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Biodiesel cold flow improvement with branched fatty acid alkyl esters (FAAE). Hydroisomerisation on bifunctional acid/metal zeolitic catalysts.

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PURPOSE OF THE ABSTRACT

INTRODUCTION

In the biodiesel production sector the methyl esters of vegetable oils (FAME) remain the major product incorporated in conventional diesel vehicles: in Europe between 2 and 7% volume according to the countries (up to 8% vol. in France and more than 10% in Latin America) with prospects of increasing percentage in the near future. Part of this demand is met by the importation of biodiesel produced from palm oil, which in 2015 accounted for 32% of total biodiesel and 2% of diesel burned in Europe. However, one of the main disadvantages of biodiesel produced from palm oil, rich in saturated fatty acids, is related to its cold flow properties compared to conventional diesel [1,2]. Among the alternatives for improving the biodiesel cold flow properties [3], we propose here a preliminary study of the branching of the hydrocarbon chain of fatty acids by hydroisomerisation (consecutive dehydrogenation and isomerization reactions), which has led to a significant improvement in the properties of cold flow of biodiesel [4, 5]. Although high yields (98%) have been demonstrated in the isomerization reaction of unsaturated fatty acids using ferrierite-type zeolitic catalysts with certain types of additives [3,6], the difficulty remains in obtaining similar yields for the hydroisomerization reaction on the saturated fatty acid chain (the main cause of poor cold flow properties) using beta zeolites [4] and platinum-impregnated ferrierite [7]. This may be due to the fact that the dehydrogenation product can be hydrogenated again without proximity of the isomerization site or because the reactant does not reach the active dehydrogenation site.

METHODS

The catalyst prepared through acid activation and wet impregnation of a commercial ferrierite with Pt was characterized by XRD, TEM, SEM, TPR, IR, NH3-TPD and N2 adsorption. The branched FAAE were prepared in two stages (Figure 1). First, branching of the fatty acids through hydroisomerization reaction over Pt/ferrierite catalyst and second acid esterification with different alcohols. Hydroisomerization reaction was carried out in batch mode at temperatures between 250 and 300 °C and pressures between 1.0 and 3.0 MPa. Reaction products were characterized through NMR and GCMS analyses. The branched FAAE were used as additives in palm biodiesel in concentration between 5 and 15% and their CFP's were determined.

RESULTS

FAAE produced from isobutanol showed the lowest freezingpoint (FP) (isobutyl oleate: -41°C), 20°C lower than

methyl esters FP whereby they were selected. Due to the catalyst treatments, new mesoporosity was created, facilitating the diffusion of the FAAE to the active sites, whereby a high conversion was obtained but with low selectivity. Reaction products showed better cold flow properties than unbranched FAAE (Figure 2). Using these branched FAAE as the additive (15%) in palm biodiesel it was possible to decrease its PP's in more than 10°C.

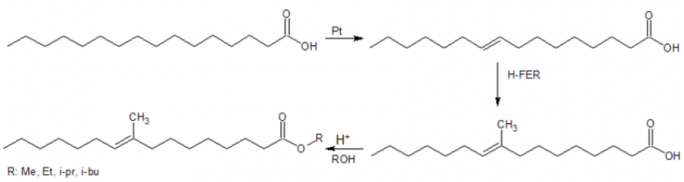
CONCLUSION

Using the Pt/ferrierite catalyst it was possible to obtain branched FAAE from saturated and unsaturated fatty acids with higher yields than previously reported for hydroisomerization reaction. The reaction products have better CFP than unbranched FAAE and permitted to enhance palm biodiesel PP.

PERSPECTIVES

Taking into account that branching of the hydrocarbon chain of saturated and unsaturated fatty acids and their esters has led to improvement of the cold flow properties, further studies will be necessary to develop a selective catalyst for the hydroisomerization reaction of alkyl esters of fatty acids and their derivatives in order to obtain better cold flow properties. The competition between the hydroisomerization of the alkyl chain, the hydrogenation of the ester function and other secondary reactions will however be the biggest challenge in the further catalyst development.

FIGURES



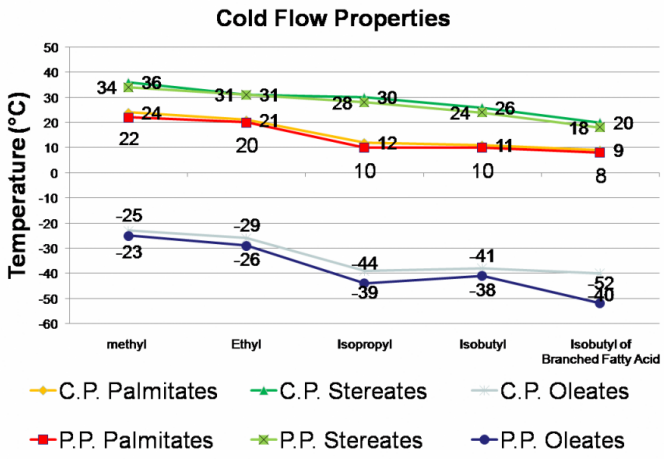


FIGURE 1

Schema of branched FAAE synthesis.

The branched FAAE were prepared in two stages. First, branching of the fatty acids through hydroisomerization reaction over Pt/ferrierite catalyst and second acid esterification with different alcohols.

FIGURE 2

Cold Flow Properties.

Isobutyl esters from branched fatty acids shows the best cold flow properties, with a cloud point from 15 to 26°C lower than methyl esters, and a pour point from 14 to 27°C lower than methyl esters.

KEYWORDS

biodiesel | hydroisomerization | Heterogeneous catalysis | fatty acid esters

BIBLIOGRAPHY

[1] S. Hoekman, A. Broch, C. Robbins, E. Ceniceros y E. Natarajan, «Review of biodiesel composition, properties, and specifications» Renewable and Sustainable Energy Reviews, nº 16, pp. 143-169, 2012.

[2] G. Dwivedi y M. P. Sharma, «Impact of cold flow properties of Biodiesel on engine performance» Renewable and Sustainable Energy Reviews, nº 31, pp. 650-656, 2014.

[3] J.-F. Sierra-Cantor, C.-A. Guerrero-Fajardo, «Methods for improving the cold flow properties of biodiesel with high saturated fatty acids content : A review», Renewable and Sustainable Energy Reviews, vol. 72, pp. 774-790, 2017.

[4] S. J. Reaume, Cold Flow Improvements to Biodiesel through the use of Heterogeneous Catalytic Skeletal Isomerization. Ph. D. Thesis, 2013.

[5] J. Rodrigues, F. Cardoso, E. Lachter, L. Estevão, E. Lima y R. Nascimento, «Correlating chemical structure and physical properties of vegetable oil esters» vol. 83, nº 4, pp. 353-357, 2006.

[6] H. L. Ngo, E. Hoh y T. A. Foglia, «Improved synthesis and characterization of saturated branched-chain fatty acid isomers» European Journal of Lipid Science and Technology, vol. 114, nº 2, pp. 213-221, 2012.

[7] J. F. Sierra-Cantor, Ésteres Alquilicos de Ácidos Grasos Isomerizados como Aditivos para el Mejoramiento de las Propiedades de Flujo en Frio del Biodiesel. MSc Thesis, 2016.