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2. *Executive publishable summary*

Objectives:

The general objective of this project aimed to reduce pollutant emissions by developing an advanced and innovative process to produce clean transport fuels precursors coupling low temperature autothermal catalytic oxidation of natural gas and an advanced Fischer-Tropsch reaction system. The main R&D objectives in the syngas production were the development of improved catalysts and the application of chemical reaction engineering advanced concepts to design a new reaction system with optimal methane conversion, catalyst stability and heat management. The main R&D objectives in the Fischer-Tropsch synthesis step were the development of improved catalysts using modified supports and the design and testing of a continuous dewatering selective membrane module to be included in the FT reaction system to increase the conversion of syngas to hydrocarbons.

Description of the work:

The work developed can be divided in four packages. The first one includes: i) new methane autothermal CPO catalysts preparation, characterisation and lab scale activity testing with special emphasis in those able to operate at relatively low temperatures (producing CO₂ rich syngas); ii) the testing under realistic conditions of the more promising catalysts (Ni supported on Mg doped α -alumina and Ru supported on alumina) and the comparison of their performance with commercially available CPO catalysts, and iii) the application of advanced chemical reaction engineering concepts to design an autothermal CPO reaction system with optimal heat management to avoid coke formation and to get high methane conversions and catalytic stability. The second one includes: i) the development (preparation, characterisation and lab scale activity testing) of new Fe- and Co- based FT catalysts using modified supports (hydrophobicity, high thermal conductivity, monoliths); ii) the optimisation of the activation procedures of these FT catalysts; iii) again the testing of the most promising catalysts (Fe promoted by K, Cu, Ce, Mn, and/or Zn) under realistic conditions and the comparison of their performance with commercially available FT catalysts, and iv) the development of water selective membrane modules and their testing at FT reaction conditions to continuously extract water from the reaction mixture and to boost syngas conversion to hydrocarbons. The third one includes a technical and economic assessment of the new GTL process resulting from the integration of all the successful innovations developed in the previous work-packages. The fourth one deals with all the co-ordination efforts required to maximise the synergies among all the partners and to control that the expected milestones are fulfilled.

Expected results, dissemination and exploitation plans:

The final results obtained in this project are the following: i) an innovative low temperature wet partial oxidation process to produce syngas from NG has been developed and the experimental data gathered and the simulation results indicate that it is 15 % cheaper (capital costs) than the conventional syngas producing technologies from NG commercially available; ii) advanced FT synthesis catalysts and an innovative chemical reaction system coupling catalytic fixed-bed reactors and dewatering selective membranes have been developed and experimental data proved that, using Fe-based catalysts, this approach can deal with CO₂-rich syngas reaching conversions and selectivities similar to the ones obtained in commercial processes; iii) when the low temperature syngas production process and the advanced FT synthesis reaction system were coupled to build a GTL process the simulation results and the techno-economic evaluation showed that both capital and operating costs are higher but near the ones calculated for the base-case initially selected from commercial process data available. These results indicate that these approaches to GTL technologies will start being of commercial interest when better dewatering selective membranes are available. Even though the ones developed in this project are an excellent basis for further research and development. The commercial applications of this project results are not only relevant from the point of view of GTL technologies, they also present significant developments very useful for BTL (biomass to liquid technologies). For example biomass gasification produces syngas with significant amounts of CO₂ and as a result the innovative approach to FT synthesis developed in this project can be of paramount importance. Seven co-ordination progress meetings took place. One of it was held in each of the cities where the partners are located (Madrid, Petten, Messina, Karlsruhe, Villigen, Lyon and Bilbao). Other more specialized meetings were held for specific topics related to some aspects of the project development. From all the common activities performed and the scientific and technological discussions held a solid research partnership has been built.

2. Objectives of the project

The main objective of this project was the development of a more efficient process to produce clean liquid fuel precursors from natural gas (Gas-to-Liquid or GTL). This new process includes innovations in its two main stages. Along the three years of project work all these initial innovations have been investigated and some promising results have been reached. This development is of special interest for the general energy balance of the European Union due to a possible new way to produce part of the transport liquid fuels diversifying the raw materials. The European oil refining companies have also a special interest in producing clean gasoline and diesel oil from different resources. The tendency in the long-term must be addressed to produce these fuels or to substitute them by other energy resources of renewable origin. Most innovations developed in this project can be applied to new areas. For example some of the advancements reached in syngas production at low temperatures could generate new insights to innovate in some syngas production processes from renewable resources. The innovations in the Fischer-Tropsch synthesis could be applied with more or less adaptations to the conversion of syngas produced from biomass.

For the syngas production from natural gas an innovative low temperature approach development (<700°C using noble metal catalysts or <800°C using non-noble metal catalysts) was the main objective. Lower temperatures than the usual ones in this type of processes imply lower investment and operating costs. This innovation could allow a cheaper and a more efficient production of syngas not only for liquid hydrocarbon synthesis but also for other applications (alcohol synthesis, hydrogen production for different uses including fuel cells, ...).

The objective of the second stage in the GTL process was the development of an innovative Fischer-Tropsch synthesis reaction system. In this case the partial objectives included the development of more active and stable FT catalysts able to deal with the relative high CO₂ contents appearing in the syngas produced at low temperature. It also included the integration of a continuous dehydration membrane module in order to end with higher syngas conversion to liquid hydrocarbons. These innovations developed could find applications outside the main objective of this project:

- A catalytic Fischer-Tropsch process able to simultaneously convert CO₂ to CO (reverse water- gas shift reaction) and to convert CO to hydrocarbons. It could be an innovation to be applied in other processes where CO₂-rich syngases are produced avoiding the costs of intermediate reactors.
- New dehydration membranes able to operate with good water selectivity and at temperatures in the range of the Fischer-Tropsch synthesis (200-300°C) will find many different applications in membrane reactors for all sort of chemical processes where water is a by-product and its extraction allows higher conversions and/or yields.

The results accumulated showed that as a consequence of all this research not only a new GTL process has been developed but also other objectives/impacts for new hydrogen production processes and for catalysts and membranes manufacturers could be reached like the ones indicated in the previous two paragraphs.

4. Scientific and technical description of the results

4.1 Low-Temperature Syngas production from NG

Main objective of the investigations in WP 1 was the development of **novel catalysts** and **advanced reaction engineering concepts** for the synthesis gas production from natural gas at relatively low temperatures ($\leq 800^\circ\text{C}$, wet CPO concept):



In practice, more water than (1-x) has to be added to achieve high methane conversions at these lower temperatures.

In practice, the synthesis gas composition must meet certain criteria to enable an efficient conversion to Fischer-Tropsch (FT) liquids. The following targets were set in the project:

- The amount of inerts (diluent) must be minimized. Since CH_4 is regarded as inert in the FT synthesis, the highest possible CH_4 conversion must be targeted.
- Pure oxygen is preferred to air as oxidant because when using air, for every mole of oxygen 4 moles of nitrogen have to be fed and compressed. Moreover, N_2 - diluting the syngas - prevents FT tail gas recycling and thus lowers the efficiency of the FT synthesis.
- For an optimal conversion of all feed carbon, the ratio $M = (\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$ should be close to 2.1

Because of thermodynamic limitations on the chemical equilibrium, these requirements imply working at low pressures (1-2 bar, abs).

Task 1.1: Preparation and characterization of catalysts

Synthesis and characterization of noble and non-noble metal catalysts with emphasis on metal-support effects and in situ techniques under reaction conditions (ICP-CSIC, PSI)

The activity of **Partner 2 (ICP-CSIC)** was focused on the preparation of catalysts based on non-noble metals, specifically nickel, their characterization, the assembly of a micro reactor for the screening of the catalysts, and on the testing these catalysts in the microreactor. Besides the base catalysts of alumina supported nickel (of different nickel content), two series of catalysts were prepared: Nickel supported on alkaline (Ca, Mg) doped alumina and on red-ox metal (Mn, Mo, Sn) doped alumina. The characterisation of the precursors of these systems allowed to obtain detailed information regarding the preparation process, followed by TGA and XRD, showing that the behaviour of Ca-doped systems presented specific characteristics due to the formation of the corresponding carbonate during successive impregnation after doping. The characterisation of the calcined catalyst by means of TPR and MS has provided data on the stability of the metallic nickel (active phase) of the different catalysts, and how the different doped aluminas modify its reducibility. In this sense, Mn-doped systems showed high reducible nickel, whereas Mg-doped ones presented nickel species very difficult to reduce. These results were also confirmed by TGA and XPS.

The final crystalline phases in the catalysts were identified by XRD, showing different phases on function of the elements present in the alumina surface. In Mg-doped catalysts the presence of a Ni-Mg solid solution was identified. It was also found that the crystal size depends on the doping metal, with the redox metal doped aluminas producing a higher crystallinity than the alkaline ones. The specific surface composition was determined by XPS, showing important differences between systems regarding the surface carbonate species.

One of the most important objectives of Partner 2 was to find a stable nickel catalyst. Most of the systems containing nickel with enough loading have high activity during few hours on stream, but only some of them keep this activity unchanged after some hours. In order to characterise the

stability of the catalysts prepared in the project, their behaviour under methane pulses, followed by MS, and the TGA analysis of the catalysts after reaction, in reducing and oxidizing conditions, was performed. From this set of data, and taking into account the previous characterisation, fast catalytic screening, and the durability data obtained by Partner 1 (ESIB), the Mg and Mo doped catalysts were found to be the most promising systems as CPO nickel catalysts (Milestones 1 and 2, and Deliverable 1).

15Ni/Al₂O₃-10Mg catalyst, which is very stable under CH₄ + O₂ + H₂O mixtures, was selected as the catalyst for the Deliverable 2 (large catalyst preparations). This catalyst was prepared at the same particle size than that used in the micro-reactor (0.42-0.62 mm). This particle size was not suitable for the reactor of the pilot system, due to the high pressure drop in the catalytic bed. Therefore, the preparation was repeated, using the support as it is commercialized by Süd-Chemie: α-Al₂O₃ in extrudes (5 mm high, 5 mm diameter). The preparation was not possible, since the magnesium precursor was not incorporated to the porous structure of the alumina when it is prepared by impregnation in excess of solvent. The same preparation was repeated using an intermediate particle size, 1.68-2.38 mm, and the result was similar, obtaining the support and the precursor in separate phases. Finally, the support was grinded to a particle size lower than 0.20 mm. By using this powder, the Mg precursor was incorporated by impregnation without problem and the catalyst was prepared. The obtained catalyst was pelletized and sized to the desired particle size (1.68-2.38 mm). The method was not optimized, since the consistence of the particles was low, and they produced fine dust. The use of some binder could be necessary in this case.

Main objective of **Partner 4 (PSI)** activities was to develop novel routes for the generation of synthesis gas ("syngas") from methane using *noble* metal catalysts. The activities were focused on noble metal based catalysts (ruthenium, rhodium, platinum) for the low temperature (T < 800°C) catalytic partial oxidation of methane to synthesis gas. The goals of the activities were (I) the evaluation of different catalysts and a pre-selection of suitable catalysts for low temperature GTL applications, (II) the optimization of reaction and process conditions and (III) design and construction of a bench-scale reactor system (thermal methane throughput: 1 kW_{th}).

Rhodium and ruthenium catalysts were prepared by impregnation techniques using aqueous rhodium and ruthenium nitrate solutions. Platinum catalysts were prepared from a Pt^{II}(NH₃)₄(OH)₂ solution. Support materials used were zirconium dioxide (DKKK, Japan) and different γ-aluminas (UOP, USA and Alcoa, USA). After impregnation and drying, the samples were calcined in air at 550°C for 3 h. The fresh catalysts were characterized by X-ray powder diffraction (XRD) to detect crystalline phases and by BET surface area measurements. The XRD patterns of the calcined ruthenium catalysts revealed the presence of ruthenium (IV) oxide, RuO₂. Rhodium phases could not be detected since the rhodium content of the samples was low (1%).

Task 1.2: Catalysts testing and screening

Catalyst activity and stability measurements for LT-CPO in microreactors at 500-800°C, 1-20 bar pressure. Co-ordination of process parameters and reaction conditions with results of FT catalyst work (CSIC, PSI, ESIB, EBI). Comparison with commercial catalysts supplied by Süd-Chemie AG (PSI, ESIB).

The catalysts prepared by Partner 2 (ICP-CSIC) in Task 1.1 were tested by **Partner 1 (ESIB)** for natural gas oxidation to produce syngas in a bench experimental installation. For the Catalytic Partial Oxidation (CPO, the experimental conditions were 1 bar and 1073 K, varying the space velocity between 600 and 1200 g_{feed}/(g_{catalyst} h). Therefore, for the more promising CPO catalysts, CPO and Wet CPO activity tests were performed at several temperatures (range of 1073-1123 K) and a total pressure of 3 bar which is an acceptable process pressure for possible industrial applications. Indeed long-term activity tests were also performed in order to study catalysts stability. The non-noble metal catalysts studied were nine catalysts of Ni supported on doped-

alumina with redox or basic promoters. These catalysts were prepared by the ICP-CSIC group and two additional commercial catalysts supplied by Süd-Chemie were also tested for comparison.

Therefore, the correlations among the characterization and the activity results were also established with special consideration to the stability of the catalysts. As a result of all the activity testing performed it was concluded that for the catalysts doped with a basic promoter the most active ones were the Mg doped catalysts and for the catalysts with redox promoters the Mo doped catalyst was the most active one. These catalysts showed a similar activity trend and similar values of the other parameters measured, like the hydrogen and CO selectivities and the hydrogen yield (H_2^{out}/CH_4^{feed}) ratio.

The characterization of the catalysts from the experiments performed by **Partner 2 (ICP-CSIC)** described above showed that the catalysts doped with molybdenum was not stable in the reaction conditions, and these catalysts were sharply deactivated after several minutes on stream. The deactivation was quicker when the partial pressure of oxygen was decreased. This correlated with the higher tendency to the oxidation of nickel when molybdenum was present in the catalysts, confirmed by TPO patterns. These findings led to the selection of magnesium-doped catalysts, which were very stable under $CH_4 + O_2 + H_2O$ mixtures, as the catalyst for the Deliverable 2. XPS of catalysts used in autothermal conditions showed a reduction of the Ni/Al surface atomic ratio compared with the fresh catalysts. This reduction was bigger in the no-doped and Mo-doped catalysts, and moderate in the Mg-doped systems. This was produced by the deposition of coke in the surface of nickel particles, producing encapsulation of the active species in the case of the no stable catalysts. Nevertheless, the presence of surface carbon is not always deactivating, since CH_x fragments are active species in the reaction mechanism, and were also detected covering the surface of the nickel in stable catalysts (15 Ni/Al₂O₃-10Mg).

Partner 4 (PSI) developed and tested ruthenium and rhodium based catalysts. With these catalysts, the reaction conditions (p, T, O/C ratio, S/C ratio) were optimized to reach the targets (see *Objectives*). Screening experiments were conducted in a thermogravimetric analyzer coupled with an infrared spectrometer (TGA-FTIR). The properties of the most promising catalysts were also investigated in a microreactor at pressures up to 1.1 MPa. In all experiments air was used as the oxidant. From these screening experiments it was concluded that two catalyst systems (5% ruthenium supported on g-Al₂O₃ doped with 5% cerium, abbreviated as 5Ru/5Ce-g-Al₂O₃ (UOP) and 1% Rh supported on ZrO₂ doped with 5% cerium, abbreviated as 1Rh/5Ce-ZrO₂) were suitable catalysts. Platinum catalysts (0.5% Pt on tin oxide, denoted as 0.5Pt/SnO₂, 0.3% Pt on g-Al₂O₃ "0.3Pt/g-Al₂O₃", and 1% Pt on g-Al₂O₃ "1Pt/g-Al₂O₃") were also included in the screening procedure. A 5% ruthenium catalyst without cerium additive (5Ru/g-Al₂O₃) was also investigated. We found the investigated platinum catalysts to be less active in the wet CPO of methane, indicated by a lower methane conversion, than ruthenium or rhodium catalysts. A higher tendency to total oxidation, indicated by a slightly higher CO₂ selectivity (above the thermodynamic equilibrium) and a lower water conversion (at 550°C water is produced), compared to ruthenium and rhodium catalysts were observed. Hydrogen yields were also lower than for ruthenium and rhodium catalysts. As a result, M factors between 0.4 and 1.6 were obtained for platinum catalysts which are too low for GTL applications (2.1 is the desired value). Thus, the three platinum catalysts were not suitable for LTCPO-GTL applications. In contrast, rhodium and ruthenium catalysts were more active. In general, the LTCPO is mainly controlled by the thermodynamic equilibrium. At a pressure of 0.3 MPa (S/C = 3; O/C = 0.85), the observed methane conversions were 60-63% at 550°C and 79-88% at 650°C. However, different hydrogen yields and M factors were observed: similar hydrogen yields of 72-74 % and M factors between 1.9 and 2.0 were obtained for 1Rh/5Ce-ZrO₂ and 5Ru/g-Al₂O₃, whereas the cerium doped ruthenium catalyst 5Ru/5Ce-g-Al₂O₃ (UOP) yielded only 63% of hydrogen and an M factor of 1.7.

The results obtained revealed that the rhodium catalyst 1Rh/5Ce-ZrO₂ and the ruthenium sample 5Ru/g-Al₂O₃ (UOP) are suitable candidates for LTCPO-GTL applications. In order to increase the methane conversion, reaction temperature and S/C ratio were increased (675°C, S/C = 4-5) and

the pressure was reduced (0.2 MPa at O/C = 0.85). With these conditions a maximum methane conversion of 91% was observed for 5Ru/g-Al₂O₃ (UOP).

Task 1.3: Reaction engineering and scale-up

Reaction engineering and scale-up with the best catalyst candidates (2-3) to optimize heat management by catalyst dilution, split O₂ (air) feeds to control hot and cold spots; deactivation studies and maximization of H₂ production for the FT step (ICP-CSIC, PSI, ESIB, EBI).

Partner 1 (ESIB) investigated the reaction engineering and future scale-up of CPO reactions of methane in the presence of steam (low temperature CPO, LTCPO) over a noble metal catalyst. For this purpose, a quasi-homogeneous one-dimensional model was developed in order to model a lab-scale fixed-bed reactor to produce syngas. In this work, autothermal reforming experimental tests were performed by the **Partner 4 (PSI)** to produce hydrogen rich synthesis gas (syngas) with a noble metal catalyst (Ru) and the modeling work was done with the helpful collaboration and advice of Prof. Schaub from the Engler-Bunte-Institut (EBI), University of Karlsruhe (**Partner 9**).

The one-dimensional quasi-homogeneous reactor model was designed for modeling the PSI lab-scale ATR reactor. This reactor model was tuned with experimental data and utilized to study potentials for optimization of the process, because it helps to get a better understanding of the significant effects of temperature gradients along the catalytic bed and of the gas feeding on the reactor performance. These model calculations contributed to the optimization of the process in order to avoid important hot spots (DT ≥ 130°).

The pre-exponential factors and the activation energy values (for a Ru catalyst) resulting from model validation showed the same order of magnitude as the ones reported in the literature for Ni and Pt catalysts. Moreover, for all the experiments the compounds outlet flow rates were fitted well with an error less than 18%. In this reaction system, the measured T-profiles were very useful in order to find the best parameters for all the cases. As it was observed, even at the same furnace temperature, depending on the flow rates and space velocity the temperature profile can be very different. The experimental and simulated profiles agreed well, although the calculated profiles reached the maximum temperature earlier following the flow direction.

It was also shown that the split of oxygen and water feed along the reactor allowed a noticeable decrease of the maximum temperature in the reactor. This enabled a more uniform temperature operation and may improve the catalyst stability. Simulation studies of the reactor operation and the determination of the kinetics remain essential for future reliable reactor design, materials selection, scale-up and operation.

The contribution of **Partner 2 (ICP-CSIC)** in Task 1.3 was the physico-chemical characterisation of catalysts working under experimentation near autothermal conditions (mixtures of CH₄ + O₂ + H₂O at different ratios), described in detail under Task 1.1, and the large catalyst preparations (Deliverable 2) for the reactor pilot system built and operated by Partner 4 (PSI).

Partner 4 (PSI) performed a scale-up corresponding to 1 kW thermal methane feed flow rate. *Autothermal* operation (no external heating once the reaction was stable) of the “MAXIPOX” reactor was successfully demonstrated. The maximum methane conversion using the best noble metal catalyst (5Ru/g-Al₂O₃) was about 70% with S/C = 2.9, O/C = 0.89, p = 0.21 MPa. The M factor was 1.97 and the exit gas temperature was 639°C. Thermodynamic calculations revealed that the conversion could not be significantly increased by adding more catalyst. The characterization of the catalyst by XRD and XPS revealed that almost *no carbon species* were present on the catalyst after the catalytic operation. However, a *loss of ruthenium* on the surface was observed.

Autothermal experiments with the best Nickel-based catalyst (15Ni/Al₂O₃-10Mg) were performed with catalyst particles, diluted with quartz sand (ca. 1:10). The best performance with the Ni catalyst was a methane conversion of 68% and an M factor of 1.86 at S/C = 1, O/C = 0.92 and p = 0.21 MPa. The exit gas temperature reached 769°C.

4.2 Advanced FT catalysts and reaction system

During the course of the project, progress in WP2 was made according to the objectives envisaged. Activities were performed according to the tasks, including both experimental work and mathematical (kinetic) modelling.

Task 2.1: Preparation, characterisation and testing of catalysts

Preparation of Fe- and Co-catalysts, characterization, measurement of reaction kinetics and selectivities, testing in lab-scale reactors for activity, product distribution and stability (CNR, CSIC, EniT, IFP, Repsol-YPF, EBI).

New iron-based catalysts to be used in Fischer-Tropsch synthesis have been prepared both in the ICP-CSIC and in the CNR-ITAE laboratories, reference Fe- and Co-catalysts in the EniT/IFP laboratories.

The ICP-CSIC group prepared various Fe-Ce and Fe-Mn catalysts using different preparation procedures. These catalysts were characterised using TGA-DTA, BET, XPS, XRD and Moessbauer or Raman spectroscopy. Their catalytic activities were measured in a high-pressure fixed-bed micro reactor and the results were compiled in a plot showing specific reactor productivity versus temperature as defined at the beginning of the project, with different synthesis feed gases. It was observed that Ce addition to Fe based catalysts enhances selectivity towards C₂-C₅ fraction and olefinicity of products. Mn addition enhances olefin and C₅-C₁₂ fraction selectivity. Also it is observed that Ce or Mn containing catalysts are less active under the initial reaction conditions than only Fe based samples, except in the case of physical mixtures. In particular, synthesis experiments were carried out with 3 selected new (and one reference) catalysts. The overall results of this work are: (a) Fe-Mn mixed oxide phases can be obtained by microemulsion. (b) Mixed Fe-Ce species can be observed in the samples prepared by continuous co-precipitation, species not observed in the physical mixture of oxides. The Fe-Ce species prepared by alternative methods (batch co-precipitation and impregnation, mixed carbonate precursor and microemulsion) show a variety of structures with signs of mixed Fe-Ce species. (c) Selectivity towards the C₆-C₁₁ fraction is enhanced over Fe-Ce catalysts. Olefinicity and selectivity to long-chain products is enhanced over Fe-Mn and Fe-Ce catalysts. (d) Potassium increased the selectivity to alkenes and long-chain products and copper improves iron usability increasing the overall activity of the catalysts.

In the CNR-ITAE laboratories, two other families of FT catalysts were prepared: a) Fe/Cu/Al₂O₃ and K/Fe/Cu/Al₂O₃, and b) Fe/Cu/CeO₂, K/Fe/Cu/Al₂O₃ and Li/Fe/Cu/Al₂O₃. These catalysts were characterized through XRF, XRD, TEM, BET and TPR techniques. The corresponding FT catalytic activities, as measured in a micro reactor, were compiled in the standard plot, as indicated above. A preliminary screening of the catalysts allowed to select three promising catalytic systems characterised by a satisfying activity towards CO₂ conversion ($X_{CO_2} > 40\%$) and specific reactor productivity close to $10^{-4} \text{ g}_{C_2+} \text{ g}_{cat}^{-1} \text{ s}^{-1}$. C₅₊ selectivities higher than 75% were obtained with CH₄ selectivity close to 9 % by operating with H₂/CO mixtures. Results indicated that the new Fe catalysts allow hydrocarbon synthesis from both CO/H₂ and CO₂/H₂ synthesis gases. The overall results from the about 30 different catalyst formulations improved the understanding of (a) the role of different active phases (Co or Fe) in FT synthesis via either CO or CO₂, (b) effects of the preparation method on the catalyst physical-chemical properties (composition, structure, surface

area, morphology), (c) the role of the carriers/promoters (K, Cu, Ce, Mn, and Zn) on the catalytic behaviour (reduction, activity and FT selectivity pathway), (d) reactivity and selectivity pathway of the FT synthesis via either CO or CO₂ hydrogenation. During the final "catalyst optimization" studies, the attention was focused on the more promising catalytic systems. Four defined Fe-based catalyst formulations showed good activity/selectivity behaviour, corresponding to chemisorption capability, product desorption energy and catalyst physical-chemical texture.

Four reference catalysts were chosen as a basis for the comparison of the new catalysts developed in this project and for the membrane studies in task 2.4 and 2.5. EniT/IFP supervised the preparation and performed the characterisation of the following reference catalysts made by a commercial catalyst manufacturer:

- GTL 1: Co/Mn/SiO₂-precipitated catalyst (100 Co/60 MnO/0.15 Pt/147 SiO₂) suggested from previous EBI experience,
- GTL 2 and GTL 3: Two Fe/Cu/K/SiO₂-precipitated catalysts with two different K contents (100 Fe/5 Cu/5 K₂O/25 SiO₂) according to the preparation developed at SASOL and considered in the open literature as the state-of-the-art,
- GTL 4: Co/Al₂O₃ conventional catalyst indicated also in the literature.

These reference catalysts cover a broad range with respect to water-gas-shift activity (close to zero activity (GTL 1 and GTL 4) and high activity (GTL 2 and GTL 3)). They are representative of commercially available FT catalysts and replace the catalysts by Sudchemie AG that were originally envisaged. The reference catalysts were provided to the partners in WP2 for comparative testing (physical characterization and catalytic activity tests).

Catalytic test results by EniT/IFP indicated the characteristic difference between Co and Fe catalysts (as measured in a bench-scale fixed-bed synthesis reactor). From experiments with H₂/CO-mixtures it is evident that Co is significantly more active. Its productivity is higher because of higher activity and negligible CO₂ selectivity (relative to a high CO₂ selectivity for Fe, due to water-gas-shift activity). On the other hand, the Fe catalyst has a lower selectivity to methane and a higher selectivity to C₂₂₊ than the Co catalysts (potassium is an important promoter for iron catalysts, increasing both activity and the average molecular weight of products). The high water-gas-shift activity of Fe is essential if a) conversion of CO₂ during Fischer-Tropsch reaction and b) enhancement by selective H₂O separation are desired. Hence, the catalyst development in WP2 was focussed on Fe catalysts. Chemical-physical characterisation of the reference catalysts based on XRD, H₂- and CO-TPR and other methods indicated that the best Fischer-Tropsch performance can be expected for GTL 3 (as Fe catalyst) and GTL 4 (as Co catalyst).

EBI carried out extensive activity tests of the reference catalysts GTL 1 and GTL 4 (Co) and GTL 3 (Fe), in particular with respect to effects of CO₂ present in the synthesis gas. The catalysts were tested for their FT and CO/CO₂ shift activity and stability. Both Fe catalysts allowed the conversion of CO₂ into the desired FT hydrocarbon products. Here, the CO₂ is first converted to CO by the CO₂/CO shift reaction, and CO subsequently reacts to FT products. Guidelines regarding the experimental conditions during catalyst testing were proposed, to be used by all partners doing own catalyst testing work. Three different syngases with defined CO₂ contents were selected, temperature was varied, and specific reactor productivity (in g_{C2+}/g_{cat}/s) served as a measure for comparing the different catalysts tested in different lab-scale systems.

With GTL 3, a four week test was performed that showed the good chemical stability of the catalyst. The Co catalyst GTL 1 did not exhibit any significant CO₂/CO shift activity that would allow conversion of CO₂/H₂ synthesis gas to hydrocarbons. As a conclusion, GTL 3 as a typical CO₂/CO shift-active Fe catalyst and GTL 4 as a state-of-the-art Co catalyst were recommended for the later membrane-FT reactor tests.

Product samples from experiments with representative Co and Fe catalysts (waxy, liquid organic and aqueous phase, delivered by EBI) were analyzed in detail by Repsol-YPF. Wax was analysed by ^1H - and ^{13}C -NMR, GC-FID and -MS and FTIR. Organic liquid samples were also analysed using the same techniques, but applying a different GC method, due to the lower molecular weight of their components. Finally, all these techniques except NMR, were applied to the aqueous sample as well. The experiment carried out with the Co catalyst yields a much “cleaner” product, in which the main compound group was n-paraffins, with a low content in olefins (mono, n- and iso-) and very low concentration of oxygenated compounds (alcohols, acids, etc.). However, in the case of the Fe/K catalyst, the main product was n-monoolefins (almost half of the product), with a quite high concentration of oxygenated compounds, mainly alcohols and acids, many of them not detected in the organic sample of the Co catalysts. The highest component identified in waxy sample of the Co catalyst was C64.

The progress made in Task 2.1 during the first half of the project allowed making the decisions required for the project work in the second half. Criteria for screening catalysts were established with respect to the desired conversion of CO_2 present in synthesis gases from LTCPO. A wide variety of new catalysts (as well as commercial-type reference catalysts) were characterized with respect to their application in CO_2 -containing syngas and membrane-FT reactor systems.

Task 2.2: Optimization of catalyst activation procedure

Tests in lab-scale fixed-bed reactor, measuring activity- and selectivity-time behaviour during initial stages of catalyst activation (CNR, CSIC, EBI)

In all catalyst test experiments, activation and start-up procedure were carried out under defined conditions. For example, in EBI's experiments Fe catalysts were reduced in-situ at atmospheric pressure in a H_2/Ar -flow heating with 2 K/min to 400 °C, and holding time 16 h. After reduction, the reactor was cooled down to 250 °C, the reaction pressure of 10 bar was adjusted. The syngas composition ($\text{H}_2/\text{CO} = 2/1$) and syngas flow were set and switched to the reactor. During a time period of several days, formation of the catalytic surface by converting Fe into carbide phases took place. In order to reach high values for the resulting steady state catalyst activity, K contents in the catalyst should not be above some critical value. Experiments showed that high K content when using CO/H_2 syngas leads to deactivation effects. When using CO_2 instead of CO in the syngas, this deactivation is less pronounced. As K content positively affects CO/CO_2 shift activity (which is important for CO_2 conversion), there appears to be an optimum value with respect to both CO_2 conversion and catalyst stability. Besides, there were other effects during catalyst activation that determine final catalyst activity (e.g. time-temperature history during reduction, kind of reducing gas).

Task 2.3: Development and manufacture of silica membranes

Membrane development and preparation of modules, physical characterization of membranes without chemical reactions (regarding H_2O selectivity, hydrothermal stability) (ECN; EniT)

ECN, during the first half of the project, tested various methylated silica membranes. Conditions herein were defined (together with EniT and EBI) to simulate Fischer-Tropsch reactor conditions (200 °C, 10 bar, gas composition $\text{H}_2/\text{CO}/\text{CO}_2/\text{H}_2\text{O} = 50/10/10/30$). For assessment of the results, target figures for water permeability and selectivity were used, calculated by means of reaction engineering calculations by EBI. Accordingly, H_2O permeance values should be at least 10^{-7} mol/(Pa m^2 s), with a minimum selectivity of 100. The silica membranes showed water permeabilities well above the target value, but the selectivities were too low. Therefore, development of new types of membranes was started, based on zirconia and on ceramic supported polymer (CSP) membrane systems.

In the case of the CSP membrane, the membrane systems were prepared by coating a mesoporous support with the appropriate polymer solution. To achieve a suitable CSP membrane system, highly cross-linked polymers with a high glass transition temperature were selected. The preparation factors varied included polymer concentration in the solution, solute, amount and type of cross-linking agent and catalyst, temperature, coating speed etc.

During this project, ECN together with EBI and EniT developed the designs of lab-scale Fischer-Tropsch reactors with integrated membrane (fixed bed and slurry reactors). As an example, the fixed bed reactor was designed starting from a pipe-in-pipe concept. The catalyst is located in the annulus between the membrane tube and the steel housing of the module, and the Fischer-Tropsch synthesis reaction takes place here. The water produced during the reaction is transported through the membrane to the inside of the inner (membrane) tube, where it is removed from the reactor using a sweep gas. For this purpose, a third tube was inserted in the centre of the membrane.

As a conclusion, ECN developed and prepared a membrane that can dehydrate a syngas mixture under simulated FT conditions. The ceramic support polymer membranes have reasonable water permeance, which is close to or above the target set on the outset of this project. Selectivities towards CO_2 and CH_4 are somewhat below target but are still reasonable. The selectivity towards H_2 is too low; however, by smart sweep gas choice this limitation can partly be overcome. Both membrane types can be operated at $200\text{ }^\circ\text{C}$ with only minor changes over time. The type of membranes developed in this project could be used in other applications, where H_2O or H_2 has to be separated from a gas mixture in which the other component is not present, such as hydrogen separation from hydrocracker or hydrotreater off-gases. Finally, the membranes developed here hold a promise to be useful in pervaporation applications.

Task 2.4: Selection of reaction system

Reaction engineering analysis of potential FT reactor systems with respect to their potential for membrane integration (EBI, EniT), mathematical model development, validation, case studies for various geometries and reaction conditions (EBI)

Target values for the performance of the membranes to be developed in Task 2.3 were calculated by EBI. Here, EBI developed a 1-dimensional, isothermal reactor model able to quantify membrane requirements (permeance, selectivity), with respect to desired increments in hydrocarbon yield and necessary degree of H_2O removal. This model was part of the mathematical simulation tools that helped to quantify the potentials of membrane integration into FT reactors.

As a result of the conceptual modelling study, the selective removal of H_2O has several favourable impacts on FT reactor performance: (i) The in-situ removal of H_2O as a side-product of the FT reaction increases (a) the partial pressure of the reactants and (b) the residence time in the reactor. (ii) In the case of the CO_2/CO -shift active Fe catalysts, the in-situ removal of H_2O enhances the shift of CO_2/CO -equilibrium towards CO which is subsequently converted to hydrocarbons.

In the case of Co catalysts, higher CO conversions can be expected in a packed bed membrane reactor (PBMR), compared to a conventional fixed bed reactor, due to higher reaction rate and a higher residence time (see Figure 3, left diagram). Although Co catalysts are not able to convert CO_2 to hydrocarbons via shift reaction, primary effects of the dewatering membrane could be studied with this kind of catalyst.

In the case of Fe catalysts, the main impact is a forced CO_2 conversion to hydrocarbons. An increased CO_2 conversion and an increased hydrocarbon yield are expected. This effect is the main objective of the development of the FT membrane reactor system.

Based on the conceptual modelling studies, a packed bed membrane reactor (PBMR) with membrane fittings was designed to combine a membrane provided by ECN and a packed bed with one of the reference catalysts (GTL 3). The tubular membranes were supplied with a flange at the top and the closed cap at the bottom. Both fittings were fixed with a special carbon sealing to the ceramic tube. A "dummy membrane", completely made out of metal, was built with a similar geometry to (a) reduce and activate the catalyst within the membrane reactor (because the real membrane is limited to a temperature up to 300 °C) and (b) to carry out experiments without membrane under similar geometrical conditions as with membrane (base case experiments). The membrane ("dummy" or real one) was inserted from the top into the steel reactor. The membrane was fixed (with a copper ring under the flange) with a steel lid to place the membrane perpendicular in the centre of the reactor. The annular gap between the membrane tube and the reactor shell (shell side) was the catalyst compartment, and the tube side was swept by sweep gas.

The reactor model, validated with experimental data from Task 2.5, was used for various case studies, regarding different geometries and reaction conditions. The first design of a scale-up for an advanced FT (AFT) reactor unit was based on a simple scale-up of the EBI lab-scale membrane reactor. Here, the membrane would be fully integrated into the reactor. For this case, ECN provided the geometric data of their pervaporisation module. Calculations indicated that the specific membrane area of this reactor configuration is too small and the total number of reactors would be too large.

Though, a fully integrated membrane has a lot of advantages in lab-scale, a commercial scale unit needs a separation of reaction zone and membrane area because very high specific membrane areas cannot be achieved in full-scale. Therefore, the N conventional packed bed reactors (PBR) and N-1 membrane units will be connected in series. Before the vapour phase of the exit stream of one PBR is sent to the next PBR, it is fed through the external membrane unit where the H₂O is removed. The results of these design studies were passed to WP3.

For the case of the slurry reactor, the effect of introducing a membrane was evaluated by IFP/EniT through a numerical model taking into account all the phenomena occurring in an industrial slurry reactor. The introduction of a membrane should allow operating the reactor at high conversion with a low water partial pressure. This should improve the conversion and the catalyst stability at the same time. A case study for the Co catalyst addressed the question how large the interfacial area must be that would lead to a removal of 53 % of the H₂O formed during Fischer-Tropsch reaction.

In separate numerical simulations, EniT/IFP studied the hydrodynamic situation inside the lab-scale slurry reactor and the effect of a membrane inserted both in terms of solid distribution and of motion field. The effect of the membrane cartridge was mainly locally limited, and no dead zones appeared where the solid should settle down, even with the bigger cartridge.

Task 2.5: Testing of reactor system and integrated dewatering membranes

Construction of a FT reactor with integrated dewatering membrane, tests with various catalysts and membranes with synthesis gases containing various amounts of CO₂, applying varying reaction conditions, reactor performance compared to a base case with no water removal (EniT, EBI, ECN)

Calculations by EBI showed that the largest effects of in-situ H₂O removal can be expected within a fixed bed membrane reactor due to the higher partial pressure gradients along the reactor axis. Furthermore, the integration of a membrane into a fixed bed reactor system appeared straightforward. The reactor was designed to fit the tubular membranes provided by ECN. The membrane reactor is described in some detail in the previous chapter. With a catalyst loading of 15 g and a membrane area of 63.5 cm², the membrane reactor offered a high weight-specific membrane area. Furthermore, with the range of 60 to 200 ml/min feed flow rate (STP), high

residence times along the membrane surface relative to the characteristic time of transmembranal transport were achieved.

Experiments by EBI included Fischer-Tropsch conditions without/with CSP membrane, with GTL 3 catalyst, variation in feed gas composition (H_2/CO_2 and H_2/CO), variations in sweep gas (H_2 , Ar), and variations in sweep gas flow ratio, pressure ratio, temperature and residence time. The results from these experiments, together with the mathematical reactor model, constituted the basis for inter- and extrapolations to other situations (catalyst activity, geometry, reaction conditions).

The component permeance values determined from the EBI-FT experiments were in good accordance with data by ECN who carried out experiments under non-reacting conditions. The following conclusions can be drawn: (a) H_2O is the fastest permeating component. The H_2O permeance is around $3\text{-}8\cdot 10^{-8}$ mol/(s m² Pa) close to the target permeance of $1\cdot 10^{-7}$ mol/(s m² Pa). (b) In the experiments, up to 70% of H_2O could be removed across the membrane. H_2O fluxes of 0.2 kg/(h m²) were achieved. (c) H_2 is the second fastest component. The required selectivity $Q_{H_2O}/Q_{H_2} > 100$ could not be reached. But the deficiency in H_2 selectivity can be minimized if a H_2 rich sweep gas is applied. (d) The loss of CO_2 and CO is not significant. Here, the membrane showed excellent properties. (e) Furthermore, the permeances/selectivities were not strongly affected by the process conditions. There is only a weak effect of temperature. The membrane was stable over time (reproducible results). (f) The effect of membrane plugging by long-chain hydrocarbons has to be investigated further.

The overall results from the fixed bed reactor with integrated membrane showed that the newly developed CSP membranes are superior to silica/zirconia membranes under FT reaction conditions. It could be shown in these experiments that the selective H_2O removal enhances CO_2 conversion to hydrocarbons. The knowledge collected in this project may be transferred to further membrane applications in Fischer-Tropsch synthesis: (a) The removal of H_2O in Co-based FT-systems can reduce the tendency of re-oxidation of the Co catalyst. In this case, less H_2O has to be removed requiring much lower membrane areas. (b) Additionally, the application of this type of membrane in water-gas-shift/reverse water-gas-shift reactors has to be investigated. WGS reactors would be necessary for the utilization of H_2 -deficient syngases (e.g. derived from biomass).

Experiments with an integrated membrane inside a stirred tank slurry reactor (by ENiT) turned out to be difficult, due to the component of the velocity vector for catalyst particles orthogonal to the membrane surface being very significant. A preliminary mechanical test was performed with a prototype membrane. It has been evidenced the necessity to implement the membrane with a connection between the top and the bottom side of the cartridge in order to avoid, in case of breakage of the membrane, serious damage of the apparatus.

4.3 Technical and Economical Integration of a novel approach to FT GTL

This report chapter describes the process and technical aspects of a low temperature catalytic partial oxidation (LTCPO) synthesis gas technology combined with an advanced Fischer Tropsch (AFT) gas-to-liquids (GTL) process. Moreover, it presents the pertinent GTL performances and the relative costs of a GTL project incorporating the novel technologies against a targeted reference generic GTL project.

Task 3.1: Analysis of present technology for Syngas generation and FT synthesis

Analysis of present technology for syngas generation and FT synthesis & new alternative scouting (EniT, IFP, Repsol-YPF)

The chosen reference base case, used for the comparative evaluation of the novel LTCPO approach to FT GTL, was based upon a conventional cryogenic air separation unit (ASU), thus pure oxygen is fed to the auto-thermal reforming reactor (ATR). The syngas produced is then introduced into a conventional slurry bubble column FT synthesis reaction process to obtain clean liquid fuel.

EniT and IFP undertook together a comprehensive feasibility study of such a hypothetical grass roots FT GTL project for making synthetic liquid distillate products. A nominal synfuels production is of 30 000 BPSD was selected for the economical evaluation. **Utilities consumption** in terms of fuel gas and steam was in perfect balance with internal production from within the project elements with the exception of **electric power** where production **exceeded** consumption by 50 MW. Thus **50 MW** of electric power was made available as export to an appropriate power grid as an additional revenue source. The specific feed gas requirement for this reference case was **8 210 SCF / Barrel of C₅ plus**. The overall investment cost, excluding site specific infrastructure, storage and loading costs, was **695 million Euros** (1st.Qt 2003 basis) giving a specific overall technical investment cost of **23 000 Euros / BPSD**. Excluding utilities, the main process investment cost was **608 million Euros**

Task 3.2: New process scheme for LTCPO-GTL route

New process scheme definition, mass & energy balances and simulations, technical & economical assessment (EniT, IFP, Repsol-YFP)

The finally chosen process configuration and conditions allowing the pair of advanced technologies to approach the reference case performance is depicted the figure below. This scheme retains the conventional cryogenic air separation unit (ASU) to feed oxygen into the new low temperature catalytic partial oxidation reactor (LTCPO), generating a synthesis gas at a lower pressure than the advanced FT (AFT) synthesis process that follows this unit. Thus synthesis gas compression is required.

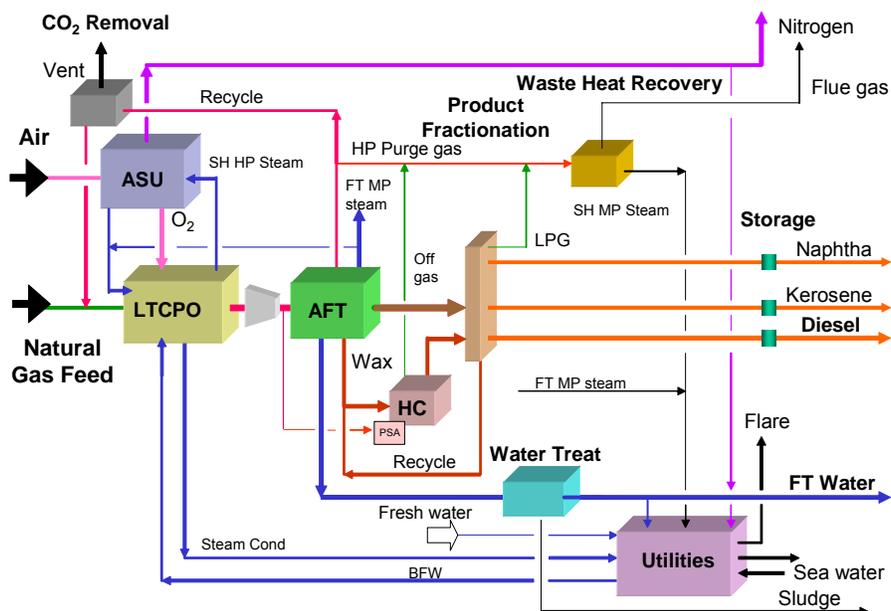


Fig. 6 LTCPO GTL Block Flow Diagram

The proposed AFT process incorporates a new reaction pathway, including de-watering membrane modules in conjunction with multi-staged fixed bed FT reactors in series. All other components in

the new process are almost the same as for the base case. But as a result of the new process conditions there is **no export of excess electric power**.

Utilities consumption in terms of steam and electric power is in perfect balance with internal production from within the project elements. However the **fired fuel gas** consumption **exceeds** production by **60 Gcal/h**. This calls for supplement of **5.0 MMSCFD** of additional natural gas feed to meet the fired fuel gas consumption of the GTL project. This factor impacts slightly on the specific consumption per barrel of C₅ plus liquid products and energy efficiency as shown below.

GTL performance expressed by energy and carbon efficiency are:

Performance	Reference case	LTCPO-GTL
Energy efficiency	58 %	57 %
Carbon efficiency	75 %	74 %
NG SCF/Barrel C ₅₊	8 210	9 000

Overall technical investment cost is determined to be **835 million Euros**. Excluding utilities, the main process investment cost is **670 million Euros**.

This gives a specific overall technical investment cost of **27 000 Euros/BPSD** to be compared with **23 000 Euros / BPSD** of the reference case.

The novel LTCPO-GTL approach to FT GTL as studied and developed by the Consortium in this European project **falls short of all proposed targets** set at the beginning of the project. However, it could be argued that these **targets were set too high as attested by commercial GTL projects being announced and beginning to come on stream** such as the Oryx project in Qatar.

Energy and carbon efficiency do find an honourable value compared to the reference base case falling only a percentage point below in both. Consequently these give an industry wide rather **respectable specific natural gas consumption of 9 000 SCF / Barrel** of C₅ plus distillates.

However, the **overall technical investment cost attributed to the novel FT GTL scheme is still too high** compared to the proven conventional approach. **It is difficult to compete with technologies and schemes which have been extensively optimized over the years.**

The simplification and **15% capital savings which could be expected for the LTCPO synthesis gas generation is not enough to compensate the complexity and 50% increased costs of the advanced FT technology** needed in this marriage. This is due mainly to the large amount and cost of the de-watering membrane material today.

5. List of deliverables

Deliverable No	Deliverable title	Expected delivery date (month)	Delivery date (month)
D1	Selection of 2-3 catalyst candidates for scale – up in the semi pilot scale facilities.	9	15
D2	Large catalyst preparations and first results with dual semi pilot reactor.	27	27
D3	Definitive selection of optimal catalyst for final pilot plant using feedback from technical and economic systems analysis.	30	27
D4	Results from catalyst improvement studies	20	26
D5	Selection of 2-3 catalyst candidates for use in reactor tests with integrated dewatering membranes	12	26
D6	Optimised catalyst activation procedures from lab-scale fixed bed reactor tests	24	27
D7	Membrane modules for testing	24	26
D8	Test results from reactor tests with integrated H ₂ O-selective membrane	33	33
D9	Selection of reactor system to be used for membrane application in FT synthesis	30	33
D10	Process integration of the syngas generation unit with the FT & Shift membrane reactor: Base case	6	8/16 ¹
D11	Techno-economic assessment of the process: Final mass & energy balances of the plant	36	39
D12	Techno-economic assessment of the process: Sizing of main equipment	36	39
D13	Techno-economic assessment of the process: Economic & Technical evaluation of the GTL process	36	39
D14, D15, D16, D17, D18	Periodic reports	6, 12, 18, 24, 30	8, 16, 21, 26, 32
D19	Final report.	36	39

¹ The second version included an annex with the contribution

6. Comparison of initially planned activities and work actually accomplished

The work performed in WP1 was mostly in accordance with the Project Work Plan, Methodology and Approach described in the proposal (part B5, page 12; and table B5 for WP 1, page 17). The Innovation depicted in part B4 of the proposal (page 9) was followed, except that referring to La additive, which was ruled out during the first experimental steps of the project. The rest of the preparation and characterization described, as well as the catalytic screening, were followed as it was proposed. Besides that, some additional characterizations, not programmed in the proposal, have been performed, since it showed of interest after evaluating the first experimental results. This produced some additional information, useful for determining the most suitable catalytic systems for CPO reaction.

According to the original project description Milestone 2 (final selection of catalysts for CPO, initial laboratory pilot plant data) should be reached after 18 months. Due to the fact that further experiments had to be conducted to reach the desired process targets, it was decided to shift Milestone 2 to 21 months. Furthermore, process analysis revealed that the use of air compared to oxygen is not economical on a large scale. The catalyst testing experiments so far had been performed with air. Therefore, additional experiments had to be performed with oxygen instead of air. This required a modification of the experimental setup.

In WP2 the FT catalytic development effort was maintained for a period longer than the one initially envisaged because of the difficulty of determine which were the optimal catalysts to be used in the final experiments and final simulations required to evaluate the new GTL technology. All the work related to membrane development followed the scheduled time table. The same can be indicated in everything concerning the design and construction of the membrane module to be integrated in a catalytic fixed bed reactor. But as it was agreed at the kick-off meeting the membrane module integration in a slurry reactor was another possible objective. This was no possible because of limitations in the CSTR reactors available in the research facilities of EniT and IFP and the time required to solve the problems related to this integration in such CSTR reactors taking care of the membrane possible erosion by the small catalyst particles and the influence of the module in the stirring system of the autoclaves.

According to the planned activities for WP3 more work than the one promised was performed. The initial selection and study of a base case or state-of-the-art GTL commercial technology was performed along the first six months of the project with the exception of the Repsol-YPF contribution dealing with the final hydrotreating units. This contribution was available with some delay (less than one year). The integration of the optimal results gathered in WP1 and WP2 implied more work than the initially planned. Instead of just one process scheme two must be considered in order to exploit up to their maximum possibilities the results reached in the low temperature syngas production and also in the advanced reaction system for the FT synthesis. This has been the reason why the research people from EniT and IFP had to work on the second process scheme along not only December 2005 but also along January and February 2006 and as a result this Final Report is submitted in April instead of before February the 28th, 2006.

7. Management and co-ordination aspects

The management and co-ordination aspects of the project correspond to the activities included in WP4. In this area the most important events were the general coordination meetings:

- The Kick-off meeting held in the Technological Center of Repsol-YPF facilities, Madrid, Spain (January 2003).
- The First Periodic meeting held in the ECN facilities, Petten, The Netherlands (June-July, 2003).
- The First Year Progress meeting held in the CNR-ITAE facilities, Messina, Italy (February 2004).
- The Mid-term Progress meeting held in the EBI facilities, Karlsruhe, Germany (July 2004).
- The Second Year Progress meeting held in the IFP facilities, Lyon, France (January 2005).
- The Second Periodic (Fifth Progress meeting) meeting held in the IFP facilities, Lyon, France (July 2005)
- The Final meeting held in the facilities of the Engineering Faculty of the Basque Country University, Bilbao, Spain (December 2005).

In these meetings both presentation of the research activities performed in each laboratory were presented and a careful discussion about which must be the following program of activities in order to advance the project in a close collaborative way. This made possible that industrial partners indicated clearer targets to be reached in WP1 and WP2 (conversions, product compositions) if an innovative and efficient GTL process must be developed in WP3.

Other collaborations well co-ordinated had permitted the development of a mathematical model for the CPO reaction system combining expertise from ESIB, PSI and EBI. The collaboration between industrial partners (Repsol, ENI and IFP) with the more basic research groups (EBI, CNR-ITAE, ICP-CSIC) allowed further advancement in the field of new FT catalysts. The collaboration of the ECN group providing initial membrane modules allowed some initial tests of FT processes including continuous dewatering.

As a result of all the collaborations indicated and all the meetings organized it has been possible to prepare and submit all the deliverables sent to the European Commission, including the corresponding Reports. In some cases with delays related to difficulties associated to the project development and in other cases to a late organization of some of the Progress meetings.

Finally, the web page of the project was permanently updated, is fully operative and contains all the relevant documents related to the project.

Concerning the follow-up of the project the names and contact details of the adequate persons follows:

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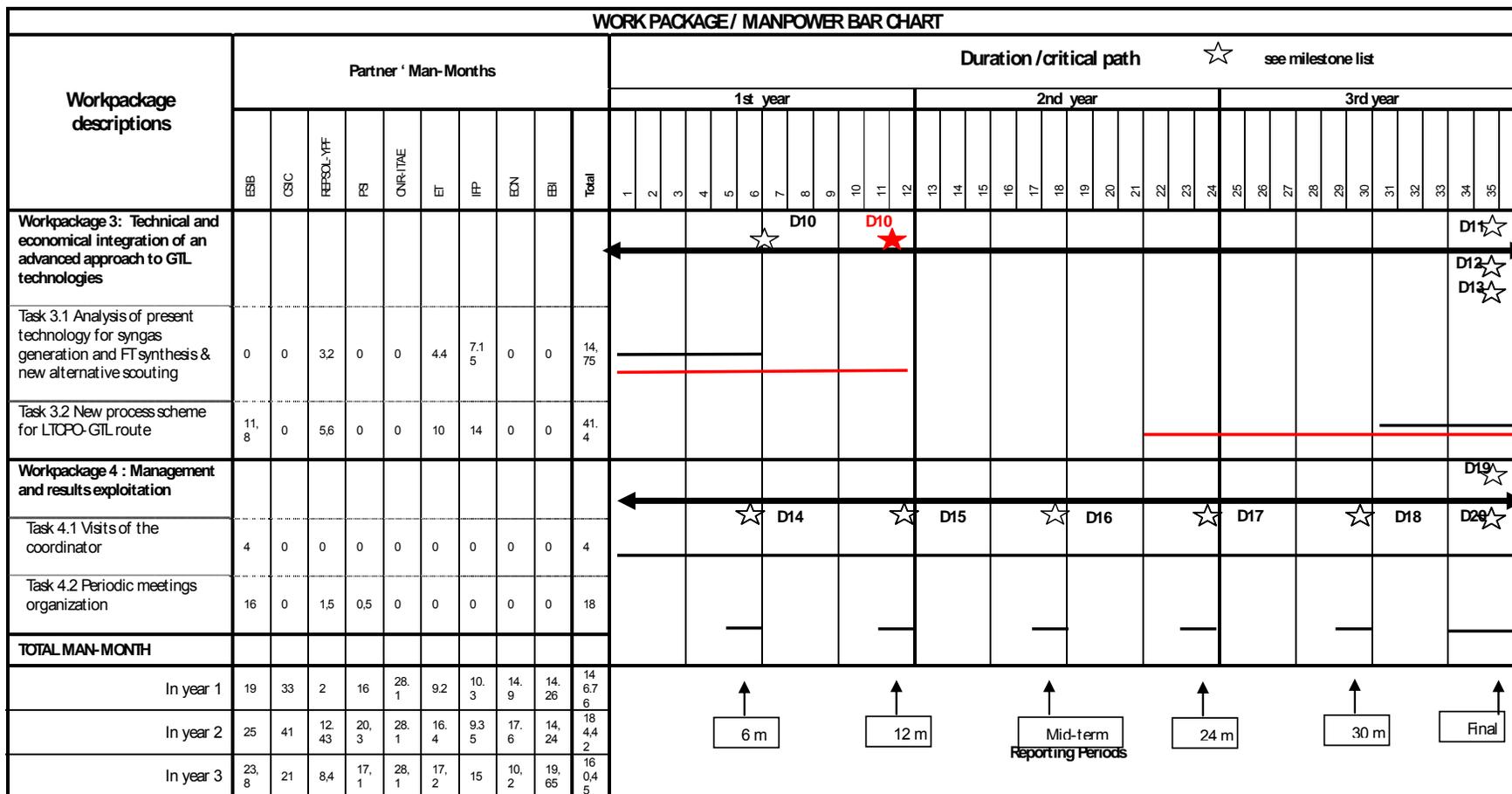
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An important role, not only as a scientific adviser, but also as a key person in all the project development was Emeritus Professor Hans Schulz from the Technical University of Karlsruhe. His enormous experience in FT synthesis, GTL technologies as well as Senior Scientist in a huge amount of related research projects was of paramount importance for the project development and management. He participated in this project as a subcontractor of partner 1.

In the following Table the intended and the final timetables are also included as a bar-chart diagram.



8. Results and Conclusions

The first significant result from this project deals with the collaboration reached among all the partners. Nine different groups with different backgrounds (industrial, research, academic) and from six different European countries have been able to build a solid partnership able to develop this project and with possible future collaborations (some of them are on-going activities).

But the main conclusions are the ones directly related to the LTCPO-GTL research project objectives: the development of a new and innovative GTL process from Natural Gas coupling a low temperature partial oxidation stage to produce the CO₂-rich syngas and an advanced Fischer-Tropsch technology able to convert this syngas to hydrocarbons including simultaneous dehydration using a selective membrane.

8.1 Syngas production

The main results and conclusions in this field are the following:

- Two new and promising catalysts have been developed, characterized and tested in the wet partial oxidation of NG. The experiments performed in a miniplant showed that autothermal operation is possible and the use of these catalysts impregnated in metallic honeycombs avoids most of the problems related to heat transfer and hot spots formation. These catalysts were a noble metal based one (Ru on alumina) and a non noble metal based one (Ni on α -alumina doped with Mg). The first one reaches acceptable conversions and hydrogen selectivity at lower temperatures (650-700 °C) than the Ni-based one (800 °C) but this second catalyst produces lower CO₂ content in the syngas.
- Applying sound chemical engineering principles a simulation model was prepared for this catalytic process. This model was extremely useful in order to establish the kinetics of the Ru catalyst and to fulfil effective strategies to avoid hot spots using conventional catalytic beds (using feed splitting).
- The technical and economic analyses of this new syngas production process (wet partial oxidation operating in autothermal conditions) could hope for 15 % cheaper capital costs than the similar commercial technologies available.

8.2 Fischer-Tropsch synthesis

The intended innovative approach had as the main objective the development of an advanced catalytic reaction system where CO₂-rich syngas can be converted to clean liquid fuels precursors. This objective was technically reached combining new catalysts (iron based) able to catalyse not only the FT reactions but also the reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$). Through this approach the carbon from the raw material (NG) can be converted into hydrocarbons even if it is present in the syngas as CO₂. The main disadvantages of this approach is the higher temperatures and the not so good conversions and selectivities as compared to the ones obtained using Co based catalysts, the requirement of the additional hydrogen necessary to convert CO₂ to CO and the higher H₂O partial pressures in the reactor due to the water produced by the reverse WGS reaction. All these disadvantages were partially solved using the following developments:

- New and promising iron-based catalysts (promoted by Ce, Mn, Cu, K and/or Zn) have been prepared, characterized and tested proving catalytic activities similar to the ones reached using Co catalysts but also catalytically active for the reverse WGS reaction to deal with a CO₂-rich syngas.

- The development of water selective membranes able to operate at the FT conditions ($T > 220$ °C) and the integration of a module with one of these membranes in a catalytic reactor where it has been proved that continuous selective extraction of water makes possible to convert not only CO but also CO₂ into hydrocarbons when using an iron-based catalyst. Further development is required in order to end with a better membrane system in terms of H₂O/H₂ selectivity and in terms of permeance.
- A simulation model was developed for a packed bed membrane reactor (PBMR). It has been extremely helpful to design the experiments of FT synthesis in the reactor with an integrated membrane module and it has been also an excellent tool to analyse the experimental results and to estimate the influence of key parameters variation and the future membrane requirements. It can be used for design studies with improved membranes possibly available in the future.
- The technical and economical assessment performed showed that this innovative approach to FT synthesis cannot compete with present available commercial technologies. This will be the case when more selective membranes with higher water selective permeance are available.

8.3 New GTL process

During the early months of this project development a GTL reference case was prepared and quantified from commercial technical and economical data available. Along the final period different partial schemes and two whole process alternatives have been considered trying to integrate all the innovations reached in the low-temperature syngas production and the FT synthesis. The best results obtained are the following:

- Utilities consumption in terms of steam and electric power is in perfect balance with internal production from within the project elements. However the fired fuel gas consumption exceeds production. This calls for supplement of natural gas feed to meet the fired fuel gas consumption of the GTL project. This factor impacts slightly on the specific consumption per barrel of C₅ plus liquid products and energy efficiency as shown below.
- GTL performance expressed by energy and carbon efficiency are:

Performance	Reference case	LTCP0-GTL
Energy efficiency	58 %	57 %
Carbon efficiency	75 %	74 %
NG SCF/Barrel C ₅₊	8 210	9 000

- On a basis of 30 000 BPSD synfuels production, overall technical investment cost, derived from "in-house" factored costing methods with instructive corrections, additions and deletions to the detailed cost estimate of the reference base case, is determined to be 835 million Euros. Excluding utilities, the main process investment cost is 670 million Euros. This gives a specific overall technical investment cost of 27 000 Euros/BPSD to be compared with 23 000 Euros / BPSD of the reference case.

The novel LTCP0-GTL approach to FT GTL as studied and developed in this European project falls short of all proposed targets set at the beginning of the project. However, it could be argued that these targets were set too high as attested by commercial GTL projects being announced and beginning to come on stream such as the Oryx project in Qatar.

Energy and carbon efficiency do find an honourable value compared to the reference base case falling only a percentage point below in both. Consequently these give an industry wide rather respectable specific natural gas consumption of 9 000 SCF / Barrel of C₅ plus distillates.

The simplification and 15% capital which could be expected the LTCPO synthesis gas generation is not enough to compensate the complexity and 50% increased costs of the advanced FT technology needed in this marriage. This is due mainly to the large amount and cost of the de-watering membrane material today.

8.4 Interesting results for other fields

Even if the objective of this project was the development of a better GTL technology using NG as raw material, the research performed and the milestones reached present results with promising applications in similar or related areas of work.

- The relatively low temperature syngas production from NG using the wet partial oxidation process can be of interest in other technologies where syngas is required as an intermediate.
- The dehydration membranes developed with thermal and structural stabilities up to more than 220 °C can be applied in any process where water continuous extraction benefits conversion, selectivity or catalyst activity and stability.
- All the knowledge obtained dealing with FT synthesis from a CO₂-rich syngas will be of paramount importance in the BTL (biomass to liquid technologies). It must be emphasized that biomass gasification produces a syngas with significant amounts of CO₂ and a H₂ deficit for FT synthesis.

8.5 Other results

Patents, publications, scientific and technological conferences contributions and presentations, scientific and technical knowledge and know-how with significant possible applications in other similar or not fields are also the result of this project development and a prove of the important quantity of experimental work performed in an complex field where many different technologies had to be considered and integrated: catalytic science and technology, catalytic chemical engineering, materials science and technology applied to membrane development, process modelling and simulation, process integration, process technical and economical assessment, etc.

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10. Glossary

Partner Acronyms:

ESIB: Escuela Superior de Ingeniería de Bilbao. The University of the Basque Country, Barrio Sarriena s/n, 48940 Leioa, Spain.

ICP-CSIC: Instituto de Catálisis y Petroleoquímica. Consejo Superior de Investigaciones Científicas. Instituto de Catálisis y Petroquímica, c/Serrano 117, Madrid 28006, Spain.

REPSOL-YPF: Repsol YPF SA, Paseo de la Castellana, 278 Madrid, Spain.

PSI: Paul Scherrer Institut, 5232 Villigen, Switzerland.

CNR-ITAE: National Research Council of Italy, Piazzale Aldo Moro 7, 00185 Roma, Italy.

EniT: Enitecnologie S.p.A., Via Felice Maritano 26, 20097 San Donato Milanese, Italy.

IFP: Institut Français du Pétrole, Avenue de Bois-Préau 1 et 4, 92852 Rueil Malmaison, France.

ECN: Energy research Centre of the Netherlands, P.O. Box 1, Westerduinweg 3, 1755 ZG, Petten, The Netherlands.

EBI: Engler Bunte Institute. Universität Karlsruhe (Technische Hochschule), PF 6980, Kaiserstrasse 12, 76128 Karlsruhe, Germany.

Abbreviations and symbols within the text:

AFT: Advanced Fischer-Tropsch process.

ASU: Air Separation Unit.

ATR: Autothermal Reforming.

BET: Brunauer-Emmett-Teller method for surface area measuring.

BTL: Biomass To Liquid.

CAPEX: Capital Expenses.

CPO: Catalytic Partial Oxidation process.

CSP: Ceramic Supported Polymer.

CSTR: Continuous Stirred Tank Reactor.

Da: Damköhler dimensionless number ($Da = k\tau$)

Dry CPO: Catalytic Partial Oxidation without steam.

FT or FTS: Fischer-Tropsch synthesis.

GHSV: Gas Hourly Space Velocity.

GTL: Gas To Liquids.

K: Kinetic coefficient.

LTCPO: Low Temperature Catalytic Partial Oxidation.

M: $(H_2-CO_2)/(CO+CO_2)$ Measures the syngas suitability for the FT process.

MS: Mass Spectrometry.

NG: Natural Gas.

O/C: Oxygen/Methane molar feed ratio.

OPEX: Operational Expenses.

P: Pressure.

PBMR: Packed Bed Membrane Reactor.

Pi: Partial Pressure of component i.

Q: Molar flow.

S/C: Steam/ Methane molar feed ratio.

SCF: Standard Cubic Feet.

STP: Standard temperature and pressure

T: Temperature.

TEM: Transmission Electron Microscopy.

TGA: Thermo Gravimetric Analysis.

TGA-DTA: Thermo Gravimetric Analysis combined with Differential Thermal Analysis.

TPO: Temperature Programmed Oxidation.

TPR: Temperature Programmed Reduction.

Wet CPO: Catalytic Partial Oxidation with steam.

WGS: Water Gas Shift.

WHSV:	Weight Hourly Space Velocity.
WP:	Work Package.
Xi:	Conversion of reactant i.
XPS:	X-ray Photoelectron spectroscopy.
XRD:	X-ray Diffraction.
XRF:	X-ray Fluorescence.
Y_{i,j}:	Yield (produced moles of species i/produced moles of species j)
α ASF:	Anderson-Schulz-Flory parameter, related to Fischer-Tropsch product distribution.
τ:	Residence time (s ⁻¹)
Ψ:	Sweep gas ratio (sweep gas flow rate/inlet reactor flow rate)
Φ:	Pressure ratio (reactor operating pressure/sweep gas circulating pressure)