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Introduction

Vegetable oils have a suitable composition for production of fuels and have been therefore extensively exploited for the production of biodiesel. However, biodiesel suffers from several drawbacks such as limited compatibility with conventional diesel engines, low oxidative stability and the need of high quality feedstocks. Thus, the direct conversion of vegetable oils to hydrocarbons (biogasoil) by different hydrotreating methods has been gaining attention and proposed as an attractive alternative, which has also been commercially demonstrated. In contrast to biodiesel, low quality triglyceride feedstocks (such as used frying oils and animal fats) can be processed by hydrotreating, lowering the cost and dependency on food grade vegetable oils.

Material and Methods

Refined high oleic sunflower oil (HOSFO) from COUSA (Montevideo, Uruguay) was used.

Hydrotreatment was performed in a HP/HT 250 mL Parr reactor at 350°C and 100 H₂ bar, for different periods, using NiMo/Al₂O₃ or PtO₂ as catalyst (added at different percentages).

During reaction period H₂ was continuously delivered to reaction system through a pressure regulator. Alternatively, regular purges from reactor head space were performed (GHSV from 13 to 27 h⁻¹), in order to evacuate the gases produced by reaction.

Liquid products were recovered after reaction period, treated with MSTFA/Py and analyzed in a GC 2010 Shimadzu, equipped with on-column injector and a capillary column OPTIMA-1TG (MACHEREY-NAGEL, 10m x 0.1µm x 0.32 mm).

Objective

Study the effect of using different catalyst and reactions conditions on the efficiency of the conversion of high oleic sunflower oil to hydrocarbons by a high pressure / high temperature hydrodeoxygenation process (HDO).

Results and Discussion

Fig. 1

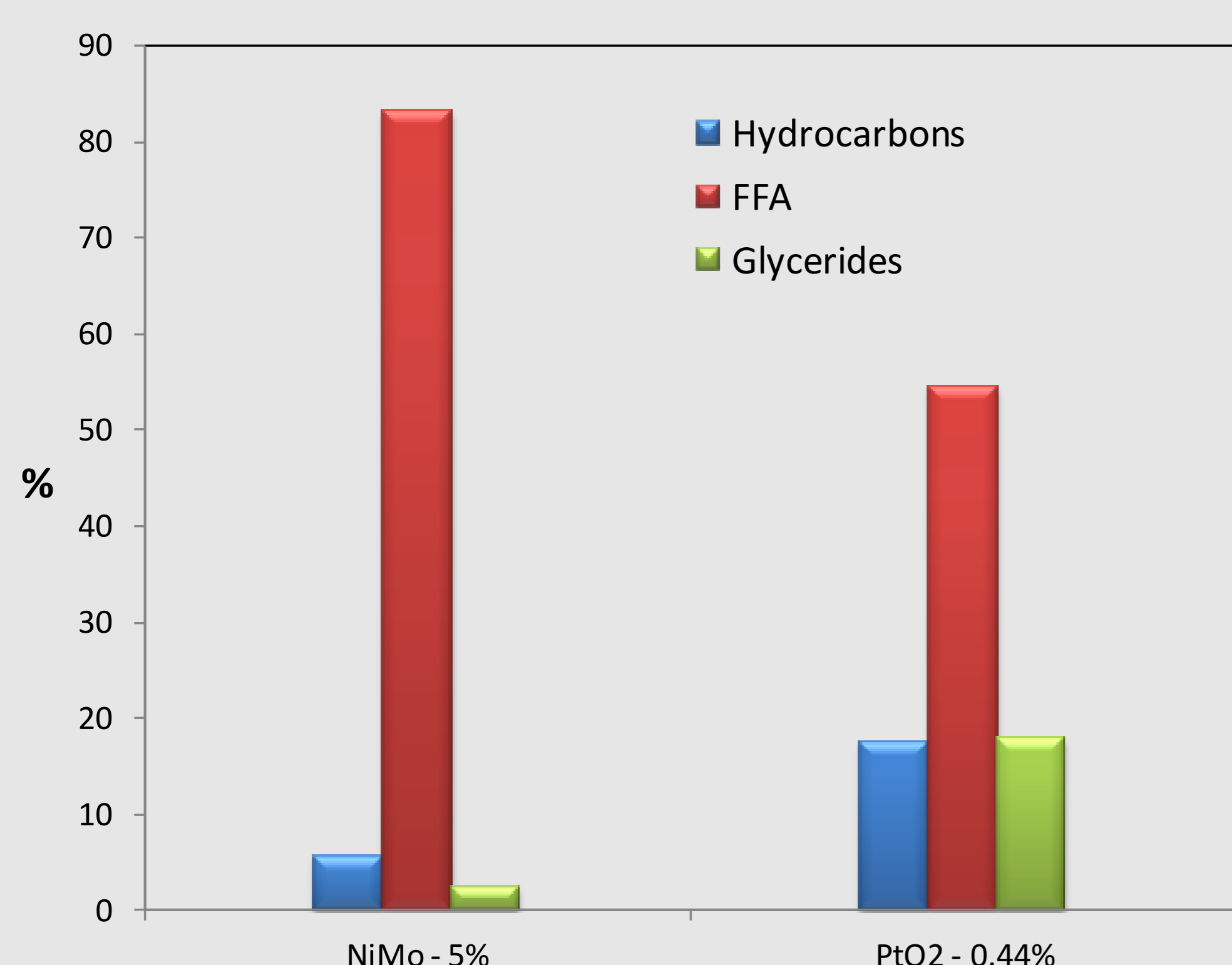
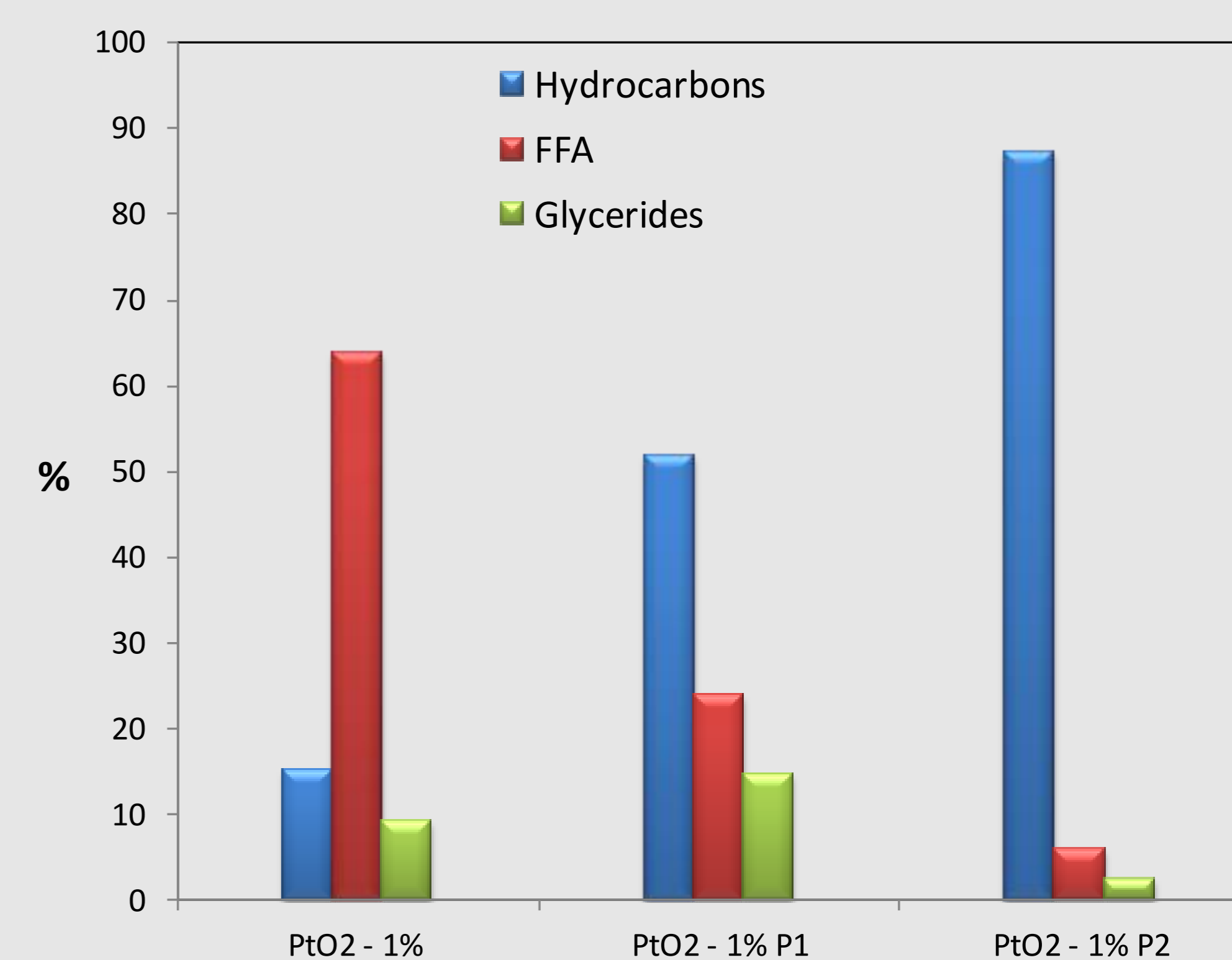


Fig. 1 shows that product from HOSFO treated at 350 °C and 100 H₂ bar catalyzed with 5% of NiMo was mostly composed by free fatty acids (FFA) and contained only 5.5 % of hydrocarbons, demonstrating that process was governed by hydrolysis instead of HDO.

But HDO efficiency clearly improved when only 0.44 % PtO₂ was used as catalyst under same reactions conditions, as shown by the increment of hydrocarbons fraction to 17.7 %, with the corresponding reduction of total FFA percentage to 54.6 %.

Fig. 2

Fig. 2 shows that although rising the catalyst percentage (PtO₂) to 1% did not improved the hydrocarbon yield. But when product (containing the used catalyst) was reprocessed for 2 additional hours performing regular purges of gas from reactor head space, hydrocarbons concentration raised to 51.3% and FFA concentration diminished to 24 % (PtO₂-1% P1). Additionally, after a third reprocessing under same conditions a product containing 87.3 % hydrocarbons and only 2.9 % FFA was achieved (PtO₂-1% P2). Hydrocarbon fraction comprised mostly C18:0 (69.2 %) and C17:0 (24.6 %), suggesting that although HDO was the main process also decarbonylation, decarboxylation and hydrocracking also should have occurred.



Conclusions

Results show that HOSFO can be efficiently converted to hydrocarbons by hydrodeoxygenation under the conditions studied. Purging the gas phase from the system produced a drastic favorable effect on process yield, suggesting that the removal of the main gas products generated by hydrotreating (H₂O, CO₂, CO and C₃H₈) permitted to increase H₂ partial pressure and shifted HDO reaction to almost completion. Further work must be done with commercial NiMo catalyst in order to improve its activity and performance on this process.

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