Full length article

Upgrading of palm oil renewable diesel through hydroisomerization and formulation of an optimal blend

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ABSTRACT

Renewable diesel is the best alternative to replace biodiesel due to its improved properties, but like biodiesel, renewable diesel has poor cold-flow properties. The hydroisomerization process improves the pour and cloud points of renewable diesel, but it worsens the cetane number and the flame point, both are regulated by international standards. In this work, desoxygenated palm oil (HDO) was produced in high yield (82 wt%) using a sulphided $NiMo/Al_2O_3$ catalyst. Then, HDO was hydroisomerized at 50 bar and 350 °C, under hydrogen, with a Pt/SAPO11 catalyst, obtaining an isomer yield of 81%. TPR and TPO analyses showed that this catalyst can be reversibly reduced/oxidized at 155–160 °C, therefore, it was completely reduced at the reaction conditions. Characterization of the isomerized product (i-HDO) showed a beneficial effect on cold-flow properties but an adverse effect on flash point, distillation range and cetane index due to light hydrocarbons formed during hydroisomerization. Light hydrocarbons ($< C_{14}$, 7 vol%) in i-HDO were distilled off at 180 °C to tune the flash point and the distillation range. The hydroisomerized and distilled product (i-HDOd) was blended with HDO to determine the required hydroisomerization level to meet the cold-flow regulations. The optimal blend consisted of 71% i-HDOd and 29% HDO and it has a cetane index of 92.4, pour point of 2.8 °C, flash point of 82 °C, distillation range of 225–321 °C and heating value of 47.3 MJ/kg.

1. Introduction

Hydrotreating of vegetable oils has become an alternative to produce biofuels with better physicochemical properties than biodiesel [1–5]. Elimination of oxygenated groups in triglycerides produces a mixture of n-alkanes between C_{12} to C_{20}, called HDO (hydro-deoxygenated) product or renewable diesel or green diesel [6]. Competitive advantages of renewable diesel over biodiesel are: a higher heating power per unit mass, better chemical storage stability, better diesel engine compatibility, low flash point, no hazes formation, higher hydrophobicity, non-detergent action, chemically inert, non-corrosive action, possibility to blend in higher proportions with petrochemical diesel and a production process that does not use water.

Hydrotreating of vegetable oils to produce renewable diesel consists of three reactions: hydrogenation (saturation of double bonds), hydrogenolysis (breaking of triglyceride molecules in propane and fatty acids) and deoxygenation. This last reaction eliminates oxygenated groups (ester, carbonyl and hydroxyl) present in fatty acids structure [7,8]. Deoxygenation occurs by three known chemical pathways: hydrodeoxygenation (oxygen elimination by H_2O formation), decarbonylation (oxygen elimination by CO production) and decarboxylation (oxygen elimination by CO_2 formation) [9,10]. Final products of the deoxygenation reactions are n-paraffins. Undesired traces of light hydrocarbons such as methane and ethane from propane cracking are also produced, due to the acidity of the HDO catalyst. Although n-paraffins can be used directly in diesel engines, it is necessary a hydroisomerization process to improve the cold flow properties, when it is required. Researchers have shown that hydroisomerization of n-paraffins to isoparaffins is the best way to improve the cold flow properties in high octane gasolines [11]. Isoparaffins not only improve the cold flow properties in high octane gasolines but also modify the viscosity of lubricant oils [12]. Catalysts for hydroisomerization have two active sites, a metallic site where the hydrogen molecule is adsorbed an on acid site where the formation of carbenium ions, by hydrogen subtraction from carbon chain, occurs [13]. Nowadays, researchers are focusing on catalytic materials with appropriate acidity and porosity properties for the selective hydroisomerization and low cracking effect. The best supports reported so far are zeolites and silicon-aluminophosphates doped with noble metals such as Pt, Pd or Rh [14–16].

Shape selectivity on hydroisomerization catalysts avoids the multi-branches formation in the main carbon chain [17] and reduces the cracking level. Researches have revealed that zeolitic catalysts have selective methyl-branch formation when the pores of the support are small, while ethyl and propyl branches are induced by medium or high-size pores [15,18]. In the n-decane hydroisomerization using zeolitic catalysts ZSM-5 or ZSM-22 with 10-ring pore, the *iso*-decane product has shown branched compounds with three methyl groups in the position 2, 4 and 5 in main carbon chain [15–17]. Moreover, n-heptadecane hydroisomerization over ZSM-22 zeolite resulted in a preferential isomers with two methyl branches [19].

SAPO11 is a silicon-aluminophosphate with medium size pore that doped with noble metals (Pt, Rh, Pd) has been used in the selective hydroisomerization of lubricant oils and waxes of medium chain [12]. The use of SAPO11 doped with Pt, Ni and Pd in hydrotreating of vegetal oils is well documented [20–25]. Formation of diverse isomer compounds from vegetable oil makes difficult the control of the hydroisomerization using Pt/SAPO11 catalyst. In this work, palm oil (stearin) was converted to a deoxygenated product by hydrotreating with Ni-MoS$_x$/Al$_2$O$_3$ catalyst under reported conditions [26–28]. Then, the HDO product was hydroisomerized using Pt/SAPO11 catalyst to produce a hydroisomerized HDO product (i-HDO). Fig. 4 shows the investigated reaction pathway. Light hydrocarbons present in i-HDO, which affect some fuel properties, were separated by distillation to obtain a better product (i-HDOd). The cold flow and fuel properties of both products (i-HDO and i-HDOd) blended with HDO were determined. Ultimately, an optimal blend that complies with Colombian standards for biofuels (EN 590:2013 [29]) was formulated.

2. Methodology

2.1. Catalysts and fuel preparation

2.1.1. Catalysts preparation

NiMo/Al$_2$O$_3$ catalyst from Johnson Matthey (Katalco 9910) was sulphided at 300 °C with H$_2$S in situ generated using sulfur (S$_8$) in a 1:8 Ni/S molar ratio at 90 bar of H$_2$ during 1 h. In the synthesis of Pt/SAPO11R, SAPO11 supplied by ACS-Materials was used as support and the platinum source was H$_2$PtCl$_6$·6H$_2$O from sigma Aldrich. 1% of platinum was supported on SAPO11 by wet impregnation, using magnetic stirring during 5 h at 20 °C. The catalyst was calcined at 400 °C/1 h (Pt/SAPO11) and reduced 1 h under H$_2$ atmosphere (20 mL/min) in a quartz tube at 400 °C; the powder was sieved (mesh #200). This reduced catalyst was named Pt/SAPO11R and it was characterized by XRD, TPR, TPD-NH$_3$, TPO, area BET and Pt dispersion by TPD-CO.

2.1.2. Synthesis deoxygenated product (HDO)

100 mL (88 g) of palm oil was blended with 8 g of (NiMo)S$_x$/Al$_2$O$_3$ catalyst in a 250 mL high-pressure reactor. The system was pressurized at 50 bar H$_2$, with H$_2$ flow 60 mL/min H$_2$, temperature 350 °C, with mechanic stirrer at 350 rpm, and a time reaction of 4 h. HDO was characterized by GC–MS and GC-FID (Agilent), acid index (NTC 218 standard), saponification (NTC 335 standard) and pour point (ASTM D97 standard). Conversion and purity were calculated as follows:

$$\%Conversion = \frac{initial\ saponification\ index - final\ saponification\ index}{initial\ saponification\ index}$$
$$\times 100$$

$$\%Purity = \frac{Mass\ of\ n-alkanes\ C_9-C_{24}}{Mass\ HDO\ product} \times 100$$

2.1.3. HDO hydroisomerization

Hydroisomerized product (i-HDO) was obtained through catalytic hydroisomerization of a deoxygenated oil (HDO). 150 mL of HDO product were hydroisomerized with a 1 g of Pt/SAPO11R in a high-

pressure batch reactor. Initial pressure was 50 bar under reductive atmosphere of H$_2$ and the temperature was 350 °C, stirring at 350 rpm was used. Characterization and quantification of products were carried out by GC–MS and GC-FID (Agilent equipment). Acid index by NTC 218 standard, saponification by NTC 335 standard and pour point by ASTM D97 were also carried out. Mass yield were calculated as follows:

$$\%mass\ conversion\ of\ isomers = \frac{Mass\ isoalkanes\ C_9-C_{24}}{Mass\ n-alkanes\ C_9-C_{24}} \times 100$$

$$\%mass\ yield\ of\ i-HDO\ product = \frac{mass\ i-HDO\ product}{mass\ HDO\ product} \times 100$$

2.1.4. i-HDO distillation

The hydroisomerized product (i-HDO) was distilled at 180 °C using a Koehler K45000 equipment. The light fraction was separated and the heavy fraction was named i-HDOd.

2.1.5. Volumetric blends i-HDO/HDO and i-HDOd/HDO

40 mL of blends i-HDO/HDO and i-HDOd/HDO were prepared in proportions 0–100% with increments of 5%. Pour points were measured according to ASTM D97. Curves were fitted using a polynomial quadratic and an optimal blend, according to B2 diesel specifications, was determinate. This optimal blend was named blend$_{opt}$.

2.2. Fuel characterization methods

2.2.1. GC FID-MS conditions

The GC method was calibrated with standards of pentadecane, heptadecane from Sigma-Aldrich and hexadecane, octadecane from Alfa Aesar. Samples were analyzed with internal standard of methyl stearate. Reaction products were quantified in an Agilent 7890 A GC with FID detector and identification was performed with a CG coupled to mass detector Agilent 5975 C. The column was a DB-5HT (30 m × 250 μm × 0.1 μm) from Agilent Technologies.

2.2.2. Relevant physicochemical fuel properties

Distillation tests were made using a distiller from Koehler, according to the ASTM D86 standard. Density, dynamic and cinematic viscosities were measured using an SVM™ 3000 Stabinger Viscometer ™ from Anton Parr, which applies the ASTM D4052 and ASTM D7042 standards. Pour points were measured according to the standard ASTM 97. Acidity and saponification indexes were determined using the standards NTC 218 and NTC 335, respectively. Flash points and cetane index were measured according to the standard ASTM D56-05 and ASTM D4737, respectively. Calorific values were measured with a 6400 isoperibol automatic calorimeter of Anton Parr.

3. Results and discussion

3.1. Pt/SAPO -11 characterization

XRD of SAPO11 shows the expected diffractogram and the same signals are present in the Pt/SAPO11R sample (Fig. 1). New signals in Pt/SAPO11R sample were assigned to metallic Pt in concordance with the PDF 2 database [30]. Results revealed that the support was unmodified by the thermal reduction treatment and by the presence of platinum. The XRD diffractogram of SAPO11 is comparable with the reported by the Jinling petrochemical Company, by Wu et al. and Ma et al. [20,31]. Wu et al. [32] reported some impurities at 8.90° and 21.20° 2θ, these impurities are also present in commercial SAPO11 and have been assigned to residues of synthesis precursors.

TPR and TPO analyses (Fig. 2) show a redox process for (Pt^{+2} ⇆ Pt^0) in the range of 155–160 °C. This TPR signal is associated with the reduction of PtO$_x$Cl$_y$ and PtO$_x$ sites formed during the calcination step [27,28]. In addition, it is possible to observe a small signal at 450 °C,