

UPGRADING OF SOLAR BIO-OILS THROUGH CATALYTIC HYDRODEOXYGENATION

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Hydrothermal processing of biomass

Bio-oils are an attractive source of energy with many advantages over the use of fossil fuels. However, bio-oils present corrosiveness, high viscosity and low heating value associated with their high oxygen content. Therefore, before its application as a transport fuel, it needs to be improved. In this sense, catalytic hydrodeoxygenation (HDO) is one of the most promising biofuel upgrading processes. However, conventional catalysts for HDO based on Co-Mo and Ni-Mo (both sulfidated) or noble metals, still have certain disadvantages. Despite their high activity, sulfidated catalysts progressively deactivate due to oxidation of the active phase in addition to promoting sulfur contamination of the final products [1]. Therefore, the development of cheap catalysts that have high resistance to deactivation and high catalytic activity is one of the main objectives of this field of research. Catalysts based on transition metal carbides improve the properties of their precursor metals avoiding their high production price. Furthermore, porous carbon supports like carbon nanofibers (CNF) have been widely applied as catalyst supports [2,3] for liquid-phase reactions due to their excellent textural properties, as well as their stability in the presence of superheated water.

- [1] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerijs, B.M. Weckhuysen, *Chemical Reviews*, 110 (2010) 3552-3599.
 [2] E. Frecha, D. Torres, A. Pueyo, I. Suelves, J.L. Pinilla, *Applied Catalysis A: General*, 585 (2019) 117182.
 [3] J. Remón, M. Casales, J. Gracia, M.S. Callén, J.L. Pinilla, I. Suelves, *Chemical Engineering Journal*, 405 (2021) 126705.

Experimental

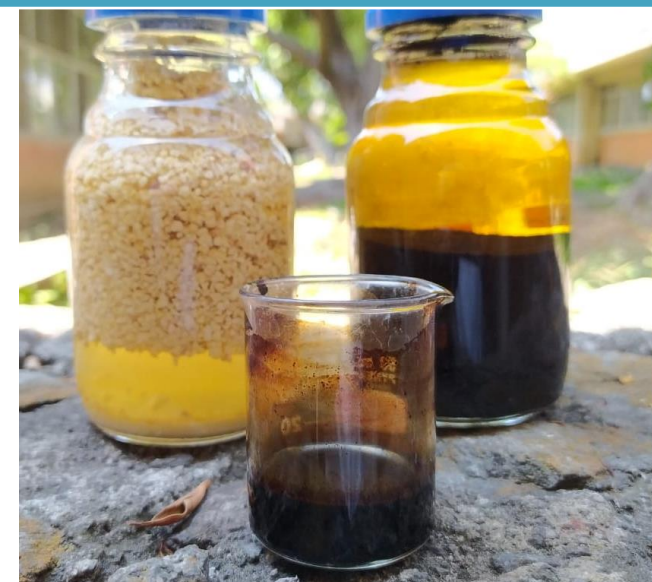
Hydrothermal processing

Agave: 250 °C for 60 min

Corn-cob: 200 and 250 °C for 90 min



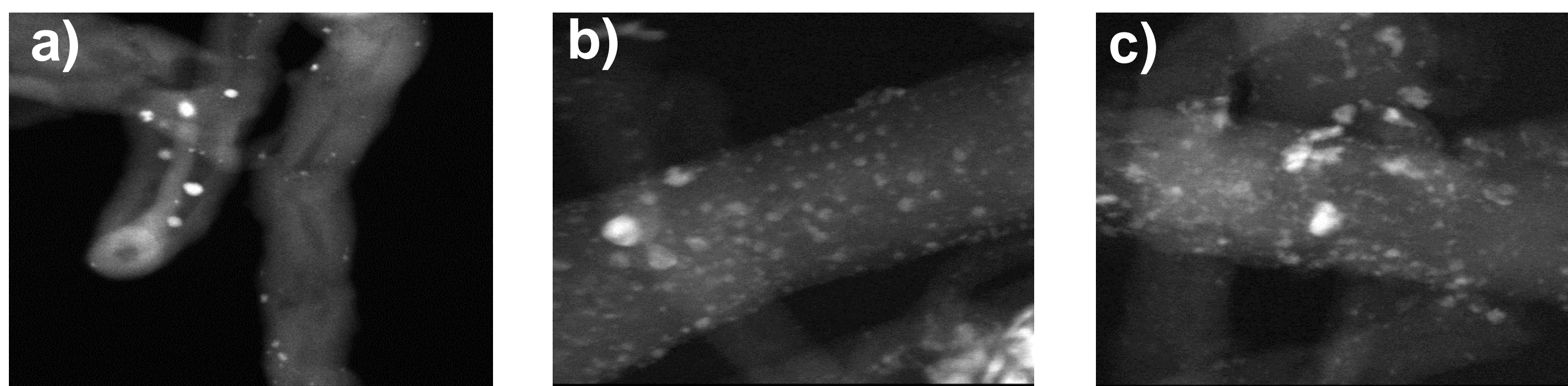
Products separation



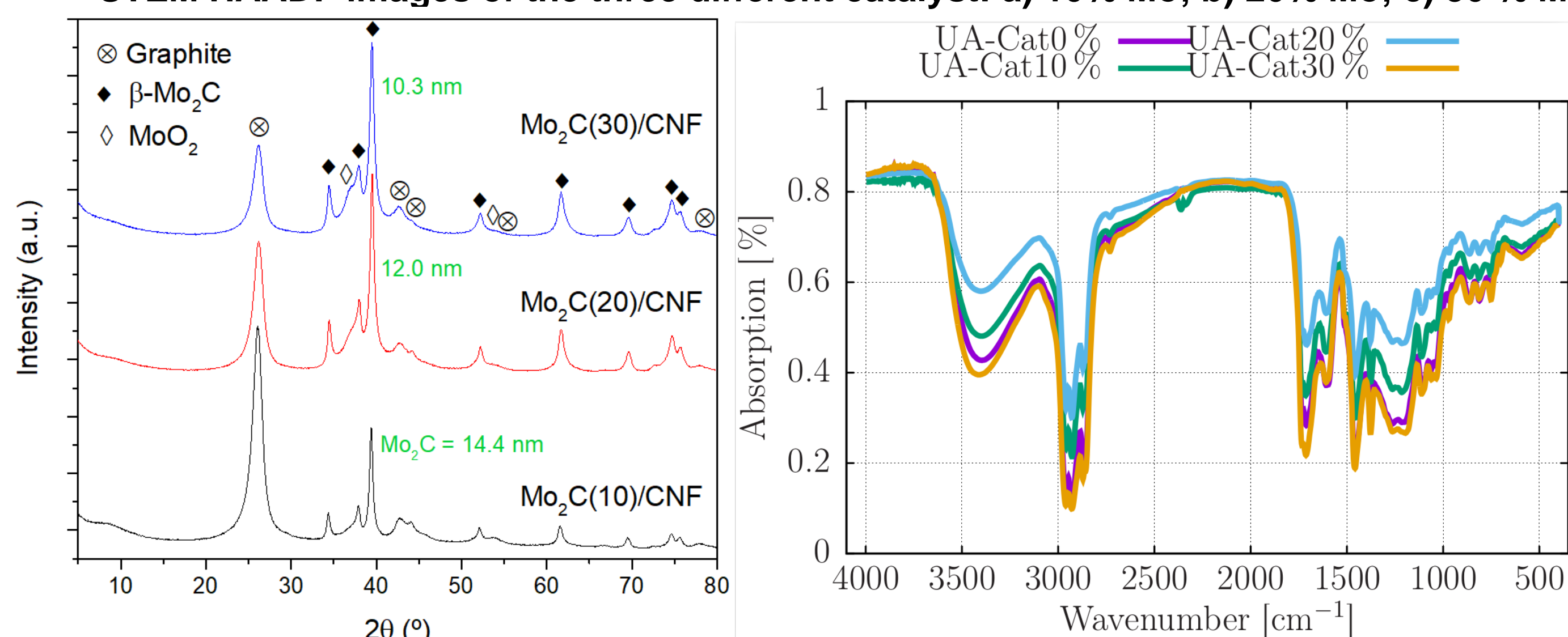
BIO-OIL (CB & AB) from Corn-cob and Agave

Catalytic hydrodeoxygenation in supercritical ethanol in a commercial Parker autoclave SS reactor of 140 mL: 350 °C for 120 min, $P_0/P_f H_2 = 10/116$ bar, bio-oil:ethanol concentration: 1:10

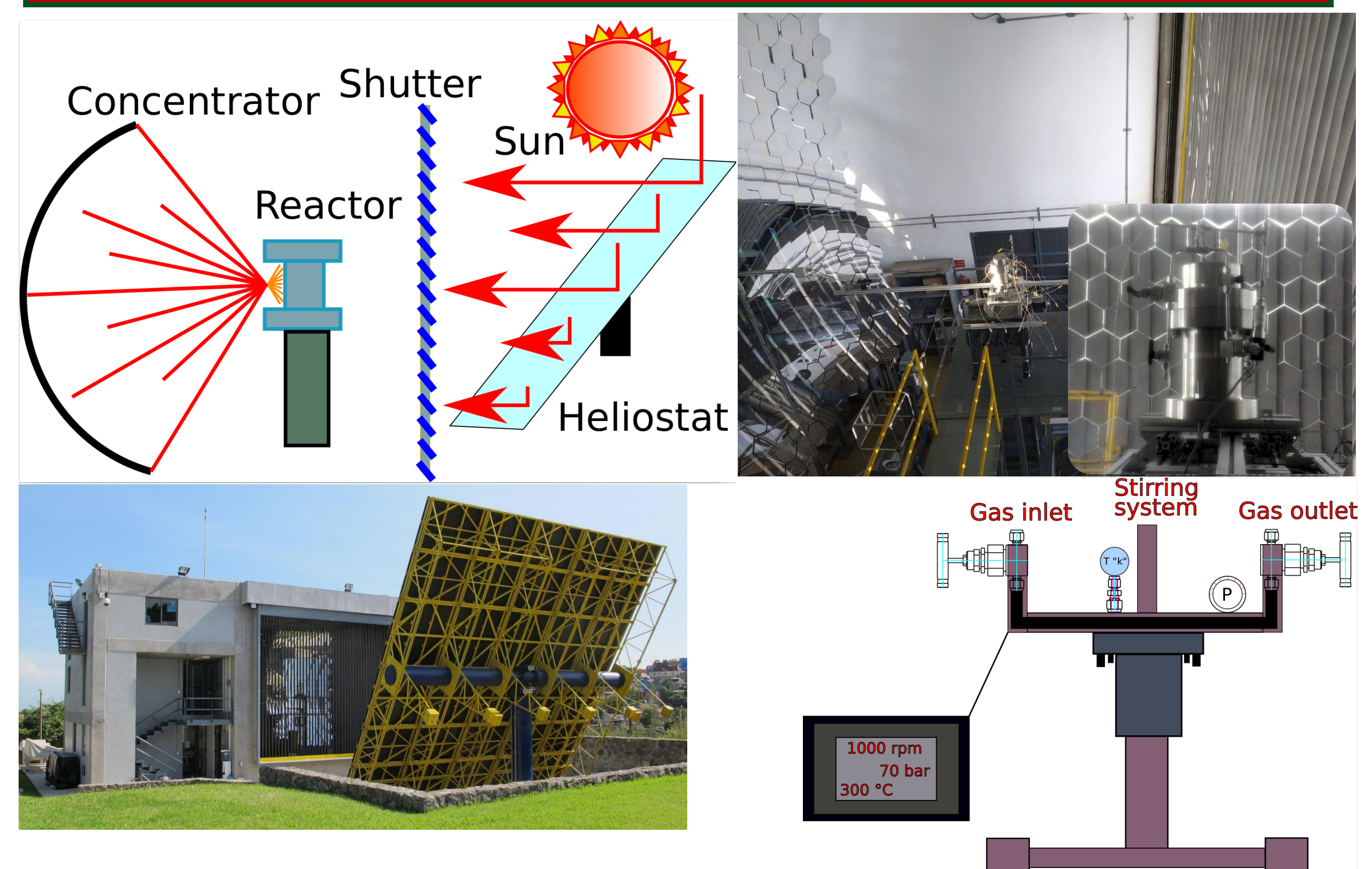
Mo₂C/CNF Catalyst



STEM HAADF images of the three different catalyst: a) 10% Mo; b) 20% Mo; c) 30% Mo.



Solar hydrothermal & HDO reactor



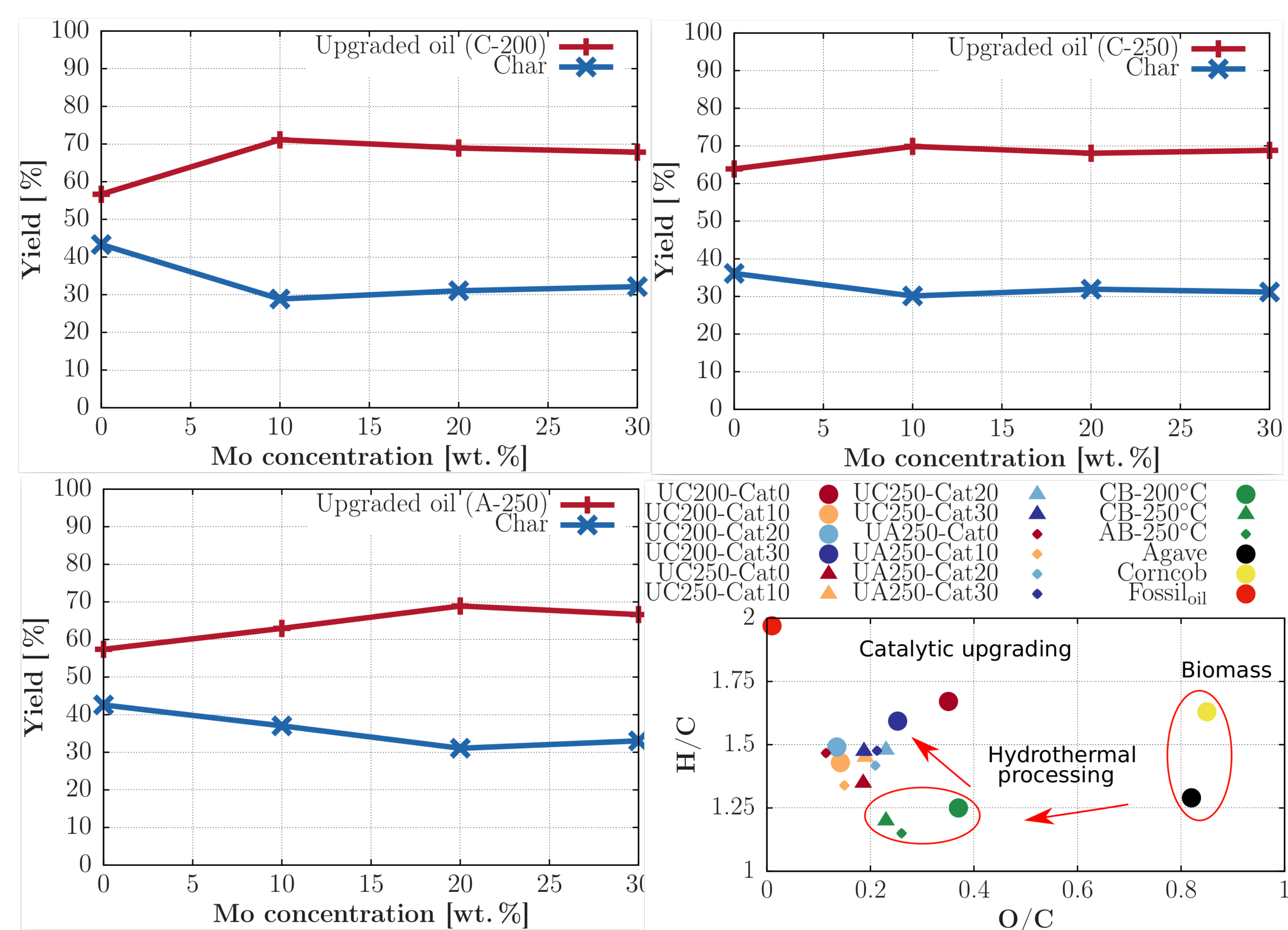
Catalytic hydrodeoxygenation in supercritical ethanol

UPGRADED BIO-OIL (U-Biomass)

Catalyst preparation Mo₂C/CNF

XRD, FTIR, Yields and CHON-S

Influence of Mo catalyst loading on the yields



Conclusions

The use of a catalyst based on Mo₂C/CNF during hydrodeoxygenation process of solar bio-oil improved the upgraded bio-oil yield up to 12%, meanwhile reduced the char formation around 11%. Catalyst with 10% Mo loading showed better improvements on the corn-cob oil yields from the oil produced at 200 °C. On the other hand, for the agave and corn-cob obtained at 250 °C the Mo concentration of 20 and 30% barely changed the oil yield. The upgraded bio-oils had lower O and higher H content as respect the original bio-oil, indicating the occurrence of deoxygenation and hydrogenation reactions.