conducted with the purpose of studying of reaction variables as hydrogen pressure and time of stream, the latter with the objective to observe the stability of the catalyst to the reaction by-products. Additionally experimental information has been compared with data obtained by an equilibrium reactor model.

2. Experimental

Hydrogenation of crude palm oil (CPO) using an industrial hydrotreating catalyst (NiMo/γAl_2O_3, Haldor Topsøe 217) intended to sulfur and metal removal was carried out. The catalyst particles are in the trilobe form and have an average equivalent size of 1.8 mm, a length of 4.1 mm, and are mixed (diluted) with spherical and inert SiC particles of different sizes, with the purpose of improving the flow pattern and help to achieve isothermal conditions. The hydrotreating activity experiments were conducted in a trickled-bed reactor unit continuously operated using pure CPO as feed. The catalyst was previously activated by a standard procedure using straight-run gas oil containing 3 wt% dimethyl disulfide for sulfiding [13]. After catalyst activation, reaction conditions were adjusted. Two process variables were investigated, i.e., hydrogen pressure and time on stream (TOS). They were varied as follows: pressure = 15–90 bar and TOS = 0–14 days using in all experiments a volume (STP) ratio hydrogen/CPO = 484 (20:1 molar). Product samples were collected and analyzed for cetane index (ASTM D-4737), kinematic viscosity at

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doi:10.1016/j.cattod.2009.11.015

Table 1
Properties of crude palm oil (CPO).

Property	Units	CPO
Cetane index	Cetane units	–
Kinematic viscosity at 40 °C	mm^2/s	40.33
Density at 15 °C	g/mL	0.9139
API gravity	°API	23.3
Flash point	°C	275
Cloud point	°C	23
Pour point	vC	12
BSW	vol%	0.3
Bromine number	g Br$_2$/100 g	52.9
Acidity	mg KOH/g	7.392

40 °C (ASTM D-445), density (ASTM D-4052), flash point (ASTM D-93), cloud point (ASTM D-2500), pour point (ASTM D-97), Corrosion (ASTM D-130), Color (ASTM D-1500), acidity number (ASTM D-664), thermal stability (ASTM D-6468), carbon and hydrogen (ASTM D-5291), bromine number (ASTM D-1159), simulated distillation (ASTM D-7213) using an Agilent 6890 GC equipped with a fused silica 10 m × 0.53 mm × 0.9 μm column and a calibration mixture from C3 to C60; Properties of CPO provided by a local extractor plant are given in Table 1.

After reaction products are separated in a biphasic separator where the reaction pressure is reduced to almost atmospheric pressure. Liquid products are collected in the separator and gases are measured with a Ritter TG-3 and collected in a stainless steel container. The liquid products, i.e., aqueous phase and the less dense organic phase (hydroprocessed product) are then separated by decantation.

In addition to all analysis previously described, the hydrogenated product was analyzed by GC–MS using a gas chromatograph Agilent 6890 connected with a mass spectrometer Agilent 5973N equipped with a HP5-MS 60 m × 0.25 mm × 0.1 μm column. The temperature in GC oven was programmed from 30 to 300 °C at a heating rate of 3 °C/min. The reaction gases were analyzed using an Agilent 6890N GC equipped with FID/TCD detectors using multidimensional chromatography.

3. Results and discussion

3.1. Hydrogenation of CPO varying hydrogen reaction pressure (P)

GC–MS analysis of hydrogenation products varying the hydrogen pressure are shown in Fig. 1. As it can be seen the reaction pressure P has an appreciable influence on product selectivity. As the P is decreased not only the yield of products with higher boiling points (retention time longer than 34.7 min that corresponds to the n-C18 paraffin) increases but also the yield of products with lower boiling points (retention time shorter than 28.0 min time that corresponds to the n-C16 paraffin). At lower retention times lighter products would correspond to the paraffin series from C3 to C14. At longer times (>34.7 min) a higher yield of heavier products as the reaction pressure decreases is observed. Along with this behaviour the main peaks corresponding to the n-paraffins C15–C18 become broader indicating that co-elution of isomers of these products and other reaction products, is occurring. A zoom of the chromatogram on this range of retention times shows clearly the effect of decreasing the hydrogen pressure in the reactor (see zoom right). Only the two extreme pressures are plotted, i.e., 15 and 90 bar. As observed the number of products increases dramatically as the pressure is reduced. Unfortunately the peak purity for some of these compounds at low hydrogen pressure was very low and they could not be identified.

We have combined quantitative information from GC-FID techniques and semi-quantitative analysis from GC–MS, especially considering the higher peak resolution of GC–MS compared to distillation chromatography obtained from GC-FID analysis, to interpret the results of this study. Thus, we have used fraction yields in terms of gasoline (IBP-221 °C), middle distillate (221–344 °C) and 344 °C+.

Between the reaction products obtained at low pressures, and preliminary identified by GC–MS, and observed at higher retention times (>34 min) are octadecenes (35 min), octadecanol (36.2 min), n-hexadecanoic acid (37.8 min), octadecanal (38.9 min), and hexadecyl hexadecanoate (58.5 min), and octadecyl hexadecanoate.

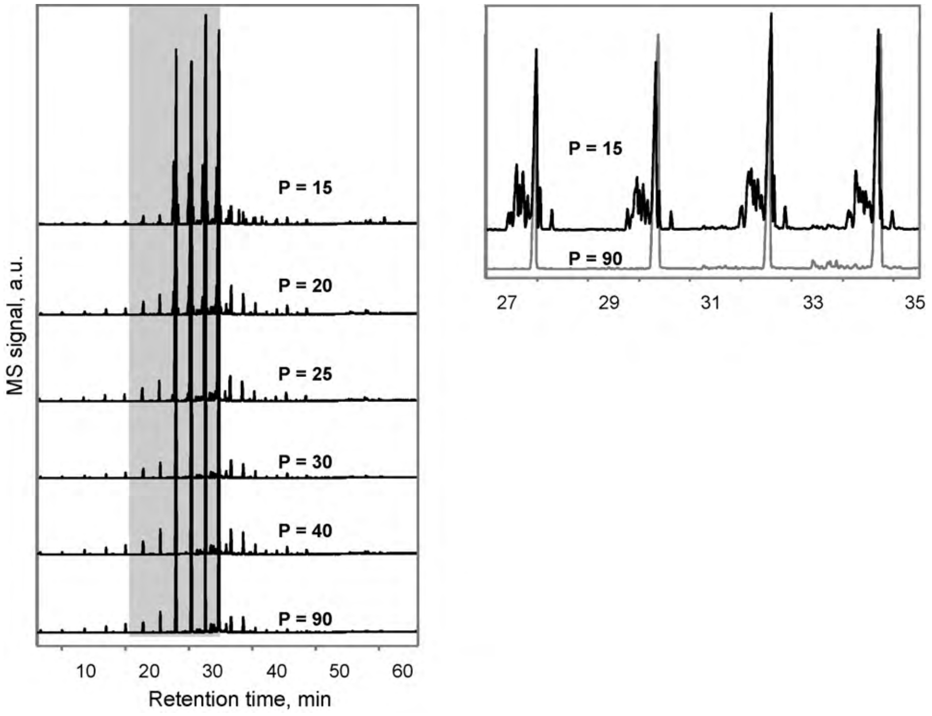

Fig. 1. GC–MS of CPO hydrogenation products varying reaction pressure from 90 to 15 bar.