

# GOLD

Growing energy crops on contaminated  
land for biofuels and soil remediation

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## D2.7 High temperature autothermal pyrolysis and upgrading



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<b>TUM</b> - Technische Universität München, Germany
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<b>IBFC</b> - Institute of Bast Fiber Crops, Chinese Academy of Agricultural Sciences, China
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### Statement of Originality

This deliverable contains original unpublished work except where clearly indicated otherwise. Acknowledgement of previously published material and of the work of others has been made through appropriate citation, quotation or both.

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## Executive Summary

There are three advanced components in this deliverable:

1. Catalytic pyrolysis of biomass contaminated with heavy metals: a doctoral student and part-time work of 3 professionals (mechanics, electrical and data acquisition)
2. Dry reforming (simulated pyrolytic fluid and CO<sub>2</sub>) using two new catalysts: a doctoral student and part-time work of 3 professionals (mechanical, electrical and data acquisition)
3. Fischer-Tropsch synthesis of liquid biofuels from biogas produced in step 2: a doctoral student and part-time work of 3 professionals (mechanics, electrical and data acquisition).

Deliverable D2.7 has been completed at the 90% level of completion. Process configurations, conditions, start-up and steady operation protocols have been finalized. Commissioning revealed some technical problems which are now fixed and a full 1<sup>st</sup> ATP (autothermal pyrolysis test will be performed early in 2024). These problems and their remediation are provided with in the next sections of this report.

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## Introduction

There are **three advanced components** in this deliverable:

1. Catalytic pyrolysis of biomass contaminated with heavy metals: a doctoral student and part-time work of 3 professionals (mechanics, electrical and data acquisition)
2. Dry reforming (simulated pyrolytic fluid and CO<sub>2</sub>) using two new catalysts: a doctoral student and part-time work of 3 professionals (mechanical, electrical and data acquisition)
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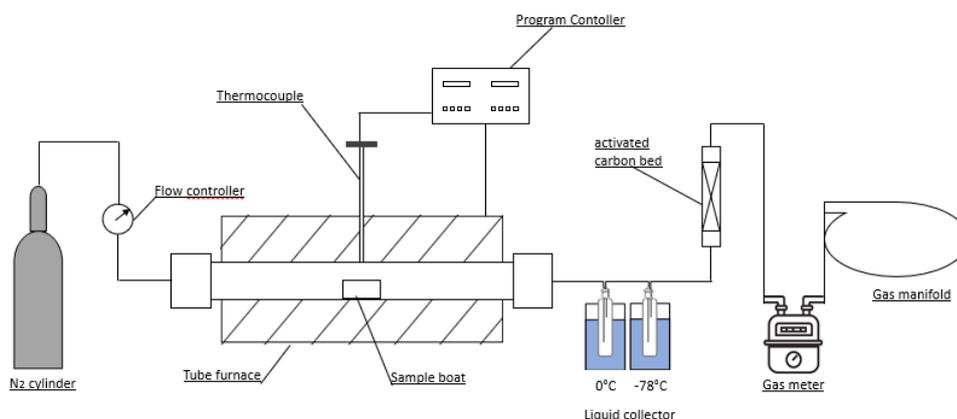
Deliverable D2.7 has been completed at the 90% level of completion. Process configurations, conditions, start-up and steady operation protocols have been finalized. Commissioning revealed some technical problems which are now fixed and a full 1<sup>st</sup> ATP (autothermal pyrolysis test will be performed early in 2024). These problems and their remediation are listed below:

- Preheating of the unit (transient state): this critical step encompasses the use of pyrolysis simulated gas product to be burned at the lower part of the ATP. The maximum allowable power is relatively low, thus rendering the transient state typically lengthier than 18h.
- The gas distribution plate built on exotic alloys proved inappropriate due to excessive relatively fast oxidation. It has been replaced by hard ceramic plates whose composition (based on zirconia) and geometry have been studied towards optimization. The optimized plate will be tested within the next month.
- Problems with the feeder encountered. The geometry of the flights is studied and an optimized design is now adopted. It will be also used soon for the full-scale runs.

Thus: the products distribution and quality and contamination content in all derived product phases are available at g-lab batch runs and reported here, but the full-scale runs results will be available before the end of the winter 2023-2024.

## **1** Catalytic pyrolysis of biomass contaminated with heavy metals

The pyrolysis reactor used is a fixed bed on laboratory scale (g-lab) which operates in batch mode. This is a pyrolysis furnace with controllable temperature and heating speed, composed of a horizontal quartz tube 90cm long and 9cm in diameter inside which is deposited an alumina crucible containing the biomass under inert atmosphere (nitrogen). The nitrogen flow rate is set at 0.2 SLPM after purging and the biomass particle size is <1mm. The volatile compounds are carried towards the outlet with the flow of nitrogen where they are cooled to two different temperatures (0 and -78°C) to ensure maximum recovery of condensable component (bio-oil). The outlet gas flow rate is determined by a gas meter connected to the outlet. Figure 1 is a block diagram of the set-up used.



**Figure 1: Batch catalytic pyrolysis set-up**

Approximately 13g of previously washed, dried and crushed biomass are used for each pyrolysis test. An experimental plan (Box-Behnken optimization plan) was established varying the temperature (between 500 and 800°C), the heating rate (between 2 and 10°C/min) and the residence time at the maximum temperature (between 20 and 60 min) for the pyrolysis of switchgrass biomass. The biomass used contains  $43.5 \pm 2.21\%$  carbon (elemental analysis SC632) and has an ash content of 1.4% (ASTM-e1755 method). According to our ICP analyses to check the level of contamination of this biomass, it contains 34.8 ppb in Cu, 499.8 ppb in Fe and 57.8 ppb in Sb; other heavy metals are in trace amounts.

The mass yields of biochars are between 21% for high heating rates and 26% for low heating rates. Elemental analysis gives a carbon content of 85 to 90%. Bio-oil yields are maximum (29%) for average temperatures (650°C) and average heating rates (6°C/min). The quantity of gas (volume) increases with the temperature, and is favored with low heating rates. The maximum quantity of gas produced for 13g of biomass is 21.44 liters at 800°C and for a heating rate of 2°C/min; the minimum quantity being 3.58 l (650°C and 10°C/min). Nearly 90% of all contaminating metals remain with the solid (biochar).

The kg-lab autothermal pyrolysis unit has been commissioned, technical problems solutions are near completion and the tests are under way. Figure 2 shows the ATP fluidized bed and Figure 3 some publicly available details of the heat providing lower part of the ATP reactor. Finally, Figure 4 shows details of the micro-combustion chamber at the lower part of the ATP reactor.



Figure 2: ATP reactor drawing

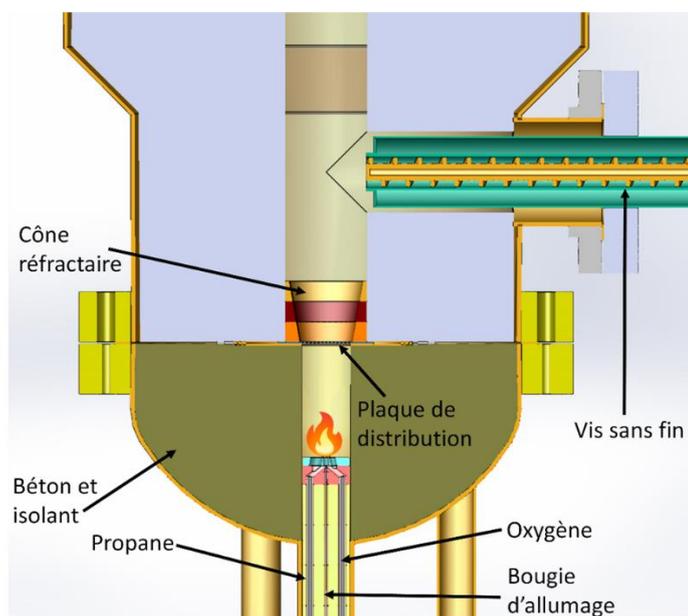


Figure 3: Heat providing lower part of the ATP reactor

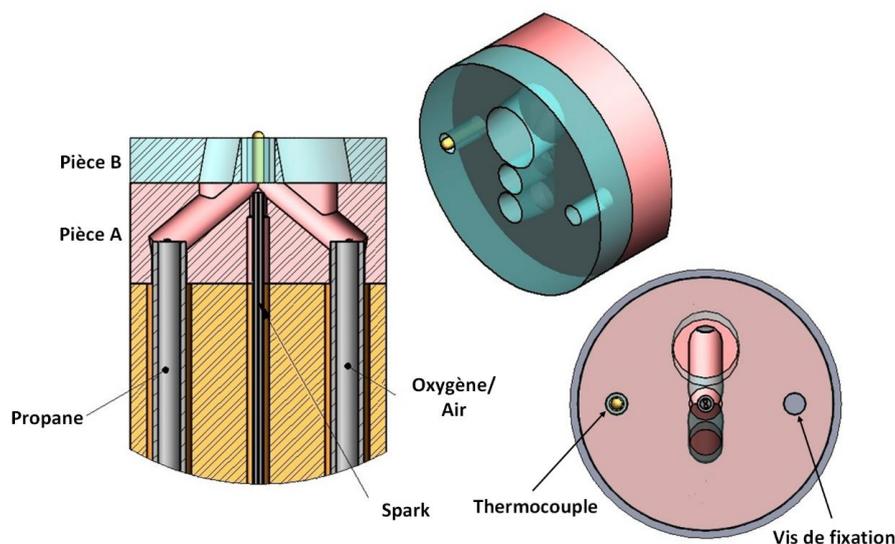


Figure 4: Micro-combustion chamber at the lower part of the ATP reactor

## 2 Dry reforming (simulated pyrolytic fluid and CO<sub>2</sub>)

Most academic studies work on dry reforming (DRM) catalysts at atmospheric pressure, industrial applications require high pressure systems. The current study focuses on the use of the patented Ni-based catalyst supported on UGSO in the form of cylindrical granules (4-5 mm in length) at pressures between 1 and 10 atm. The kg-lab scale setup in Figure 5 is used to study the effect of pressure on the activity and selectivity of the catalyst in the fixed bed reactor. The working variables and reactor conditions are described in Table 2. These experiments are conducted at a temperature range of 700-800 °C, at a pressure range of 1-10 atm in a fixed bed reactor (1.5 m long and 6 cm internal diameter). The reactor is charged with 300 g of the catalyst, maintained in the reaction zone using inert alumina ceramic beads. A preheater was used to preheat the feed until 450 °C before injecting the reaction mixture (hydrocarbons, CO<sub>2</sub>) into the reaction chamber. A paper is now submitted.

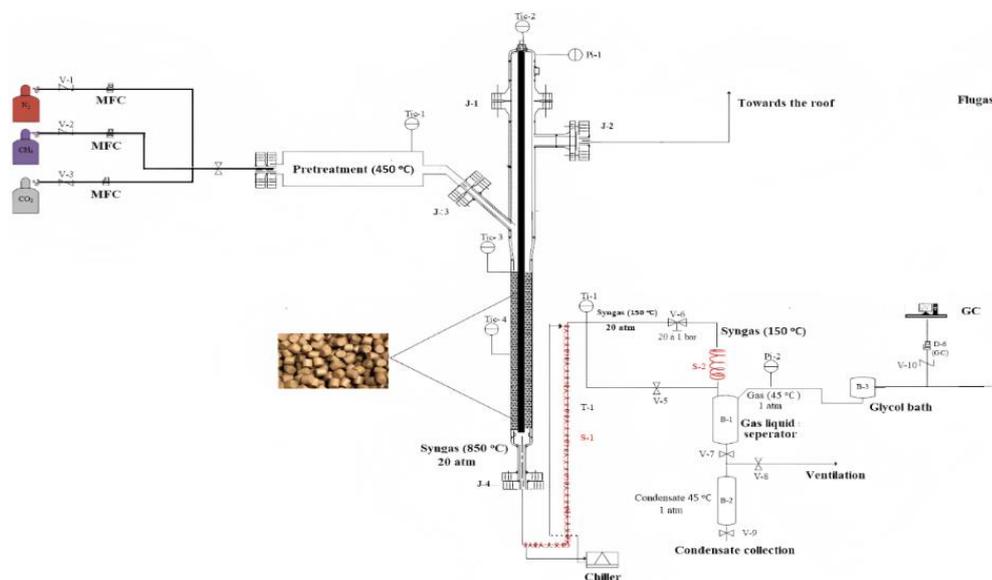


Figure 5: DRM kg-lab scale setup

The main findings are summarized in Figure 6 below. All mechanistic explanations are available in the upcoming paper.

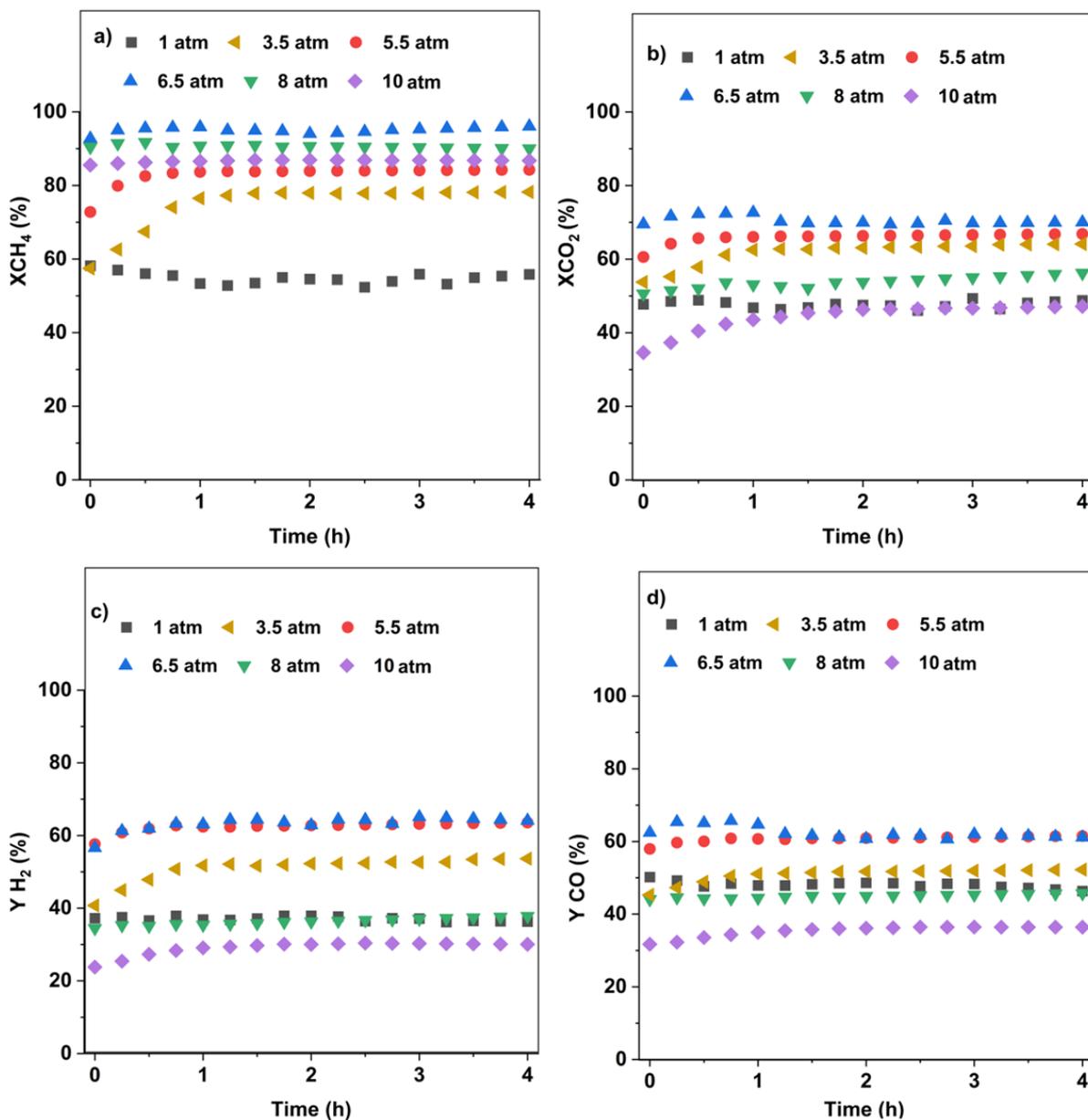


Figure 6. The Ni-UGSO pellet performances in DRM reactions (a) Conversion of CH<sub>4</sub> (%); (b) conversion of CO<sub>2</sub> (%); (c) yield of H<sub>2</sub> (%), (d) yield of CO at 800 °C, feed composition CO<sub>2</sub>/ CH<sub>4</sub> = 2:1, GHSV: 810 L/(h\*kg<sub>cat</sub>), P: 1-10 atm.

## 3 Fischer-Tropsch synthesis (FTS) of liquid biofuels from biogas produced in 2

A series of experimental tests are carried out in a 3- $\phi$  CSTR reactor with the aim of optimizing in parallel different parameters (catalyst formulation and operating conditions), for better conversions of CO, CO<sub>2</sub> and yields of liquid hydrocarbons.

Figure 7 shows the PFD diagram of the experimental setup. The principle consists of suspending the catalyst in an inert solvent, the reactive gas is then introduced at the bottom of the reactor and distributed in the solvent. Vigorous agitation is applied to maintain CSTR conditions as well as to have a homogeneous system temperature. The reaction is carried out at a pressure in the range of 10 to 30 atm and a temperature of 200 to 300°C. Unconverted syngas and light products exit the reactor in gaseous form, while heavy liquid hydrocarbons remain in the reactor. The heat is removed through cooling coils mounted inside the reactors. The mixture (gases and light liquids) passes into a cold trap to capture the liquid products and separate them from the non-condensable vapors. A flow meter (Omega) is located at the outlet to measure the total gas flow. The gas and liquid samples are analyzed by a gas chromatograph (TCD-FID SCION Instruments 456 GC).

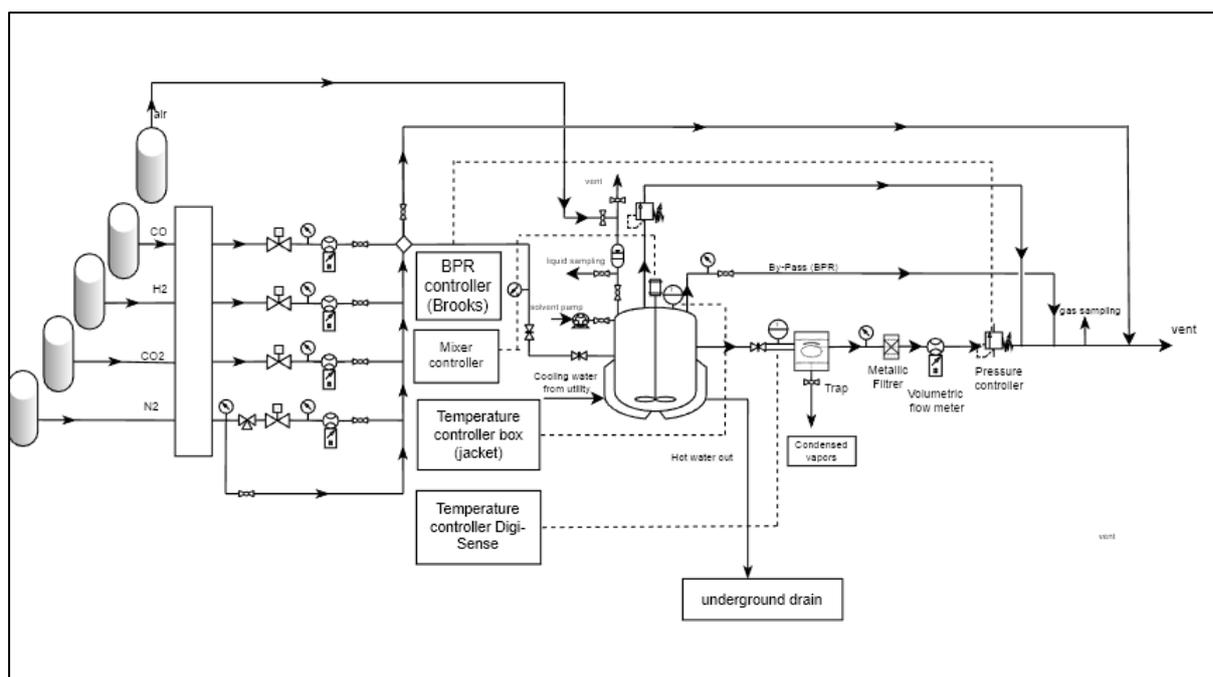


Figure 7: Process Flow Diagram of the used FTS set-up

The initial catalytic test for the Co/HAp-based catalyst was carried out for 6 hours in the CSTR 3- $\phi$  reactor, at a pressure of 20 atm and a temperature of 230°C. The results, presented in Table 1, show that the CO conversion, which is around 40%, remains stable during the 6-hour reaction. Selectivity towards liquid hydrocarbons (C<sub>5</sub>+) was high, at around 55%, and tended more towards the petrol fraction (C<sub>5</sub>-C<sub>12</sub>). Table 1 shows these results.

Table 1

CO Conversion and FTS products selectivity for the catalyst

Co/HAp (at P=20bars, T=230°C, TOS=6h, H<sub>2</sub>/CO=2)

t (min)	X <sub>CO</sub> (%)	Y <sub>CH<sub>4</sub></sub> (%)	Y <sub>C<sub>2</sub>-C<sub>4</sub></sub> (%)	Y <sub>C<sub>5</sub>+</sub> (%)
30	10,81	60	0,00	40,24
60	43,03	14	13,48	72,67
90	46,38	16	35,96	47,99
120	43,97	12	36,58	51,24
150	42,83	9	27,34	63,42
180	40,21	10	13,10	77,28
210	40,64	10	12,97	77,09
240	43,26	11	28,71	60,22
270	42,45	9	28,44	63,03
300	44,00	9	35,44	55,68

## 4 Key findings and policy relevant messages

### 4.1 From the ATP runs

The mass yields of biochars are between 21% for high heating rates and 26% for low heating rates. Elemental analysis gives a carbon content of 85 to 90%. Bio-oil yields are maximum (29%) for average temperatures (650°C) and average heating rates (6°C/min). The quantity of gas (volume) increases with the temperature, and is favored with low heating rates. The maximum quantity of gas produced for 13g of biomass is 21.44 liters at 800°C and for a heating rate of 2°C/min; the minimum quantity being 3.58 l (650°C and 10°C/min). Nearly 90% of all contaminating metals remain with the solid (biochar).

The kg-lab autothermal pyrolysis unit has been commissioned, technical problems solutions are near completion and the tests are under way.

### 4.2 From the DR runs

The Ni-UGSO pellet achieved higher performance than the Ni-UGSO powder because of better Ni dispersion due to surface silicate formation. 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, high 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.

### 4.3 From the FTS runs

The initial catalytic tests for the Co/HAp-based catalyst show that the CO conversion, which is around 40%, remains stable during the 6 h reaction. Selectivity towards liquid hydrocarbons (C<sub>5+</sub>) was high, at around 55%, and tended more towards the petrol fraction (C<sub>5</sub>-C<sub>12</sub>).

## 5 Conclusions and further steps

The D2.7 has been delivered on time with a degree of completion 90% due to some extended commissioning delays. However, additional work covering works to be delivered later are clearly in advance of the expected completion. These are all materials reported here in point 2 and 3.