GOLD

Growing energy crops on contaminated land for biofuels and soil remediation

D2.8 “CC - Process configurations, conditions, products distribution and quality”

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Partners

CRES - Centre for Renewable Energy Sources and Saving Foundation, Greece
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UDES - Université de Sherbrooke, Canada
IBFC - Institute of Bast Fiber Crops, Chinese Academy of Agricultural Sciences, China
CTD - Society for Economic and Social Studies, Center for Technology and Development, India

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Introduction

The aim of this deliverable was the cracking to carbon nanofilaments. CC has been replaced by CR (reforming) because the preliminary testing has shown that it is more efficient. The results regard CH_4 as surrogate reactant. Pyroproducts, which are now produced in the kg-lab scale unit (4-5 litres per run of about 5 h at steady state), are being tested and the full results will be available until the end of the project (in the 3rd reporting report of the project since are not part of this deliverable). However, we intend to perform the cracking also; there is a delay due to technical problems with the cracking unit and the full results must be available by the end of 2024.

1 Configuration of Catalytic reforming kg-lab scale test rig

The performance of Ni-supported UGSO powder and the pellets (4-5 mm in length) is measured using the kg-based 1.37 m long continuous flow fixed bed reactor containing a 0.83 m long cylindrical tube (reaction chamber) with 60 mm i.d. The reactor was charged with 300 gm of the catalyst, held in the reaction zone using the inert alumina ceramic balls. A preheater was used to preheat the feed until 400°C before injecting the reacting mixture (CH_4, CO_2) into the reaction chamber. The schematic diagram of the reactor is shown in Figure 1. The reactor is equipped with K-type multiple thermocouples placed inside the reactor tube to monitor the reactor temperature up to ten separate locations. The pressure was controlled using the pressure relief valve calibrated for each set of pressure.

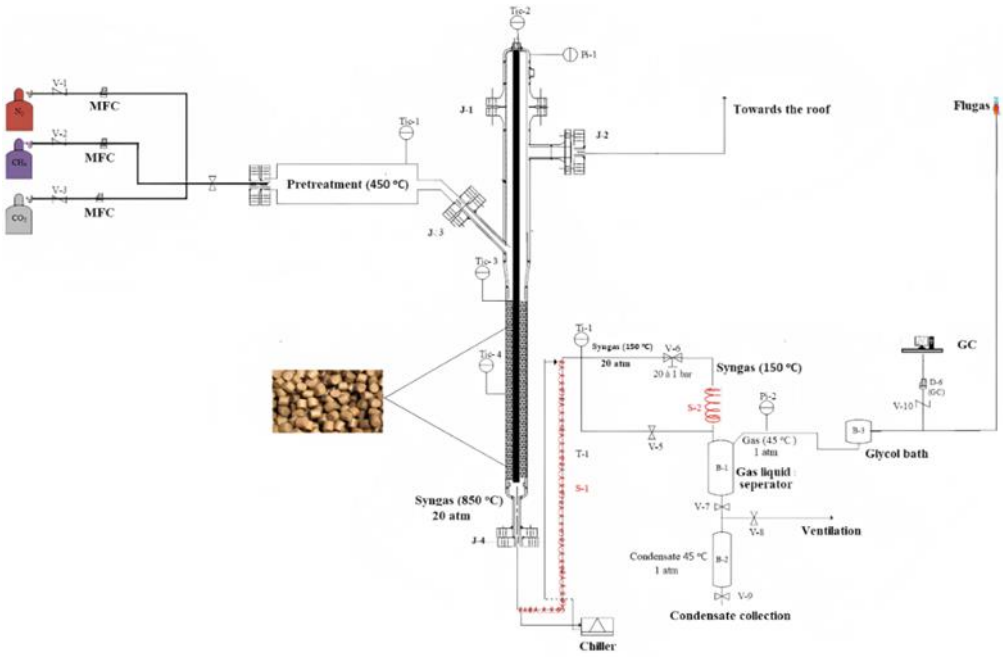

Figure 1: Catalytic reforming test process flow diagram

2 Conditions

2.1 Catalyst preparation

The Ni-UGSO pellets are produced using the wet agglomeration process. Initially, the UGSO was sieved to get the 53 µm size particles. Afterwards, sieved UGSO, the clay (25%), water contents and certain amount of nitrate hexahydrate salt Ni $(NO_3)_2{\cdot}6H_2O$ depends upon the desired percentage of nickel were milled for 10 minutes to get

a homogenous mixture. Finally, the resulting slurry (mixture) was introduced into the extrusion machine (Thermo Scientific Process 11 Parallel Twin-screw Extruder), and the feeder rate, temperature (120°C), pressure and the RPMs (110) of screws were accurately adjusted to get cylindrical granules in 4-5 mm length at the exit of the die. The granules were afterwards dried in the oven at 105 °C for 4 hours and calcined at 1100 °C for 3 hours. We used 20, 25 and 30% binder (clay) contents under the 3 and 6 h calcination times to target pellets with higher breaking strength and surface area. The Ni-UGSO powder had a 4.1 m^2/g surface area, and it is observed that whatever the calcination time is (3 or 6 h), the 85-90% reduction in surface area of the pellet ($0.24 m^2/g$ – $0.62 m^2/g$) was observed. Since there was not much difference in their activity, the pellet with 389 N (Newton) breaking force prepared from 25% binder and 13 %Ni formulation was chosen for the DRM test, and the results are reported in this deliverable.

2.2 Tests conditions

Initially, pure N_2 flow was passed from the catalyst bed for approximately 3 h until the preheater was heated to 400°C and the reactor bed to 800°C. After that, the CO_2 and CH_4 in a 2:1 ratio at GHSV 810 L/h.kg_{cat} were injected under different pressure regimes (1, 3.5, 5.5, 6.5, 8 and 10 atm) depending upon the experimental conditions. The gaseous samples were collected using the syringe every 15 min from the beginning of the reaction until the 4 hours, and product samples were analyzed in the GC (company name) with Ar (purity of 99.99%) as carrier gas. The catalytic performance of the catalysts was evaluated using the following equations.

$$X_i(\%) = \left[\frac{F_i\,(in) - F_i\,(out)}{F_i\,(in)} \times 100\,, \qquad i = CO_2 \text{ or } CH_4\right] \qquad (1)$$

$$Y_{co}(\%) = \left[\frac{(nCO)_{produced}}{(nCH_4 + nCO_2)_{in}} \times 100\right] \qquad (2)$$

$$Y_{H2}(\%) = \left[\frac{(nH_2)_{produced}}{2 \times (nCH_4)_{in}} \times 100\right]$$

2.3 Metals mapping on the pellet (SEM-EDXS)

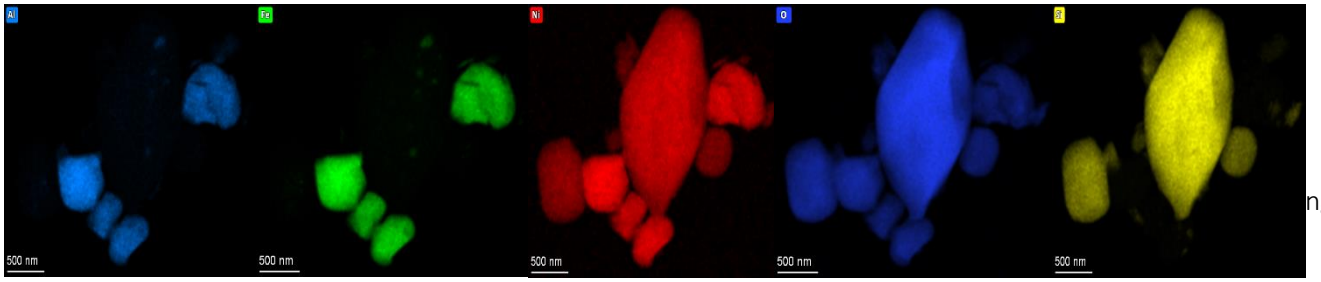

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Figure 2: The metals mapping on the pellet

3 Products distribution and quality

In Figures 2 the performance of the catalyst at various P conditions including conversions and products distributions are presented.

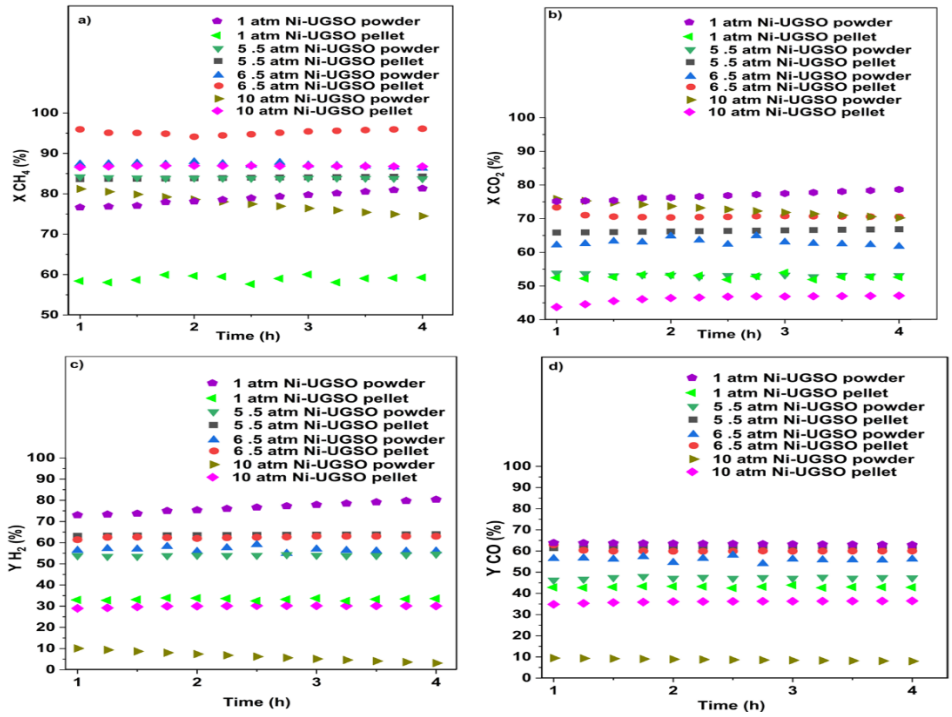

Figure 3: Reforming reactants conversions and products distributions and yields at various P

4 Conclusions and further steps

In summary, we have characterized the Ni-supported UGSO pellet promoted with clay binder by the wet impregnation method. Our results demonstrated that despite the lower surface area, the Ni-UGSO pellet achieved higher performance than the Ni-UGSO powder because of better Ni dispersion due to surface silicate formation. Figure 4 shows the better dispersion in pellets. The pellet synthesis method enhanced the surface basicity and lattice oxygen by providing Mg-based surface silicates and maintained the robust interaction between Ni and the spinels, which improved the Ni resistance to the coke and enhanced the activity and selectivity of the catalyst until 6.5 atm and provided remarkable results; however, at higher pressure, increased extent of inevitable exothermic coke formation reactions promotes particle agglomeration and enhance the surface temperature thus deactivates the catalyst surface. Increasing the pressure from 6.5 atm leads to lower activity and selectivity of the pellet in DRM. It forms the crystalline graphitic carbon and ultimately disintegrates the pellet particles. A proper combination of thermodynamic analysis to investigate the coke-free zones and additional research for well-dispersed, higher mechanical strength and optimum surface area-based catalytic pellets is critical to mitigating the coke deposits at higher pressure.

The next steps planned based on D2.8 are:

1. Evaluation of the same catalysts at the same high pressure and temperature conditions under steam reforming conditions: a scientific article is submitted for review.
2. Evaluation of the same catalysts at the same high pressure and temperature conditions under autothermal POX conditions: tests completed; the results are interpreted and a scientific article will be submitted for evaluation shortly.

3. Cracking of pyroliquids to produce carbon nanofilaments by dry reforming and by plasma-assisted cracking: tests underway in October (it is related to MS10) and results will be evaluated and another scientific article will be submitted for review.

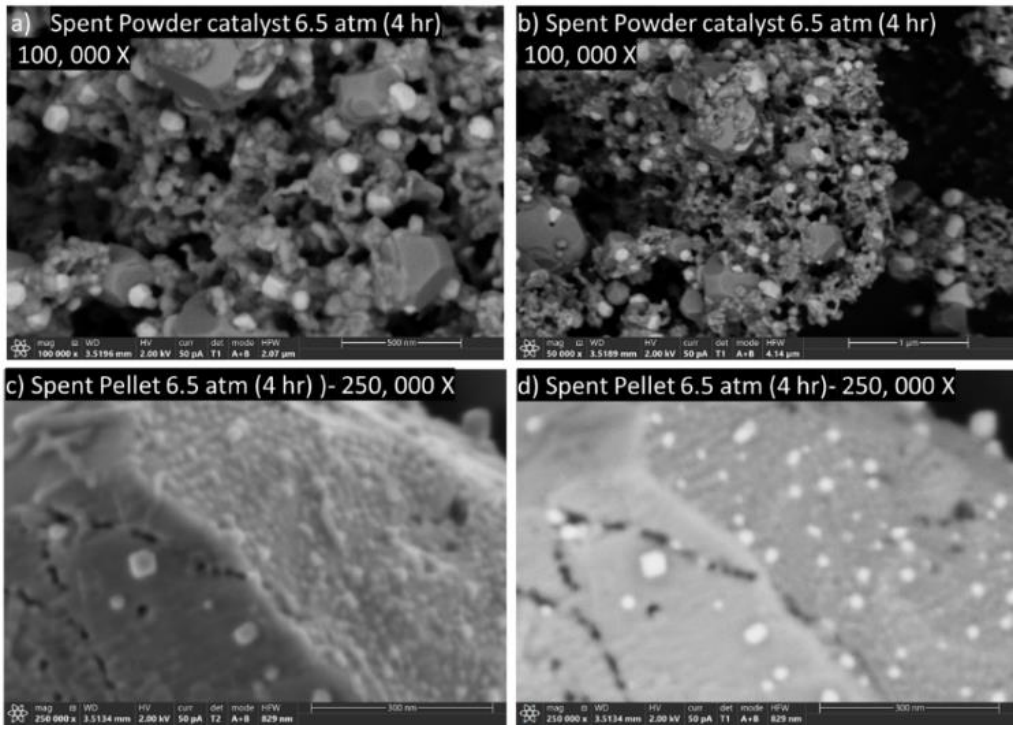

Figure 4: The SEM analysis validating better dispersion in pellets (bright spots are metallic species (Ni, Fe)