

Industrial Perspectives in H₂ generation through short contact time - catalytic partial oxidation technologies

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Two research groups in the US¹ and in India² reported almost contemporaneously in 1992, findings concerning the catalytic partial oxidation (CPO) of methane for producing synthesis gas. These findings showed that the reaction was promoted by reducing the contact time condition at values below few milliseconds and immediately attracted the attention of other researchers working in industrial environments^{3,4}.

It was then discovered that the fast catalytic reactions occurred inside an incandescent solid-gas inter-phase zone at temperatures higher than the equilibrium adiabatic temperatures and higher than the gaseous phase temperatures⁵. This physical chemistry condition was a consequence of a combination between fast chemical reactions and heat and mass transfer limitations⁶.

A long term fundamental investigation matured an awareness on the possibility of applying these conditions in industrial technologies for producing synthesis gas and H₂. Here we will discuss this industrial potential. Moreover we will report on the out comings of experiments performed in laboratory, bench-scale, the pilot scale and demonstrative plants⁷.that have channelled th industrial development of three production technologies named:

Technology 1 – Air Blown SCT-CPO of gaseous hydrocarbons

Technology 2 – Oxygen Blown SCT-CPO of gaseous hydrocarbons

Technology 3 – Oxygen blown SCT-CPO of liquid hydrocarbons

In this work we will discuss their characteristics after briefly mentioning some of the main physical chemistry characteristics of these processes. Firstly we mention that some aspects of the reactivity involved in the synthesis gas production processes can be commented by observing the equations [1-7]. Among these the exothermic oxidation reactions [1-2] would have highest probability to occur at the beginning of a catalytic bed of a “plug-flow” reactor fed with a relatively cool CH₄ and O₂ mixture.

Instead the WGS [3] and the endothermic steam (SR) and CO₂ (CR) reforming reactions [4-5] would have the highest probability of occurring in following zones since these reactions require heat and reactants produced with total oxidation reactions.

¹ H. Hickman and L.D. Schmidt, *J. Catal.* **267** (1992), p. 138.

² V.R. Choudary, A.S. Hamman and S.D. Sansare, *Angew. Chem. Int. Ed. Engl.* **31** (1992), p. 1189

³ K.A. Vonkeman, L.L.G. Jacobs, EP0576096

⁴ L. Basini, D. Sanfilippo, M. Marchionna, US Patent 5,856,585.

⁵ L. Basini, *Catal. Today* **117** (2006), pp. 384 -393

⁶ M. Bizzi, L. Basini, G. Saracco and V. Specchia, *Ind. Eng. Chem. Res.* **42** (2003), pp. 62–71

⁷ L. Basini, K. Aasberg-Petersen, A. Guarinoni and M. Østberg, *Catal. Today* **64** (2001), pp. 9–20

The slightly exothermic and direct partial oxidation reaction [2] would instead be favoured at high temperature values provided that the oxygen would not be entirely consumed by total oxidations.

These general consideration can be assisted either by thermodynamic calculations and by surface science studies. These last have shown that surface temperature has the most relevant role in determining the product selectivity. In particular it has been shown that common surface intermediates can be recombined originating total combustion products at "low surface temperatures" ($T < 1000$ K) and partial oxidation products at high surface T values^{8, 9}.



It is now underlined that it would be useful in industrial practice, a condition in which the total oxidation reaction [1] could proceed at an extent sufficient to raise the catalyst temperature at values (above 1000 K) in which are prevailing of the mildly exothermic partial oxidation reaction [2]. This would avoid the complexities required to manage a combination of strongly exothermic total combustion reactions and strongly endothermic steam and CO₂ reforming reactions.

Hence the temperature profile of a "dream" reactor would imply a fast but controlled temperature raise followed by a smoothed high temperature "plato". Indeed at short contact times (below 0.01 s) and with a proper design of the reactor, catalyst and thermal shields, it has been possible, even at high pressures (5-40 ATM) to produce these temperature conditions.

⁸ a) L. Hanley, Z. Xu and J.T. Yates, Jr. *Surf.Sci.Letters* **1991**, 248, L265, b) M.B. Lee, Q.Y. Yang, S.T. Ceyer *J.Chem.Phys.* **1987**, 87, 2724, c) J.D. Bekerle, Q.Y. Yang, A.D. Johnson, S.T. Ceyer, *J.Chem.Phys.* **1987**, 86, 7236, d) T.P. Beebe, Jr., D.W. Goodman, B.D. Kay, *J.Chem.Phys.* **1987**, 87, 2305, e) T.P. Beebe, Jr., D.W. Goodman, B.D. Kay, J.T. Yates, Jr. *J.Chem.Phys.* **1987**, 87, 87, f) C.T. Au, M.S. Liao and C.F. Ng, *J.Phys.Chem* **1998**, 102, 3959, g) E. Shustorovich and A.T. Bell, *Surf.Sci.* 1992, 268, 397

⁹ a) D. Mantell, K. Kunimori, S.B. Ryali, G.L. Haller, J.B. Fenn, *Surf.Sci.* **1986**, 172, 281, b) K. Kunimori, H. Uetsuka, T. Iwade, T. Watanabe, S. Ito, *Surf.Sci.* **1993**, 283, 58, c) H. Uetsuka, K. Watanabe, T. Iwade, K. Kunimori, *J.Chem.Soc. Faraday Trans.* **1995**, 91, 1081, d) K. Kunimori, T. Iwade, H. Uetsuka, S. Ito, T. Watanabe, *Catal.Lett.* **1993**, 18, 253

The reactor designs solution have been broadly based on know-how and experimental experience and have also utilised numerical reaction/reactor models¹⁰. These last have been developed considering a diffusion-reaction system in which transport phenomena and chemical kinetics are interrelated in a transfer controlled operating regime where local T differences are originated between the catalyst surfaces and the gaseous phase. In this regime the oxygen transport from the bulk gas phase to the catalyst surface has been considered as the rate limiting step.

We do not enter into the details of the works extensively reviewed in reference¹¹ but we deem it useful, for the following of the discussions, to mention that the occurrence of solid gas temperature differences, and relatively flat temperature profiles following a steep temperature increase can be interpreted by utilising a formalism discussed in literature since 1971¹², considering the contribution of “enthalpy recirculation effects”. These can occur with a radiative particle-by-particle heat transfer from the hotter to the cooler catalyst particles with a mechanism that is much more efficient of the convective heating of the gaseous phase that remains “chemically cool”.

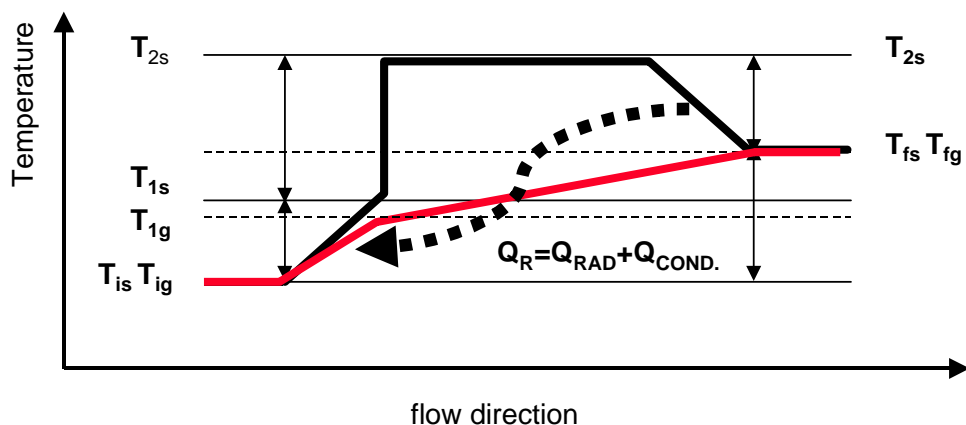


Figure 1. Qualitative scheme of the temperature vs. distance diagrams for the solid and gaseous phases produced during CPO under stationary flow conditions in an adiabatic reactor (solid phase - black line, gas phase - red/gray line). T_{1g} , T_{1s} inlet temperatures of the gas and solid, T_{1g} , T_{1s} ignition temperatures affected by the heat recuperation term (Q_R), T_{2g} , T_{2s} reaction temperatures, T_{fg} , T_{fs} final exit temperatures.

Figure 1 schematise a system in which the reaction heat is partially distributed from the hotter towards the cooler catalyst particles located at the very beginning of the catalytic bed. This allows the ignition of the reactions at higher enthalpy and temperature values and

¹⁰ a) Bizzi M., Basini L., Saracco G., Specchia V., Chem. Eng. J., **90** (1-2), 97-106, **2002**, b) Bizzi M., Basini L., Saracco G., Specchia V., Ind. & Eng. Chem. Res., **42**, 62-71, **2003**, c) O. Deutschmann, L.D. Schmidt AIChE Journal, **44**, 2465, **1998**, d) G. Groppi, E. Tronconi, Cat. Today, **105**, 297 **2005**, e) Bizzi, M.; Saracco, G.; Schwiedernoch, R.; Deutschmann, O.; AIChE Journal **50**(6), 1289-1299, **2004**

¹¹ M. Maestri; “Short Contact Time – Catalytic Partial Oxidation of Methane on Rh: Reactor Analysis and Microkinetic Modeling”, Ph.D. Thesis, Dpt. of Materials Chemistry and Chemical Engineering, Politecnico di Milano

¹² E.J. Weinberg, Nature, **1971**, **233**, 239

originates local surface temperatures higher than the final adiabatic temperatures of the products. Moreover the “super-adiabatic” surface temperatures determine a non-equilibrium reactivity.

Accordingly Figure 2 shows the experimental temperature profiles measured with IR thermography and thermocouples, in a small quartz reactor during the SCT-CPO phenomena.

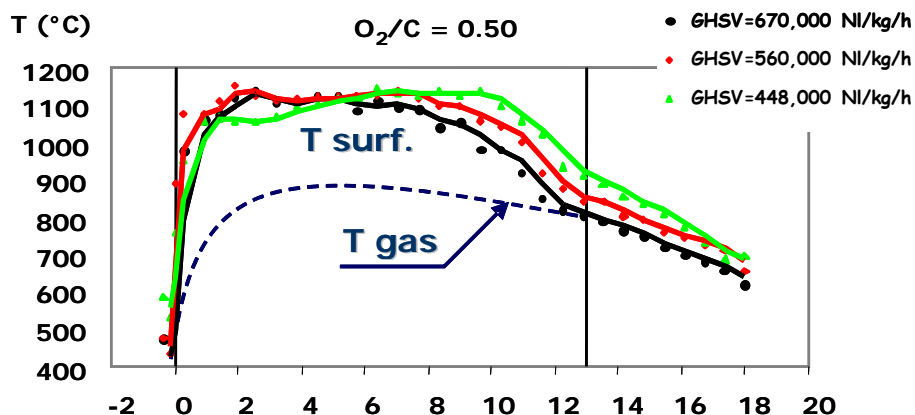


Figure 2. Surface and gas temperature profiles measured with thermocouple and IR thermography means inside laboratory scale reactor

This peculiar physical chemistry situation has been utilised for designing an industrial technology with reduced pre-heating requirements and with a reactivity produced in local environments in which the temperatures are higher than the thermodynamic equilibrium temperatures.

Technology 1: Air Blown SCT-CPO of gaseous hydrocarbons

The presence of N_2 has two relatively negative effects that need to be considered when designing and operating an Air Blown SCT-CPO process. The first negative effect concerns the convective cooling the catalytic surface. The second concerns the reduction of the O_2 partial pressure that in turn reduces the amount of heat liberated at the surfaces by the chemical reactions.

The surface temperatures reduction below 1000 K could reduce the reaction rates and the selectivity towards partial oxidation products and need to be avoided. However the low partial pressure of O_2 also reduces the risk of flame ignition and the propagation of the reactions into the gaseous phase.

The negative effects related to the presence of N_2 are less relevant with scale-up and currently two small plants are on stream producing H_2 from NG and from mixtures of NG and LPG.

The first is a Pilot Plant with a maximum capacity of $500 \text{ Nm}^3/\text{h}$ of synthesis gas and is located in Milazzo (Sicily). This has been designed and realised as a multi-purpose experimental pilot plant. It allows the testing of both Air Blown and O_2 Blown technologies by simply changing a Mixer placed at the top of the same reactor body (see Figure 3).

The second (see Figure 4) is a small Air Blown demonstrative plant located inside a multi-fuel station and produces an extremely pure H_2 flow (CO content < 0.2 ppm) that is

utilised by Fuel Cell vehicles (FCV) and by a stationary 15 kW Polymeric Electrolyte FC (PEMFC). The multi-fuel station is located in the city of Mantova and contemporaneously distributes H₂ and the “conventional” hydrocarbon fuels. This activity has been developed in the framework of an European Union project named ZeroRegio (www.zeroregio.com).



Figure 3. Image of the multi purpose pilot plant in which it is possible to test Air, Enriched Air and Oxygen blown SCT-CPO technologies also utilising gaseous and liquid hydrocarbon feedstock



Figure 4. Image of the Air blown SCT-CPO plant located in multi-fuel station in the municipality of Mantova distributing H₂ to FCV and NG, gasoline and Diesel to ICE within the framework of the ZeroRegio project sustained by the European Union (www.zeroregio.com).

The use of Air instead of Enriched Air or pure Oxygen, leads to a high energy consumption. This is mainly related to Air compression. It is in fact necessary to reach a pressure of at least 20 ATM in the Air flow for producing a synthesis gas stream from which the H₂ can be recovered through Pressure Swing Absorption (PSA) at a reasonable “recovery factor”. This indicates that Air Blown SCT-CPO could be applied for producing H₂ in small plants (F<1000 Nm³/h); hence in situations that would not justify the cost of producing/consuming pure Oxygen. Alternatively the Air Blown SCT-CPO could be utilised in medium size H₂ production plants in situations in which for location factors (e.g. stranded locations) or safety reasons (e.g. off-shore) the production and/or the utilisation of oxygen is not feasible. In conclusion it is mentioned that Air Blown SCT-CPO could also find application in ammonia production plants¹³.

Technology 2: O₂ Blown SCT-CPO of gaseous hydrocarbons.

The use of Oxygen or of Enriched Air (90% v/v of O₂) instead of Air widens the applicability of SCT-CPO technologies both in H₂ and in all the other via synthesis gas processes.

In these cases the advantages of SCT-CPO would mainly follow from: i) its flexibility versus the feedstock composition, ii) its flexibility versus the variation of the production capacity, iii) the easy operability, iv) the catalyst robustness to thermal and mechanical shocks and to chemical poisons v) the small dimensions and the technological simplicity.

This last point can be appreciated by comparing the characteristic of SCT-CPO reactor and heat exchanger with those of Steam Reforming; a technology that is utilised for obtaining the 96% of the H₂ worldwide production. Figure 5 is included for facilitating this comparison and shows that a SR for producing 55,000 Nm³/h of pure H₂ from NG and LPG would occupy a total volume of about 11,000 m³. Moreover the SR furnace would include 178 reforming tubes and 21 Tons of pre-reforming and reforming catalysts are required for operating the plant.

The SCT-CPO reactor and the synthesis gas cooler required for producing the same amount of H₂ would instead occupy a total volume of 70 m³ and would include 0.8 Tons of catalysts.

Clearly the relevant reduction of the dimensions, catalyst volume and the technological simplicity would allow a relevant reduction of investment costs while the simplicity of the technology and its easy operability would have a relevant impact in operation and maintenance costs.

Despite the small dimensions the SCT-CPO technology would allow a wide flexibility towards the feedstock composition and production capacity. Indeed the flexibility of a SCT-CPO plant would never be bottlenecked by the reactor/syngas cooler system but by the flexibility of the surrounding equipments. For what it concerns the feedstock composition it is reported that virtually all refinery off-gas streams can be accepted and some liquid streams too. Noteworthy the high catalyst surface temperatures prevent poisoning effects in presence of sulphur, aromatic and many other compounds that cannot be tolerated in SR.

This statement is based on a 3500 lifetime test performed at 25 ATM in a pilot plant utilising NG also including mercaptanes and thiophene.

¹³ L. Basini, A. Saggini, F. Saviano, D. Sanfilippo, DE10232970A1

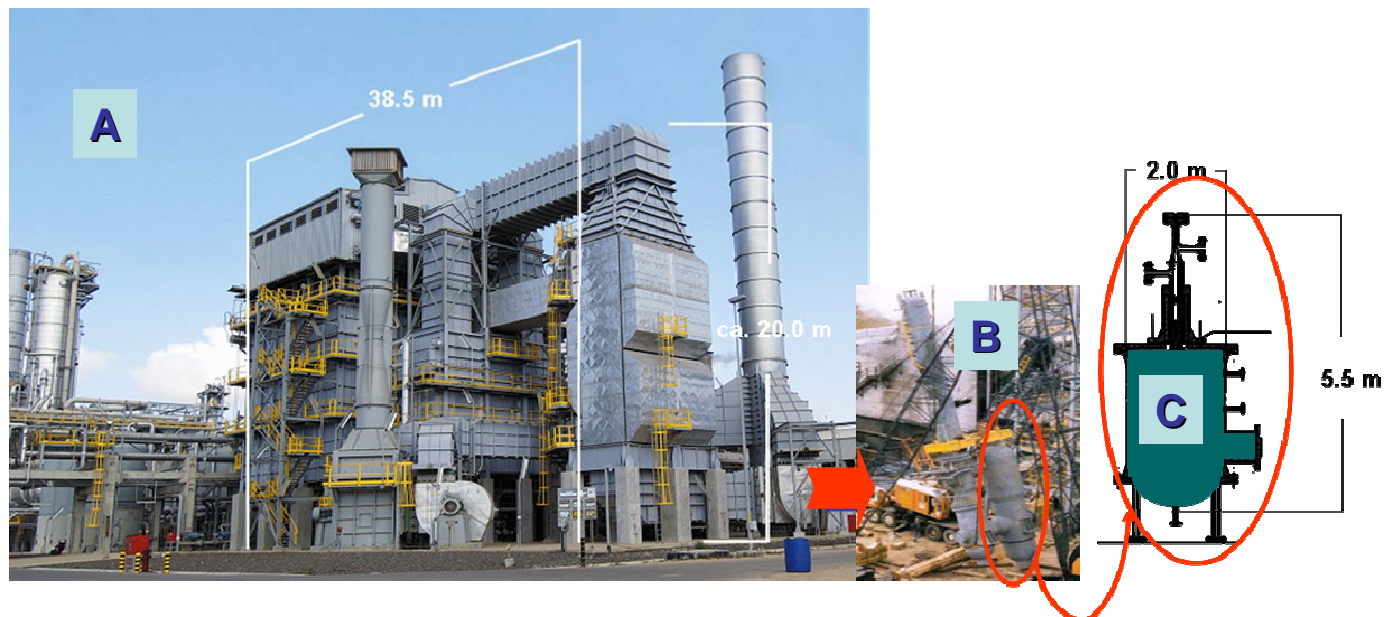


Figure 5. Picture of a 55,000 Nm³/h SR reactor (A) and of a reactor and synthesis gas cooler (B) that would resemble a O₂ blown SCT-CPO unit with an analogous production capacity. The drawing (C) details the main dimensions of the SCT-CPO reactor system.

Another characteristic of SCT-CPO concern the possibility of defining a process schemes in which the associated CO₂ production can be removed at percentages comprised between 95-98%. The level of CO₂ removal in SR could instead reach values around 70%.

SCT-CPO costs are instead penalised vs. SR costs by O₂ costs and moreover SR variable costs could take advantage from a high valorisation of the Steam export that could be quite relevant in some process scheme solutions utilising SR furnaces.

A detailed discussion of the economics cannot be given here but appear clear that many situations does exist for applying SCT-CPO to H₂ production and to synthesis gas production for MeOH, Fischer-Tropsch, CH₃COOH and other via synthesis gas processes.

Technology 3: O₂ Blown SCT-CPO of Liquid and Gaseous feedstock.

The research on this process is relatively new compared to the two preceding cases and is still performed into the bench-scale. However we have acquired enough information for the scale up of a technology that could utilise hydrocarbons such as naphtha and light middle distillates or oxygenate feedstock such as glycerine and alcohols that can be vaporised at temperature below 650 K. Indeed the vaporisation of the feedstock is not completely necessary since the reaction can be produced also utilising a nebulised liquid fuel into a gaseous stream¹⁴. This possibility is currently utilised for studying the SCT-CPO of heavy hydrocarbons with final boiling points higher than 850 K. In this case however the reactor solutions are quite different from those utilised in the technology fed with gaseous reactant or with liquids with a low boiling point and their reliability still need an extensive R&D work to be confirmed.

¹⁴ Equipment for the atomization of a liquid stream for effecting catalytic partial oxidations. Bartolini, Andrea; Basini, Luca; Lupi, Giancarlo WO 2006034868 A1 20060406

Conclusions

After more than 15 years two SCT technologies have reached the maturity for being utilised in industrial practice and a third technology is progressing. The first matured technology is the Air Blown SCT-CPO of gaseous hydrocarbons with application in small scale H_2 production plants, ammonia synthesis or for producing H_2 and synthesis gas in locations in which for safety and for other reasons Enriched Air or pure Oxygen flows would not be available.

The second technology is the Oxygen Blown SCT-CPO of gaseous hydrocarbons that has several advantages vs. the existing technologies; the most striking one concerns the drastic reduction in the complexity and dimension of the reactor and of the synthesis gas cooling systems. Other advantages would follow from flexibility towards feedstock composition and synthesis gas productivity and from the catalysts insensitivity to poisons like sulphur containing compounds and aromatic hydrocarbons.

The maturity of a third technology able to utilise heavy hydrocarbon fuels is less advanced and is still progressing at the bench scale level.

In conclusion it appears that the SCT-CPO would widen the possibility of producing H_2 and synthesis gas by reducing the production costs and by rendering available a new technological key for opening new production pathways.

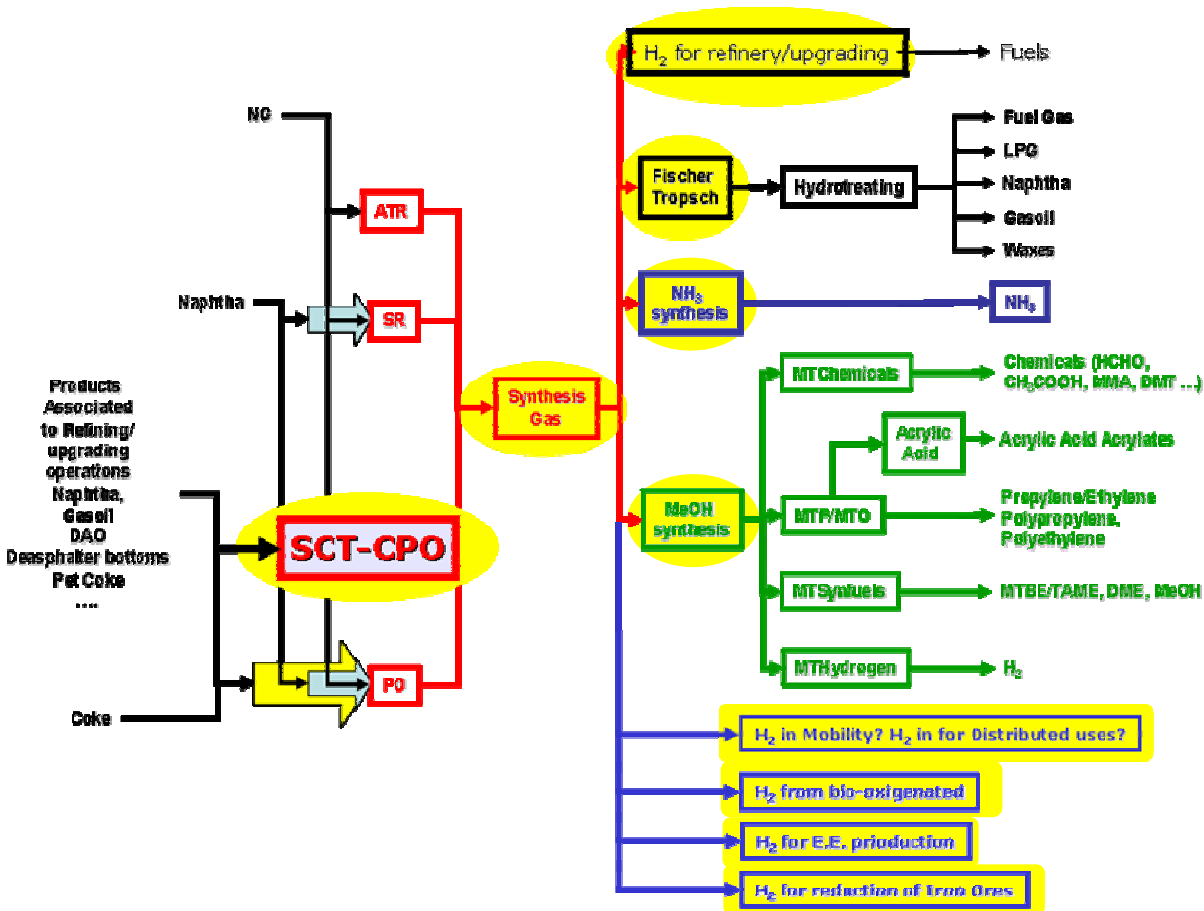


Figure 7. Scheme of the possible application of the SCT-CPO synthesis gas and H_2 production method.