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A Disruptive Innovation for Upgrading Methane to C3 Commodity Chemicals

Technical challenges faced by the C123 European consortium

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<ABSTRACT>

C123 is a 6.4 M€ H2020 European integrated project running from 2019 to 2023, bringing together eleven partners from seven different European countries.

There are large reserves of stranded natural gas waiting for a viable solution and smaller scale biogas opportunities offering methane feedstocks rich in CO₂, for which utilization can become an innovation advantage. C123 will evaluate how to best valorise these unexploited methane resources by an efficient and selective transformation into easy- to- transport liquids such as propanol and propanal that can be transformed further into propylene and fed into the 6B\$ polypropylene market. In C123 the selective transformation of methane to C3 hydrocarbons will be realized via a combination of Oxidative Conversion of Methane (OCoM) and hydroformylation (HF), including thorough smart process design and integration under industrial relevant conditions. All C123 technologies exist at TRL 3, and the objectives of C123 will result in the further development of this technology to TRL 5

with a great focus on the efficient the overall integration of not only the reaction steps but also the required purification and separation steps, incorporating the relevant state-of-the-art engineering expertise.

Introduction

Methane market opportunities will keep emerging; most energy forecasts currently predict that natural gas will play an important future role in the global energy sector. Projected long-term growth rates for gas are around 2% per year and analysts are expecting natural gas to overtake coal in the global energy arena in the next two decades (1,2). Security of supply is improving to meet this demand with USA becoming a large liquid natural gas (LNG) export player in recent years as the price of natural gas continues to drop while liquid petroleum gas (LPG) and carbon exploitation associated costs increase. All these scenarios could also allow for economically viable opportunities for stranded gas and biomethane utilisation. Sustainable exploitation is a key driver of natural gas consumption's future growth. The role of natural gas as a crucial stage strategy vector to reduce emissions could be supported by carbon pricing policies with the development of low carbon technologies where natural gas is implemented. Sustainable gas sources combined with renewable energy applications and process efficiency innovations are all required to tackle global emissions. Some of these first and second generation lower carbon or fuel switch technologies are expected to merge and support future methane applications and opportunities. (3,4,5).

An extensive technoeconomic and viability review paper was presented in parallel by the partners in C123, the reader is directed there for further details (6). In the present paper, technical progress and remaining challenges are reviewed.

Disruptive technologies need to evolve to support new challenges including biomethane composition (higher amounts of CO₂ in the gas), alternatives to NG flaring, transformations to easy-to-transport chemicals, hydrogen production, and carbon capture, utilisation and storage (CCUS). Current stranded natural gas reserves opportunities include compressed natural gas (CNG), gas to liquids (GTL), gas to solids (GTS or solidified natural gas SNG), and gas to wire (GTW). GTL increases the ease of transport through a physical change of the natural gas into a liquid (7). Two additional state-of-the-art utilization options include GTP (gas to polymers) and GTO (gas to olefins). For both GTO and GTP, natural gas is converted into syngas, which is used to produce methanol as the feedstock source for the MTO (methanol to olefins) process. The olefins, i.e. ethylene and propylene, are then converted into polymers, polyethylene (PE) and polypropylene (PP).

C123 "Methane oxidative conversion and hydroformylation to propylene" is a 6.4 M€ EU H2020 project running from 2019 to 2023. The consortium consists of 11 partners from 7 different European countries (Norway, Belgium, France, United Kingdom, Germany, Azerbaijan and The Netherlands) with 6 industrial partners, 2 Research and Technology Organisations, 2 Universities and 1 association, all of whom have extensive previous experience in national and international research and innovation projects. C123 will evaluate how to best valorise unexploited methane

resources by an efficient and selective transformation into easy-to-transport liquids such as propanol and propanal. In C123 the selective transformation of methane to C3 products will be realized via a combination of Oxidative Conversion of Methane (OCoM) and hydroformylation (HF). The C123 process aims to validate the implementation in two energetically and economically relevant, complementary and sustainable routes depending on the natural gas source exploited:

- Add-on route targeting propylene production as an add-on to large existing facilities (>140 kt/y of propylene – equivalent to >200kt/y propanol).

- Modular route targeting decentralised modular production unit (~10 kt/y) of high value propanol or propanal that can be either easily transported for further transformation into propylene or other products.

C123 will explore and evaluate the viability of this technology for biogas, associated gas and marginal gas fields, all with different challenges. Biogas is produced from organic matter such as sewage sludge, cow manure, agricultural waste and the organic fraction of municipal solid waste. Large concentrations of CO₂, about 36 %, and impurities such as hydrogen sulfide (100-10000ppm) are usually found in biogas. Associated petroleum gas (APG), is a form of natural gas found with deposits of petroleum, either dissolved in the oil or above the reservoir. Associated gas is often wasted by flaring, under-utilized in low value applications, such as on-site electricity generation or reinjection for enhanced oil recovery or sold. Marginal fields are abandoned or non-developed fields that can have limited economic viability,

unfavourable crude oil characteristics or high gas and low oil reserves. Marginal gas reserves account for approximately 15 % of the world's proven gas reserves.

All C123 technologies exist at TRL 3, and the objectives of C123 are their further development to TRL 5 by an optimized integration of catalyst and process. The C₃ commodity chemicals propanal and propanol can be transformed further into propylene and fed into the 6B\$ polypropylene market or transformed into other valuable chemical products. The breakthrough innovation is the replacement of propylene production via the very energy intensive steam cracking process with production by less energy demanding and more selective build-up from smaller molecules.

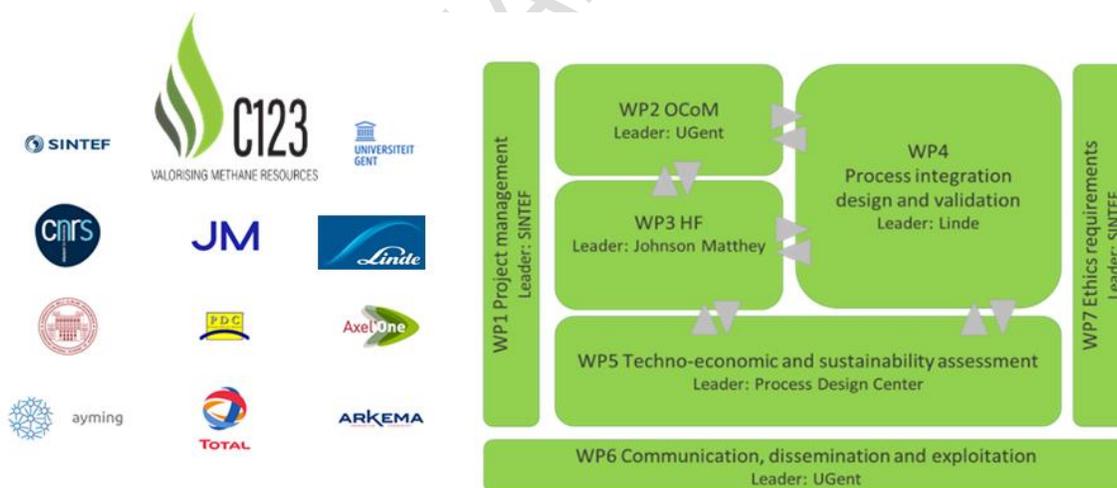


Fig.1 C123 Work package structure and consortium partners: Johnson Matthey, SINTEF, CNRS, Ghent University, Total, Linde, Axel'One, Process Design Centre, Arkema, Ayming, and Azerbaijan Academy of Sciences.

The C123 transformation of methane into C3 chemical building blocks will be developed through in the technical work packages WP2, WP3 and WP4 described in Fig.1. The goal will be optimization of the overall carbon and energy efficiencies and cost effectiveness of the integrated OCoM and HF processes through the application of a set of collaborative technologies involving both catalyst development and formulation and reactor design.

The expected major advancements in WP2 OCoM with respect to the state-of-the-art are the achievement of a higher methane conversion per pass, simpler heat management, higher energy efficiency, better carbon utilisation and an optimum product stoichiometry for an efficient HF process. The latter will be realised by tuning the output of the OCoM process to provide the optimal ethylene/CO ratio. Some H₂, required for HF and also processes downstream of the HF step, will be formed during OCoM, but optimizing the amount of H₂ is not part of the overall targets of OCoM. Any extra H₂ for the overall process will be supplied externally. The HF step will need to tolerate CO₂ in the reactor feed, as that is provided by both the feed gas and the by-product recycle. C123 will thus improve the atom economy and will circumvent the bottlenecks of the state-of-the-art Oxidative Coupling of Methane (OCM) process which optimizes only the ethylene production.

The goal of WP3 is production of the liquid C₃ intermediates propanol and propanal through the development of a heterogeneous HF catalyst and process optimised for conversion of the OCoM effluent. This is advantageous for transportation and can be used for on-demand production of propylene by dehydration of propanol, or for

further conversion of propanal to valuable downstream chemicals propionic acid.

While industrial HF is a homogeneous process, a heterogeneous catalyst for the C123 HF is envisaged, allowing simplified separation and global process integration with OCoM.

WP4 will comprehensively develop and optimize process concepts from the simultaneous tuning of the catalyst properties, the operating conditions and the reactor configuration. It includes an innovative integrated reactor design that optimizes heat management and transfer, mass transfer and recycling, thus improving energy and carbon efficiency, as well as achieving high product yields. This requires an optimal combination of the two processes, including possible equalisation of the operating pressure (around 10 bars) of both OCoM and HF in order to minimise the costs of pressurisation and improve reactor integration efficiency. Further, the additional reaction steps, the hydrogenation of propanal and dehydration to propylene, as well as appropriate purification and separation steps need to be efficiently included. The C123 process innovation is expected to result in an increase in carbon efficiency of at least 25%. Overall, at least 30% of fossil fuel consumption can be saved, and this can potentially increase up to 100% when any external hydrogen required by the overall process is electrolytically generated with electricity from renewable energy sources.

Oxidative Conversion of Methane

For about four decades, i.e., since the pioneering work of Keller and Bhasin, (8) OCM into ethylene has been a kind of Holy Grail in the petrochemical industry. It has

made scientists and industrials dream of converting a low-value feedstock, c.q., fuel, such as natural gas/methane into ethylene, i.e., the base chemical with the highest global production volume. The promising perspectives offered by this reaction came with severe challenges. Indeed, methane oxidative coupling products such as ethane and ethylene are more easily activated than the reactant methane by the typically employed metal oxide catalysts, such as Li/MgO, Sr/La₂O₃ and NaWMn/SiO₂.⁽⁹⁾ Basicity was recognized as an interesting catalyst property to reduce the interaction between ethylene and the catalyst. Nevertheless, C₂⁺ yields seldomly exceeded 20% not to mention 30% which, at times, was considered as a minimum threshold value for commercial viability, see Figure 2. The oxidative character of the reaction comes with a pronounced exothermicity, rendering temperature control difficult and triggering parasitic phenomena at the high reaction temperatures, i.e., 800 °C or higher, such as wall effects in the case of improper reactor material selection.

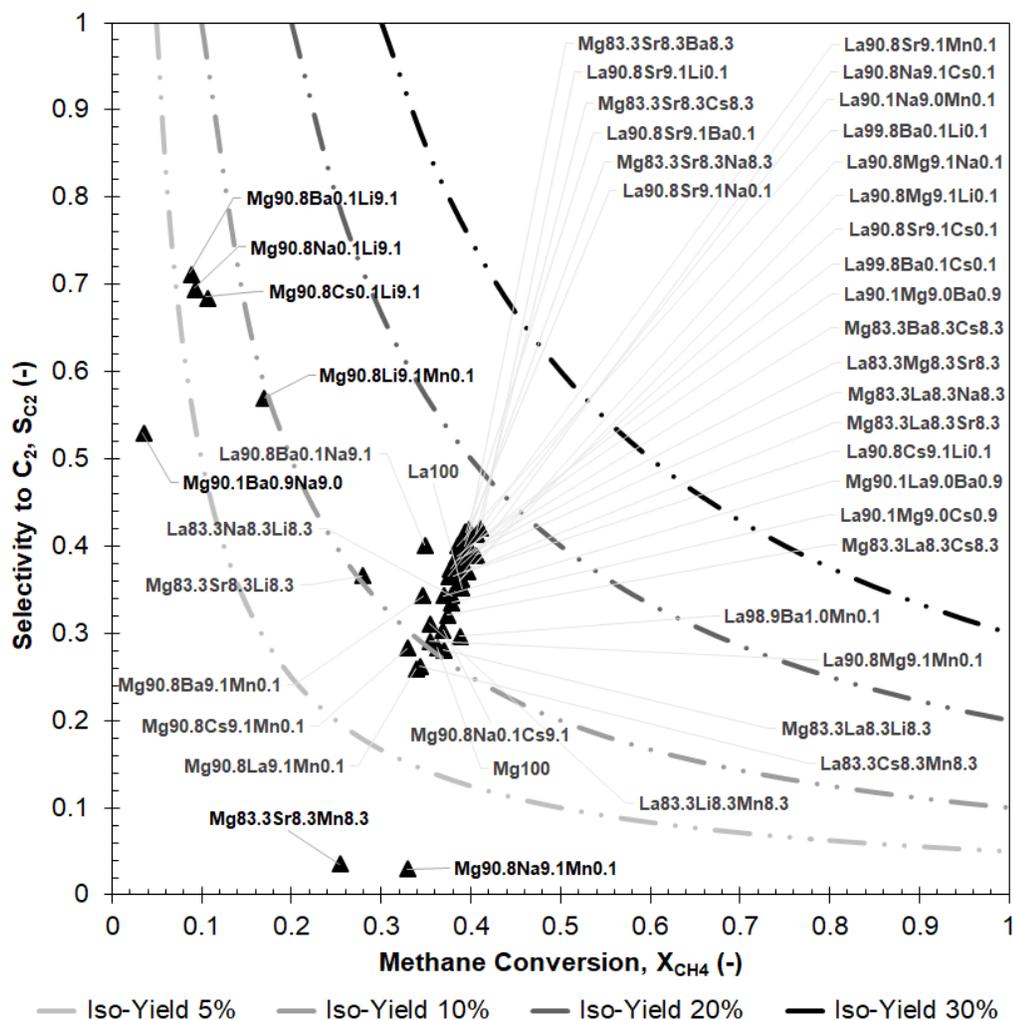


Figure 2 C_2 selectivity as a function of the methane conversion for the OCM catalyst library gathered by Kondratenko et al.(9,10)

Almost the entire periodic table has been probed for finding the best suited elements to be included in OCM catalysts (11). Li/MgO and its Sn promoted version belonged to the first generation of investigated catalysts and provided good perspectives, despite shortcomings with respect to stability. La_2O_3 and SrO_2 were other catalysts that resulted in high activities at the expense of the C_2 selectivity. More recently, NaWMn on SiO_2 has been identified as a more moderately active but more selective catalyst. These catalysts have been studied in a series of European integrated

projects, including, among others, TOPCOMBI and OCMOL, and within C123 they constitute the benchmark materials.(12,13). In addition to a better understanding of these catalysts in these projects, the perception arose that no adequate combination of catalyst and operating conditions was available to allow an economically viable, single-pass conversion of methane into ethylene via oxidative coupling with a sufficiently high selectivity. It became clear that, rather, an entire process concept would be required to meet this purpose, an aspect which was also recognized by Siluria who were the first to implement OCM technology at the pilot scale. The necessity of a proper process concept was already recognized before. The OCMOL project proposed the integration of OCM with (dry) methane reforming, mainly to recuperate the heat provided by OCM, see Figure 3.

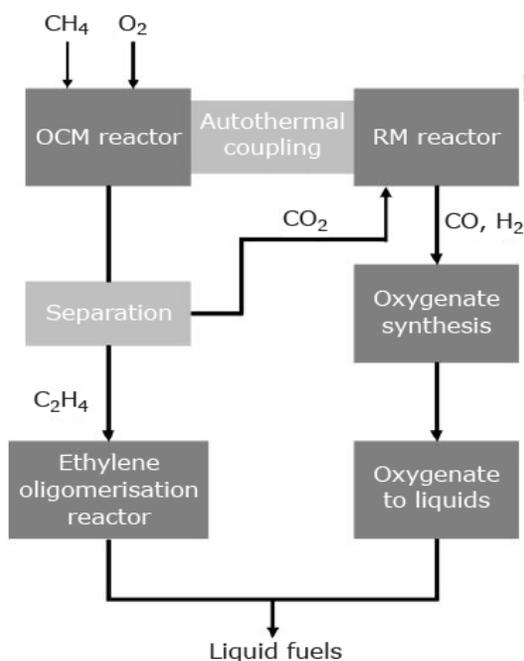


Figure 3: Simplified process flow sheet for the OCMOL process concept. (12)

The resulting syngas was subsequently valorised by methanol synthesis and MTO

conversion. Whereas each of the individual process steps could be designed in a

competitive manner, the needs imposed on the separation proved to go significantly beyond the state of the art. Moreover, only about 10% of the carbon in the end products was the result of oxidative coupling, while 90% was incorporated by the conventional syngas route. Siluria took advantage from the presence of non-negligible amounts of ethane in shale gas to accommodate a post-bed ethane cracking zone in their process concept, which of course imposes constraints on the feedstocks that should be processed.

Considering the lessons learned from the work on OCM, the following

C123 hypotheses/constraints were put forward:

- OCM remains an interesting route for methane upgrading
- Exploration of OCM catalysts and operating conditions has not resulted in an outstanding combination and is unlikely to do so in the near future, if at all
- The key towards economic viability is situated in an adequate process concept, provided that separation efforts can be properly tailored

As an answer to the above, the concept of the oxidative *conversion* of methane was conceived, still critically relying on oxidative *coupling* of methane, yet potentially embodying a variety of alternative methane conversion routes not just to maximize the C₂ yield, but to produce an effluent suitable for HF. Apart from an OCM reactor, the OCoM process will also take advantage from methane conversion via reforming and partial oxidation and by incorporating a water-gas shift reactor. The heat produced by OCM can still drive the reforming reaction as it was the case in the OCMOL project, however, the goal in C123 is to mix the effluents into an adequate proportion for HF rather than perform difficult separations. Achieving full oxygen

conversion in the OCM reactor will be key to achieve this goal. The CO₂ produced can be recycled to the OCM reactor for CO₂ induced OCM or to the reforming reactor for dry reforming. Ethane formed can be dehydrogenated oxidatively or by interaction with CO₂. Subsequent HF to propanal and propanol efficiently combines products formed in relatively high amounts, i.e., CO and ethylene, which would, otherwise, require difficult separation steps.

In order to establish a proper C123 process implementation, research advances are required along various directions. A suitable combination of catalytic material and operating conditions is required. However, this time the goal is not to maximize the per pass ethylene yield but to produce the most promising product spectrum, c.q., H₂, CO and ethylene, for subsequent HF. As a result, an innovative process concept is required for the efficient conversion of methane into a HF feedstock (14). The common denominator, serving both challenges, is the fundamental modelling of the reaction and transport phenomena involved, both at the catalyst pellet and the reactor scale, see Figure 4. Such a fundamental model is the mathematical translation of the experimental insight into the investigated system. The goal is not to prove the model, but rather to indicate when the model (hypotheses) is not adequate and, hence, it is an extremely useful tool to assess the potential validity of model assumptions.

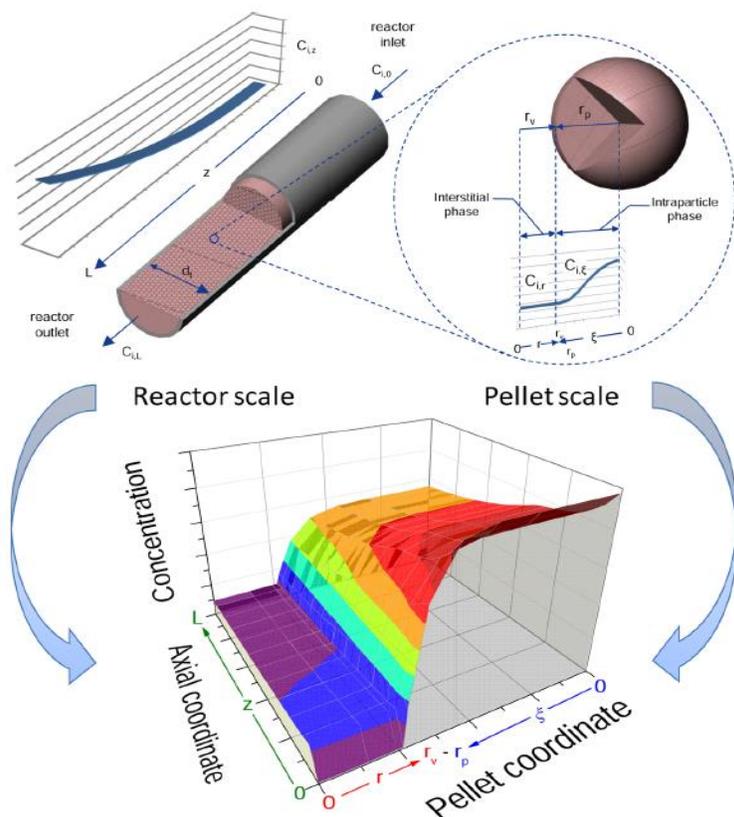


Figure 4: Scheme of the heterogeneous reactor model accounting for transport limitations Reprinted (adapted) with permission from Kechagiopoulos et al. Copyright (2014) American Chemical Society.

Within C123, the activities on OCoM are, hence, focused along three lines, i.e., (i) further catalyst development and operating conditions screening, (ii) microkinetic modelling of the OCoM reactions and (iii) process concept development. As evident from the above, the further catalyst development and operating conditions screening mainly serves the need of providing the relevant information for evaluating various alternative process concepts and, of course, as a basis for the training of the OCoM microkinetic model. 3 Benchmark catalysts, i.e., 2 Sr/La₂O₃ catalysts and 1 NaWMn/SiO₂ catalyst have been shared among the project partners by JM. A crucial aspect for a proper performance evaluation is the pretreatment of the catalyst

samples. Bosch et al.(13,15) specifically focused on the crystal phases obtained in nanoparticle catalysts and identified some interesting differences as a function of the calcination atmosphere, i.e., whether or not it contained oxygen, see Figure 5.

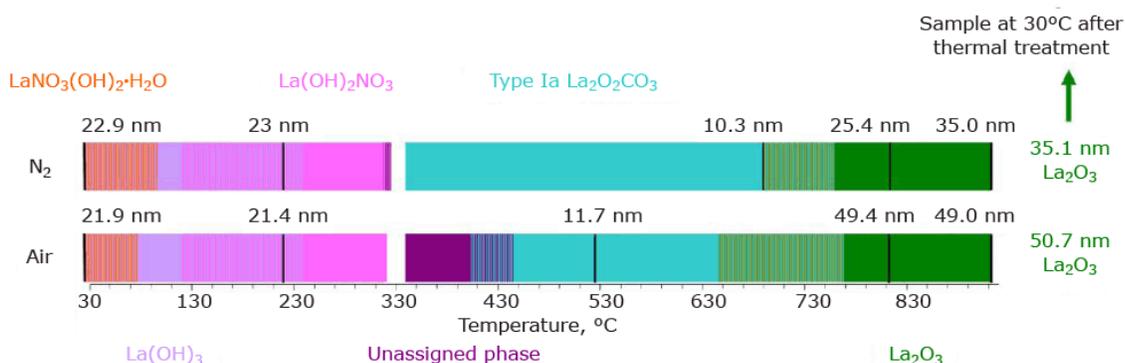


Figure 5 In situ XRD analysis for La₂O₃ with increasing temperature under a nitrogen or air atmosphere

The microkinetic model, see Figure 4, accounts for intraparticle gradients for reactants, products, radicals and surface species. Particularly for the most reactive radicals and surface species, significant gradients were found to develop, even if reactant and product concentrations had a negligible gradient. According to the model, methane is mainly activated by oxidized sites on the catalyst surface. Practically no methane activation occurs in the interstitial phase, i.e., outside of the catalyst particles. The coupling steps, on the other hand, do proceed homogeneously, both in the catalyst pores (intraparticle phase) and between the catalyst pellets (interstitial phase). Highly porous catalyst materials appear to hold a lot of promise, on the conditions that sufficient surface sites remain for the methane activation. More particularly within C123, the impact of CO₂ in the feed on the catalyst performance is assessed. Limited experimental information is available and, at present, both positive and negative impacts are reported. Hence, additional

experimentation at intrinsic kinetics conditions will be performed to elucidate the true behaviour. In the meantime, preliminary simulations have already been performed to probe the capability of the available microkinetic model to account for the effects induced by CO₂. Indeed, CO₂ formation is included already in this model, see Table 1 for the considered elementary steps. However, now that CO₂ is assuming the role of the reactant, c.q., oxidant, there may be a need for tailoring the rate coefficients of the already included steps involved in the production and consumption of CO₂ and incorporation of additional reaction steps. For the time being, a moderating effect on the methane conversion has mainly been observed after including CO₂ in the considered feedstock.

Table 1: Elementary reaction steps contained in the OCM microkinetic model.

Gas phase reactions		
$\text{CH}_4 + \text{O}_2 \rightleftharpoons \text{CH}_3\bullet + \text{HO}_2\bullet$	$\text{CHO}\bullet + \text{M} \rightleftharpoons \text{CO} + \text{H}\bullet + \text{M}$	$\text{C}_2\text{H}_4 + \text{CH}_3\bullet \rightleftharpoons \text{C}_2\text{H}_3\bullet + \text{CH}_4$
$\text{CH}_4 + \text{H}\bullet \rightleftharpoons \text{CH}_3\bullet + \text{H}_2$	$\text{CHO}\bullet + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2\bullet$	$\text{C}_2\text{H}_3\bullet + \text{M} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}\bullet + \text{M}$
$\text{CH}_4 + \text{O}\bullet \rightleftharpoons \text{CH}_3\bullet + \text{OH}\bullet$	$\text{CO} + \text{HO}_2\bullet \rightleftharpoons \text{CO}_2 + \text{OH}\bullet$	$\text{C}_2\text{H}_3\bullet + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_2 + \text{HO}_2\bullet$
$\text{CH}_4 + \text{OH}\bullet \rightleftharpoons \text{CH}_3\bullet + \text{H}_2\text{O}$	$\text{C}_2\text{H}_6 + \text{H}\bullet \rightleftharpoons \text{C}_2\text{H}_5\bullet + \text{H}_2$	$\text{C}_2\text{H}_3\bullet + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CHO}\bullet$
$\text{CH}_4 + \text{HO}_2\bullet \rightleftharpoons \text{CH}_3\bullet + \text{H}_2\text{O}_2$	$\text{C}_2\text{H}_6 + \text{OH}\bullet \rightleftharpoons \text{C}_2\text{H}_5\bullet + \text{H}_2\text{O}$	$\text{C}_2\text{H}_5\bullet + \text{CH}_3\bullet \rightleftharpoons \text{C}_3\text{H}_8$
$\text{CH}_3\bullet + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}\bullet + \text{O}\bullet$	$\text{C}_2\text{H}_6 + \text{CH}_3\bullet \rightleftharpoons \text{C}_2\text{H}_5\bullet + \text{CH}_4$	$\text{C}_3\text{H}_8 + \text{H}\bullet \rightleftharpoons \text{C}_3\text{H}_7\bullet + \text{H}_2$
$\text{CH}_3\bullet + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O}\bullet + \text{OH}\bullet$	$\text{C}_2\text{H}_5\bullet + \text{HO}_2\bullet \rightleftharpoons \text{CH}_3\bullet + \text{CH}_2\text{O} + \text{O}\bullet$ $\text{H}\bullet$	$\text{C}_2\text{H}_4 + \text{CH}_3\bullet \rightleftharpoons \text{C}_3\text{H}_7\bullet$
$\text{CH}_3\bullet + \text{HO}_2\bullet \rightleftharpoons \text{CH}_3\text{O}\bullet + \text{OH}\bullet$	$\text{C}_2\text{H}_5\bullet + \text{M} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2\bullet$	$\text{C}_3\text{H}_7\bullet \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}\bullet$
$\text{CH}_3\bullet + \text{CH}_3\bullet + \text{M} \rightleftharpoons \text{C}_2\text{H}_6 + \text{M}$	$\text{C}_2\text{H}_5\bullet + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2\bullet$	$\text{O}_2 + \text{H}\bullet \rightleftharpoons \text{OH}\bullet + \text{O}\bullet$
$\text{CH}_3\text{O}\bullet + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{H}\bullet + \text{M}$	$\text{C}_2\text{H}_4 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\bullet + \text{HO}_2\bullet$	$\text{O}_2 + \text{H}\bullet + \text{M} \rightleftharpoons \text{HO}_2\bullet + \text{M}$
$\text{CH}_2\text{O} + \text{OH}\bullet \rightleftharpoons \text{CHO}\bullet + \text{H}_2\text{O}$	$\text{C}_2\text{H}_4 + \text{H}\bullet \rightleftharpoons \text{C}_2\text{H}_3\bullet + \text{H}_2$	$\text{HO}_2\bullet + \text{HO}_2\bullet \rightleftharpoons \text{O}_2 + \text{OH}\bullet + \text{OH}\bullet$
$\text{CH}_2\text{O} + \text{HO}_2\bullet \rightleftharpoons \text{CHO}\bullet + \text{H}_2\text{O}_2$	$\text{C}_2\text{H}_4 + \text{OH}\bullet \rightleftharpoons \text{C}_2\text{H}_3\bullet + \text{H}_2\text{O}$	$\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{OH}\bullet + \text{OH}\bullet + \text{M}$

$\text{CH}_2\text{O} + \text{CH}_3\bullet \rightleftharpoons \text{CHO}\bullet + \text{CH}_4$	$\text{C}_2\text{H}_4 + \text{OH}\bullet \rightleftharpoons \text{CH}_3\bullet + \text{CH}_2\text{O}$	$\text{HO}_2\bullet + \text{HO}_2\bullet \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$
Catalytic reactions		
$\text{O}_2 + * + * \rightleftharpoons \text{O}^* + \text{O}^*$	$\text{CH}_3\bullet + \text{O}^* \rightleftharpoons \text{CH}_3\text{O}^*$	$\text{C}_2\text{H}_3\text{O}^* + \text{O}^* \rightleftharpoons \text{CH}_2\text{O}^* + \text{CHO}^*$
$\text{CH}_4 + \text{O}^* \rightleftharpoons \text{CH}_3\bullet + \text{OH}^*$	$\text{CO}_2 + * \rightleftharpoons \text{CO}_2^*$	$\text{H}_2 + \text{O}^* \rightleftharpoons \text{H}\bullet + \text{OH}^*$
$\text{C}_2\text{H}_6 + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_5\bullet + \text{OH}^*$	$\text{CH}_3\text{O}^* + \text{O}^* \rightleftharpoons \text{OH}^* + \text{CH}_2\text{O}^*$	$\text{OH}\bullet + \text{O}^* \rightleftharpoons \text{O}\bullet + \text{OH}^*$
$2\text{OH}^* \rightleftharpoons \text{H}_2\text{O}^* + \text{O}^*$	$\text{CH}_2\text{O}^* + \text{O}^* \rightleftharpoons \text{CHO}^* + \text{OH}^*$	$\text{H}_2\text{O} + \text{O}^* \rightleftharpoons \text{OH}\bullet + \text{OH}^*$
$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O} + *$	$\text{CO}^* + \text{O}^* \rightleftharpoons \text{CO}_2^* + *$	$\text{H}_2\text{O}_2 + \text{O}^* \rightleftharpoons \text{HO}_2\bullet + \text{OH}^*$
$\text{C}_2\text{H}_5\bullet + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_4 + \text{OH}^*$	$\text{CO} + * \rightleftharpoons \text{CO}^*$	$\text{CH}_3\text{O}\bullet + \text{O}^* \rightleftharpoons \text{CH}_2\text{O} + \text{OH}^*$
$\text{HO}_2\bullet + \text{O}^* \rightleftharpoons \text{O}_2 + \text{OH}^*$	$\text{C}_2\text{H}_4 + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_4\text{O}^*$	$\text{CH}_2\text{O} + \text{O}^* \rightleftharpoons \text{CHO}\bullet + \text{OH}^*$
$\text{HO}_2\bullet + * \rightleftharpoons \text{OH}\bullet + \text{O}^*$	$\text{C}_2\text{H}_4\text{O}^* + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_3\text{O}^* + \text{OH}^*$	$\text{CHO}\bullet + \text{O}^* \rightleftharpoons \text{CO} + \text{OH}^*$
$\text{C}_2\text{H}_4 + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_3\bullet + \text{OH}^*$		

Awaiting more detailed results from catalyst development, operating conditions screening and microkinetic modelling, the process concept development has already been started by making a stoichiometric analysis. The minimum amount of methane for producing a maximum amount of HF feedstock is determined from stoichiometric considerations and idealistic conversion scenarios. Such a scenario will serve as a benchmark for comparing actual implementations in a later stage of the project, initially based on literature reported kinetics, later based on microkinetics developed as part of C123.

Hydroformylation of ethylene into C3 commodities:

Hydroformylation (HF) is the catalytic synthesis of an aldehyde from an alkene and a synthesis gas mixture. Aldehydes are convenient building blocks for a large range of organic compounds, including alcohols, carboxylic acids and amines making HF a

commercially attractive synthesis process (16). The reaction mechanism proceeds through a series of fundamental organometallic reactions, including ligand exchange, alkene insertion, oxidative addition and reductive elimination (17). Rh complexes are the most active catalysts, and although more expensive, they have generally replaced less active and selective Co catalysts. Both linear and branched aldehydes are produced from all C₃+ alkenes, and the linear/branched ratio can be controlled via the reaction conditions, particularly the phosphine ligands bound to Rh. Linear aldehydes are generally the preferred products.

The reaction parameters have been well established for nearly all alkenes, in particular propene, since the HF product from propene, n-butyraldehyde, is so industrially important. However, the literature is rather scarce on the conditions for the HF of ethylene, a simpler molecule with no stereoselectivity issues (18-21).

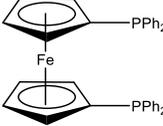
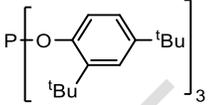
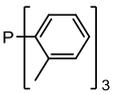
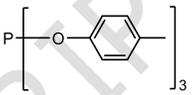
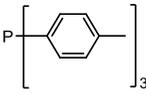
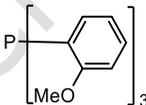
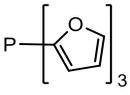
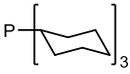
As discussed above, coupling a robust heterogeneous ethylene HF process with OCoM could disrupt the current technology. Benefits include a more circular economic process, responsible use of stranded, flared or biogas and improved transport in the value chain. The OCoM step is a high temperature (650-900 °C), atmospheric pressure reaction. When tuned properly, this OCoM process will provide an optimized feedstock of C₂H₄ and CO for the HF process, which operates around 100°C and 20-40 bar pressure in the current industrial, homogeneous processes. A suitable heterogeneous catalyst will keep both processes in the gas phase, reduce precious metal losses during operation and address corrosion issues associated with solvent use. In addition to a tuned feedstock for HF, another operational goal is the

reduction of the pressure difference between the two parts of the process (i.e. OCoM and HF). A detailed understanding of the reaction variables for homogeneous ethene HF will guide catalyst and process development of a heterogeneous version of the reaction and the overall C123 process scheme.

The integrated process will attempt to avoid inter-stage purifications and pressure switches between each step. That means that the OCoM will have to operate under pressure, but also that the hydroformylation might have to operate at lower pressure than usual, and in a stream that contains CO₂, H₂O and other impurities from previous stage such as residual methane and ethane. The HF C123 WP goals are development of stable heterogeneous HF catalysts, development of an integrated engineering concept for HF and demonstration of the process in an industrial environment at TRL 5.

A screening study, involving both batch scale and high-throughput experiments, was carried out to determine the optimum catalyst and reaction parameters for the homogeneous ethene HF. Eleven different Rh catalysts and thirteen different phosphines with varying electronic and steric profiles (see Table 2) were screened under two different CO:C₂H₄:H₂ feed gas compositions, several different pressures, different feed gas/catalyst ratios, a range of excess phosphine molar ratios and with Ar or CO₂ as diluent gas. In all cases, only propanal was detected as product. No propanol was detected, even at higher pressures and with an excess of H₂ in the feed gas.

Table 2. Phosphines screened in batch scale and high throughput studies.

Name (abbreviation)	Structure	Name (abbreviation)	Structure
Triphenylphosphine (PPh ₃)	$P(C_6H_5)_3$	Tris(pentafluorophenyl)- phosphine (P(Ph _f) ₃)	$P(C_6F_5)_3$
1,1'-Ferrocenediylbis- (diphenylphosphine) (Fcdpp)		Tris(2,4-di-tert- butylphenyl)phosphite (P(O-tBu ₂ Ph) ₃)	
Tri(o-tolyl)phosphine (P(o-tol) ₃)		Tri(p-tolyl)phosphite (P(Otol) ₃)	
Tri(p-tolyl)phosphine (P(p-tol) ₃)		Tris(2-methoxyphenyl)- phosphine (P(MeOPh) ₃)	
Tri-n-butylphosphine (P(nBu) ₃)	$P(CH_2CH_2CH_2CH_3)_3$	Tri-n-butylphosphite (P(OnBu) ₃)	$P(OCH_2CH_2CH_2CH_3)_3$
Tris(2-furyl)phosphine (P(2-fur) ₃)		Tricyclohexylphosphine PCy ₃	
Tris(diethylamino)- phosphine (DEAP)	$P[N(CH_2CH_3)_2]_3$		

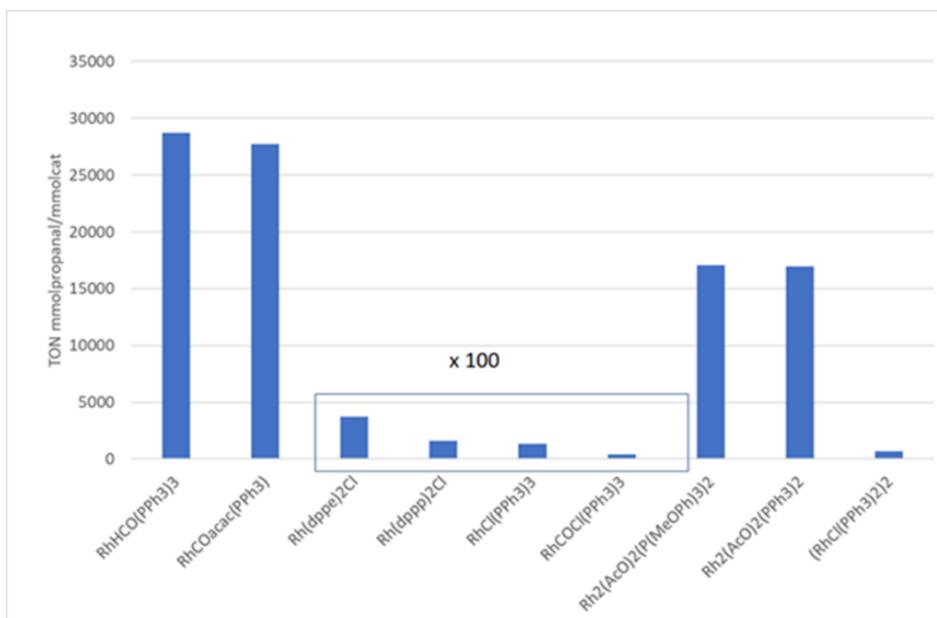


Fig.6 TON values (mmol propanal / mmol catalyst) for 9 different Rh catalysts compared during the screening process using 1:1:1 H₂:CO:C₂H₄, 20 bar, 100 °C and 1.5 h at 1000 rpm and 5 mg of catalyst in 5 ml of toluene.

As shown in Figure 6, the best catalysts are the known HF catalysts Rh(CO)H(PPh₃)₃ (**1**) and Rh(CO)(acac)PPh₃. A 10-20 fold excess of phosphine proved optimal, at least when PPh₃ was used. The high throughput screening studies showed that a 10-fold excess of the π -accepting phosphite ligands P(Otol)₃, P(O-tBu₂Ph)₃ and P(2-fur)₃ gave activities on par with the benchmark ligand PPh₃, but a definitive activity ranking of phosphines was difficult because of the high overall catalyst activity. To verify the high throughput results and investigate both the effect of CO₂ and the catalyst loading on activity, a series of batch studies were performed, and the results are given in Table 3. As can be seen from the first 6 entries in Table 3, there is very little difference in the TON for propanal formation, regardless of ligand, feed gas pressure or diluent gas. At least for the modest pressures and low C₂H₄/Rh ratios, CO₂ does not have an adverse effect on propanal TON. The enhanced effect of the π -

acid ligands is most pronounced with the highest C₂H₄/Rh ratios. While P(Otol)₃ gives slightly higher TON than PPh₃ with the highest ratios (compare entries 8 and 9 with entries 11 and 12), the effect of the ligand P(2-fur)₃ is dramatic, with this ligand giving TONs 2.5 times greater than those with PPh₃ (compare entries 8 and 9 with entries 17 and 18).

*Table 3: Effect of changes in diluent gas, feed gas pressure, catalyst loading and phosphine on TON to propanal. All reactions run with **1** as catalyst, at 100 °C for 2 h under static pressure and 8-11 equiv of the indicated phosphine.*

Entry	Phosphine ^a	P (bar) ^b	Diluent gas ^c	C ₂ H ₄ /Rh ratio ^d	TON ^e
1	PPh ₃	10	CO ₂	185	128
2	PPh ₃	10	Ar	115	130
3	PPh ₃	20	CO ₂	360	233
4	PPh ₃	20	Ar	370	268
5	P(Otol) ₃	20	CO ₂	260	219
6	P(Otol) ₃	20	Ar	295	221
7	PPh ₃	40	Ar	970	260
8	PPh ₃	40	Ar	16800	4835
9	PPh ₃	40	Ar	49400	12700
10	P(Otol) ₃	40	Ar	970	250
11	P(Otol) ₃	40	Ar	16800	6000
12	P(Otol) ₃	40	Ar	49400	13200
13	P(O-tBu ₂ Ph) ₃	40	Ar	970	320
14	P(O-tBu ₂ Ph) ₃	40	Ar	16800	5700
15	P(O-tBu ₂ Ph) ₃	40	Ar	49400	10700
16	P(2-fur) ₃	40	Ar	970	425
17	P(2-fur) ₃	40	Ar	16800	13900
18	P(2-fur) ₃	40	Ar	49400	31500

^a Refer to Table 2. ^b Feed gas 1:1:2 CO:C₂H₄:H₂ ^c Diluent gas at 10 bar. ^d Based on ideal gas law calculation at 100 °C. ^e Determined as mmol propanal/mmol Rh.

The high selectivity of the HF reaction to propanal is an important factor for the process design and impact of C123. Propanol is the preferred product over propanal since it is easier to transport and requires only a dehydration step to the valuable C3 product propene. The economic and sustainability impact of an extra hydrogenation process step for the conversion of propanal to propene will need to be evaluated. On the other hand, the selectivity for propanal even with excess H₂ will lessen the need for hydrogen from the OCoM step, which may favor the OCoM process development. Importantly, the production of only propanal in the homogeneous reaction does not guarantee that the gas phase, heterogeneous HF reaction will show the same selectivity. These results will regardless be very valuable in the design of the heterogeneous catalyst that will be developed in the next phase of the project, in addition to supporting the modelling work at UGent and in building a set of experimental data for the HF process optimisation and the WP4 process integration toolbox.

As indicated above, a gas phase HF reaction is preferred for the C123 process. While there are some examples of heterogeneous HF catalysts (19-22) the development of such a catalyst with the same activity and selectivity as the widely-used homogeneous ones remains a challenge [new]. The C123 approach for development of a heterogeneous HF catalyst will therefore involve a more traditional funnelling strategy. First generation catalysts will be synthesised by tethering appropriate organometallic Rh complexes in porous supports. Testing and iterative synthesis will provide a set of innovative, heterogeneous HF catalysts that will achieve the KPIs for TRL 4. Second generation HF catalysts will be developed from the 1st generation catalysts by using relatively well-established shaping RTD protocols to select one or

two catalysts that meet the KPIs for TRL 5. For the HF catalysts, a part of the risk management strategy will be the use of homogeneous catalysts as back-up, while still pursuing project work.

HETEROGENEOUS MATERIAL SYNTHESIS STRATEGY PROPOSED:

Johnson Matthey will functionalise high surface area silica surfaces with phenyl phosphine groups, and ultimately with rhodium complex catalysts, to form heterogeneous HF catalysts. Suitable organo silanes can interact with silica displacing surface silanol groups, creating a covalent bond. Two approaches have been selected for this functionalisation using ethoxy and methoxy silane organic precursors to anchor organic groups over the original silanol. Fumed silica, silicagel and templated mesoporous MCM41 will be used to compare the effect of pore and surface area in the silica functionalisation.

The first approach will use an amine as an anchor group to then react the basic ligand with a rhodium salt, as shown in Figure 7. Aminopropyl trimethoxy silane grafted silicas have been widely reported in the literature as they can selectively remove acid molecules such as CO₂ and H₂S (23). Direct impregnation techniques can attach propyl amines to silica, but there is evidence of more ordered surface coverages and optimisation through a toluene excess silane reflux approach over dehydrated silica. Surface secondary amines can then react with phenyl phosphine groups, attaching rhodium organometallic complexes such as Wilkinson's catalyst or **1** to the silica surface (24–26).

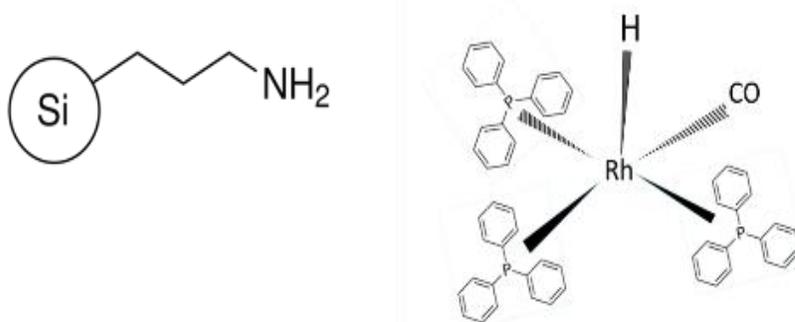


Fig.7 Example of possible interaction of a HF catalyst with amino propyl triethoxy silane functionalised silica. Silicas typically are functionalised with around 1 mmol/g amine groups(26).

The second, more ambitious approach involves incorporation of a larger monophosphine organosilane precursor, 2-(diphenylphosphino)ethyl-triethoxysilane on silica, as shown in Figure 8. The surface anchored phosphine can then be coupled to rhodium salts such as $[(\text{COD})\text{Rh}(\mu\text{-Cl})]_2$ (COD = 1,5-cyclooctadiene), $[(\text{NBD})\text{Rh}(\mu\text{-Cl})]_2$ (NBD = norbornadiene) or $[(\text{COT})_2\text{Rh}(\mu\text{-Cl})]_2$ (COT = cyclooctene) that can selectively incorporate other phosphines by sequential reaction with, for example, bis(diphenylphosphino)ethane dppe .

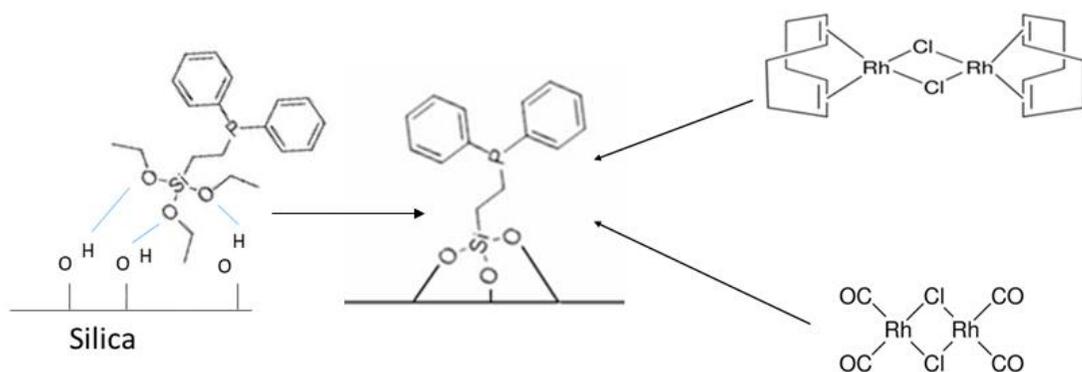


Fig.8 Organosilane silica phenyl phosphine functionalisation followed by reaction with traditional rhodium coordination complexes to prepare a tethered HF catalyst.

The goal of the SINTEF approach is to synthesize a metal organic framework (MOF) based material that has a large number of phosphines decorating the pores of the MOF. The idea is that, after introduction of Rh to the material, a traditional organometallic reaction mechanism can be accessed, in that the Rh has access to an abundance of phosphine moieties to both steer the fundamental reaction steps and prevent instability and leaching. This effect of this concept was illustrated by the incorporation of **1** into a (PTA)-MIL-1010(Cr) MOF (PTA = phosphotungstic acid). The PTA immobilized the Rh complex within the MOF pores, yet provided homogenous catalyst-like selectivities in the HF of 1-octene in toluene (27).

Rather than incorporating the necessary phosphine moieties during the demanding MOF synthesis, we will investigate a post-synthetic modification approach called solvent-assisted ligand incorporation (SALI) (28). In particular, it has been shown that a range of ligands with pendant carboxylic acid and phosphoric acid groups can

react with the μ_3 -OH functionalities of MOFs built up with $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4$ nodes. There are a wide range of MOFs with varying pore sizes and shapes that are built up from this inorganic building block, such as NU-1000, the UiO series and MOF-808 (29). Our hypothesis is that full incorporation of phosphine ligands with an appropriate tether within a Zr MOF, followed by addition of an appropriate fraction of a Rh complex such as **1**, will provide a heterogeneous version of a homogeneous HF catalyst (see Figure 9).

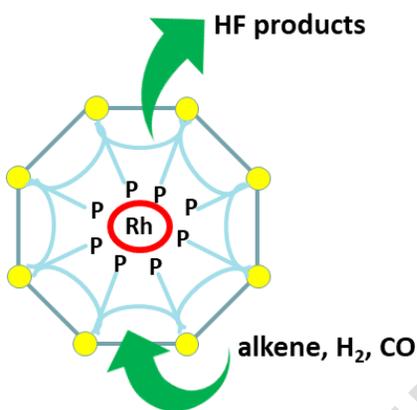
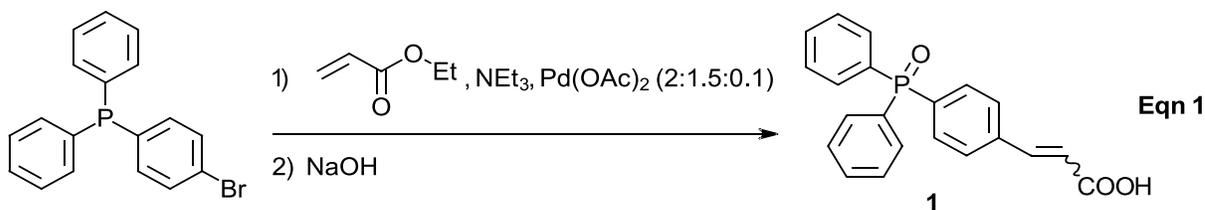


Figure 9. Schematic representation of a catalytic Rh complex immobilized within a MOF with an excess of phosphine ligands within the pores.

Our initial attempt to make a suitably tethered PPh_3 variant, specifically $(PPh_3)_2P(p-C_6H_4CH=CHCOOH)$ (see Eq 1), provided instead the phosphine oxide **2**. Reaction of **1** with the MOF NU-1000 provided evidence for incorporation of the tethered ligand into the MOF. Appropriately tethered ligands based on phosphites should be less prone to oxidation and have been synthesized.



The concept of porous macroligands, *i.e.* a porous solid acting as the organic ligand of a molecular complex, has been introduced and used recently by Canivet *et al.* at the French Centre National pour la Recherche Scientifique (CNRS) in Lyon for the heterogenization of active molecular catalysts to combine the advantages of high activity and versatility of molecular catalysts and sustainability of easy to separate and easy to recycle heterogeneous catalysts. (30) Following this strategy Canivet's team at CNRS will develop novel porous organic polymers which will embed efficient organometallic HF catalysts (31-33). Porous organic polymers formed from functionalised PPh_3 and biphosphos have already been used as supports for the Rh-catalyzed HF of 1-octene in toluene and ethylene, propylene, and 1-butylene in fixed bed reactor. Here, easily accessible phosphine or bipyridine based vinyl monomers will be used in controlled radical polymerization leading to solid porous organic matrix with high surface area and pore accessibility (Figure 10). Further functionalization with cobalt or rhodium precursors will give access to heterogenized and site-isolated hydroformylation catalyst within stable microporous structures.

The high versatility of porous organic polymers will be used to advantageously tune the hydrophilic/hydrophobic balance of the hosting pore as catalytic nanoreactor, and the confinement within the micropore will play a crucial role by influencing transport,

reaction rate and product selectivity. Moreover, the intrinsic swelling behaviour of porous organic polymers will ensure that the solubilized gaseous species will reach the active site while larger aldehydes or alcohols produced will freely transfer to the reaction medium.

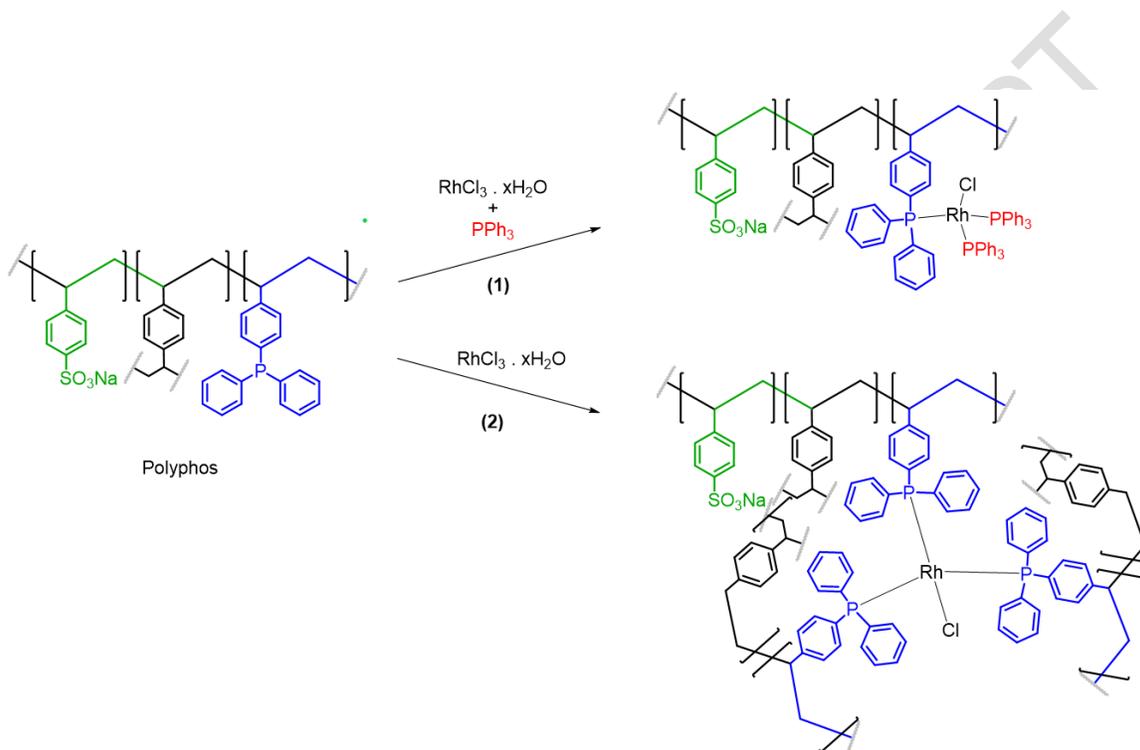


Fig.10 Synthetic strategies using phosphine-rich porous polymer Polyphos as macroligand for Rh-based catalysts.

Two microkinetic models will be developed for the HF of ethylene, i.e. one dedicated to the homogeneous and one to the heterogeneous process. The kinetic parameters will be determined via regression of the models to a comprehensive set of intrinsic kinetic data, i.e. data acquired in the absence of mass and heat transfer limitations.

By performing such a detailed model construction, i.e. no rate determining steps are

assumed, for homogeneous HF the critical steps in the selective conversion of ethylene to propanal can be unraveled. A distinction will be made between catalyst descriptors (e.g. adsorption parameters) and kinetic descriptors (e.g. activation energy). Preliminary simulations using the model developed for homogeneous HF have shown that the increase of the propanal yield with the total pressure is nicely captured by the model.

Following the same principles a microkinetic model will be developed for heterogeneously catalyzed HF, and similar relationships in terms of catalyst and kinetic descriptors will be established. This will allow the unravelling of the determining factors to optimize the heterogeneous catalyst activity and selectivity, and the models will be further used in the reactor design.

WP2 and WP3 will work in close collaboration with continuous exchange between both WPs as well as with WP4 in order to ensure overall integration. WP3 focus will be on the optimisation of the reaction and process conditions for maximised product yield and ethylene conversion, as well as achieving more active and more stable catalysts that can be operated at higher temperatures without deactivation and at lower pressures (close to those for OCoM) without decreasing conversion. This will be achieved through the combined development of heterogeneous catalysts optimised for operation in fixed reactor beds and maximum selectivity toward propanol with competitive performance with homogeneous catalysts and reactor design.

The results from OCoM (WP2) and HF (WP3) catalyst development and reactor design will be transferred into WP4 for the integrated process design and validation in relevant environment (TRL 5) for both the modular and the add-on routes, to allow a conceptual design of the fully integrated units with all process steps, and the development of a possible scheme for an integrated commercial process.

Process Tuning and Integration:

The process design of the C123 technology is characterized by the combination of several reactions which are performed under different conditions and the integration of required purification and separation steps. In addition to the OCoM and HF reactions described before as novel core elements, a hydrogenation and a dehydration reaction also have to be included in the process. Furthermore, purifications and separations need to be implemented. Although these are in principle based on state-of-the-art technologies, at this point improved or innovative concepts and solutions have to be taken into account. Only by consideration of the interaction and optimal integration of all steps and process operations can an efficient and sustainable approach matching the efficiency and sustainability targets of the C123 project be achieved. Accordingly, this chapter is focusing on the base considerations and key aspects of process design for an implementation on technical scale and under industrially relevant conditions.

Methane shows a lower reactivity towards oxygen than higher hydrocarbons and olefins are more reactive than paraffins. Therefore, it is no surprise that OCoM reactions suffer from low selectivity at high conversion. Only at low conversion are highly selective reactions, e.g. to ethane and ethylene, feasible, although the difficult

separations and high recycle ratios have an overwhelming impact on process economics.

In conventional approaches of OCoM (9,10), CO is considered an undesired by-product, requiring additional effort in process design for separation, further conversion and/or recycling. Siluria, for example, based its technology on methanation and recycling of carbon oxides in order to increase the overall process efficiency (34). In contrast, C123 is taking advantage from the CO production; by allowing the reaction to produce equimolar amounts of ethylene and CO, propanal can be further produced by HF. Subsequent hydrogenation to propanol and dehydration yields propylene as final product. Propylene is very important chemical key intermediate, and propanal and propanol could be potential value products. The challenge of a process design is the number of subsequent reaction steps which have completely different demands on conditions, which makes the process complex and requires compromises and optimization.

The OCoM reactor is under strong kinetic control (8,35). Thermal runaways leading to total oxidation are always possible and need to be avoided by a careful reactor design. A low pressure helps to push back the typically unselective gas phase reactions. Nevertheless, the reaction heat release is tremendous and requires a very effective cooling. Also, temperatures and heat recovery are challenging. While it looks attractive to use endothermic ethane dehydrogenation to recover high temperature heat after the OCoM reactor, providing the respective ethane stream requires cryogenic distillation. The process limitations affect the reactor design and vice versa.

Reaction thermodynamics already indicate the required reaction conditions for the subsequent steps. In addition, certain vapor-liquid-equilibria (VLE) separations require a high pressure. As the OCoM pressure is low, the pressure staging of the overall process is accordingly also subject to an optimization.

The HF reaction (14,36) has an equilibrium limitation at high temperature and low pressure, (fig.11) and is therefore usually performed at 15 bar or more, i.e. significantly above the OCoM pressure. While in conventional HF the reaction partners are the main components in the gas phase, for the C123 process the overall equilibrium conversion is further reduced by inert gases, as the partial pressure of the educts is decreased by inert dilution (including especially methane, ethane, carbon dioxide). Hence the process design has an impact on the maximum achievable HF conversion. The HF as targeted in the C123 project is designed as a heterogeneous system. In contrast to a homogeneous system, the catalyst is immobile and remains in the reactor avoiding dedicated efforts for catalyst separation and recycling.

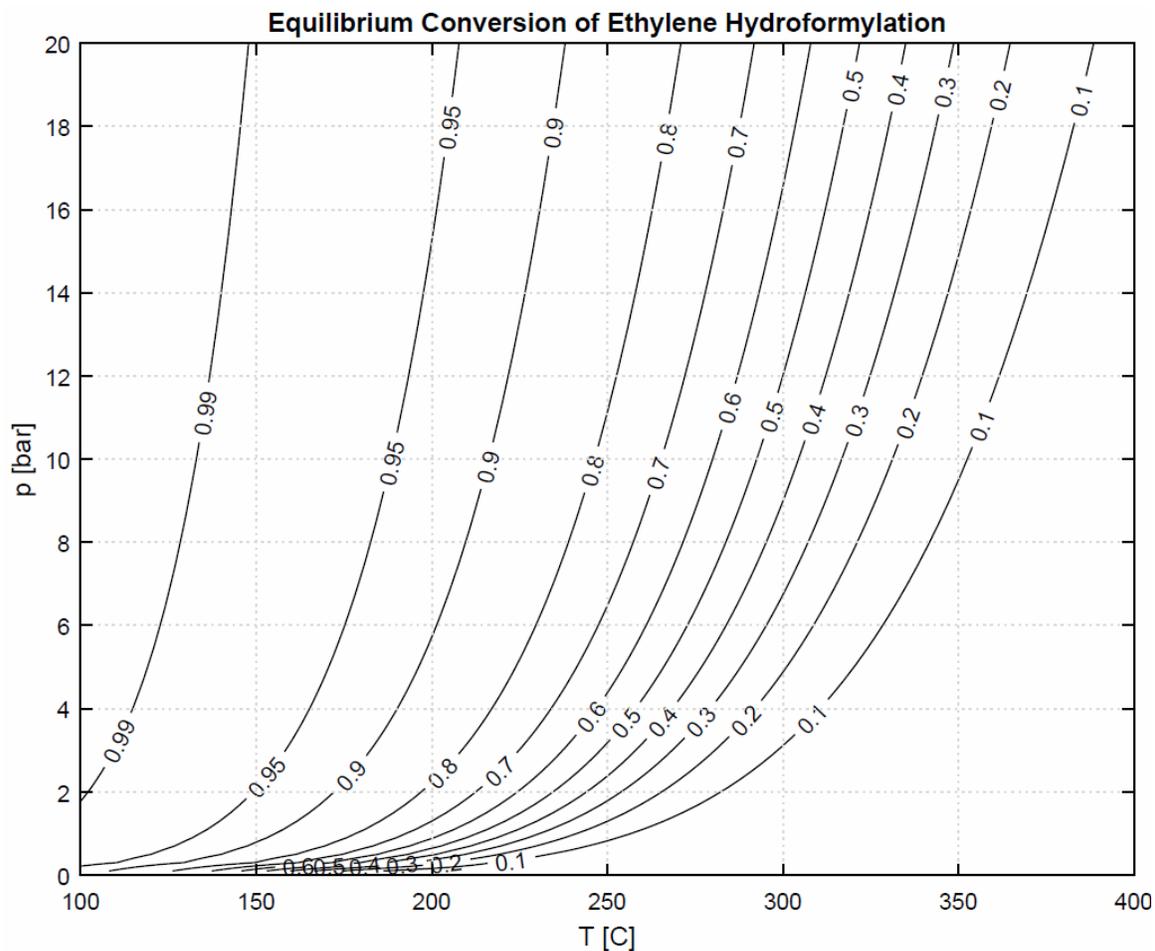


Fig 11: Equilibrium conversion of the hydroformylation reaction.

The propanal hydrogenation is again an equilibrium limited reaction performed at elevated but still limited temperature. In order to maximize the conversion, sufficient pressure is required (fig.12). To provide the overall hydrogen demand for both steps (HF and hydrogenation) an external hydrogen source needs to be considered which is preferably based on renewable resources or energy.

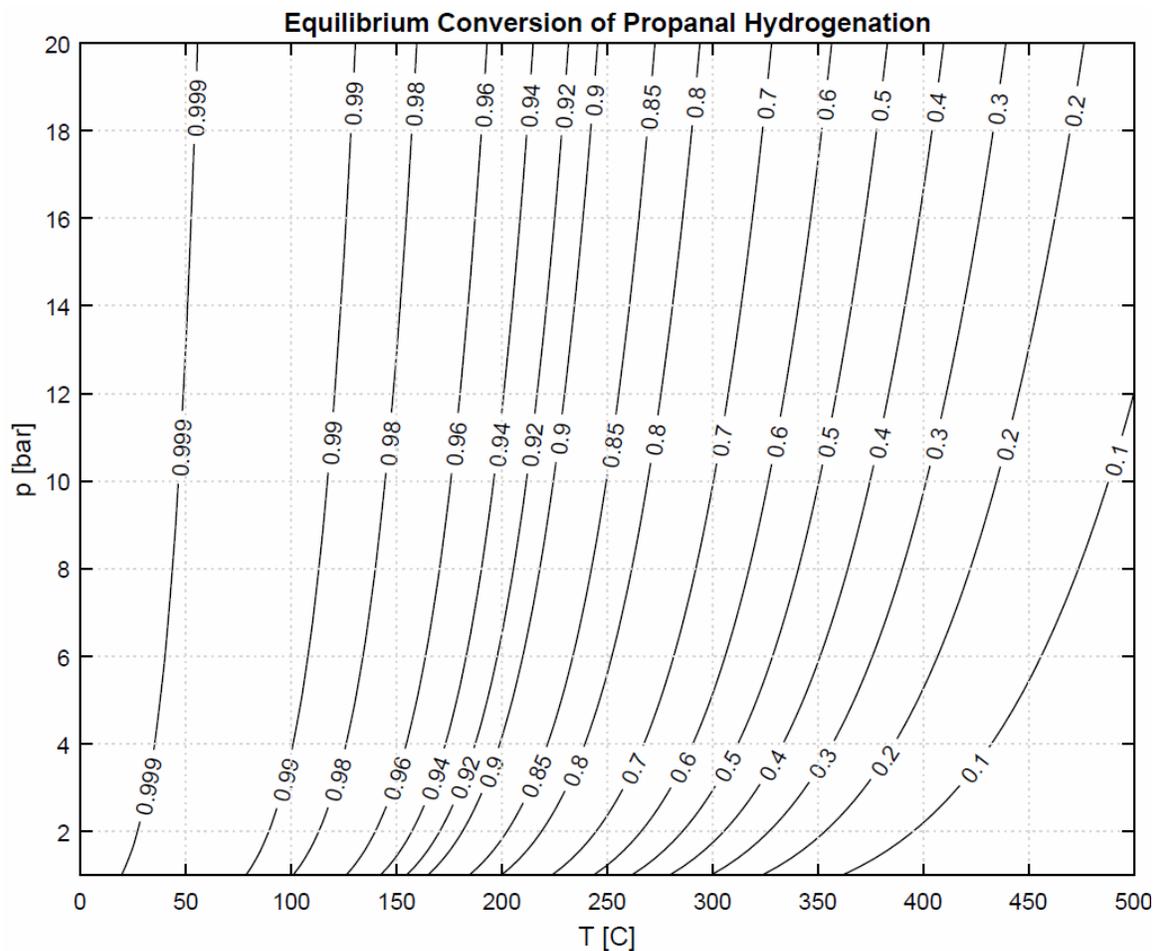


Fig. 12: Equilibrium conversion of the hydrogenation reaction

The dehydration is preferably performed at lower pressure and elevated temperature (fig.13). Next to a beneficial increase of reaction rates and equilibrium conversion, typical catalysts for this reaction require a minimum temperature of $>250^{\circ}\text{C}$. The endothermic dehydration from propanol to propylene can be performed in a heated reactor (e.g. tube bundle fixed bed reactor) or in an adiabatic multi-stage reactor with intermediate cooling.

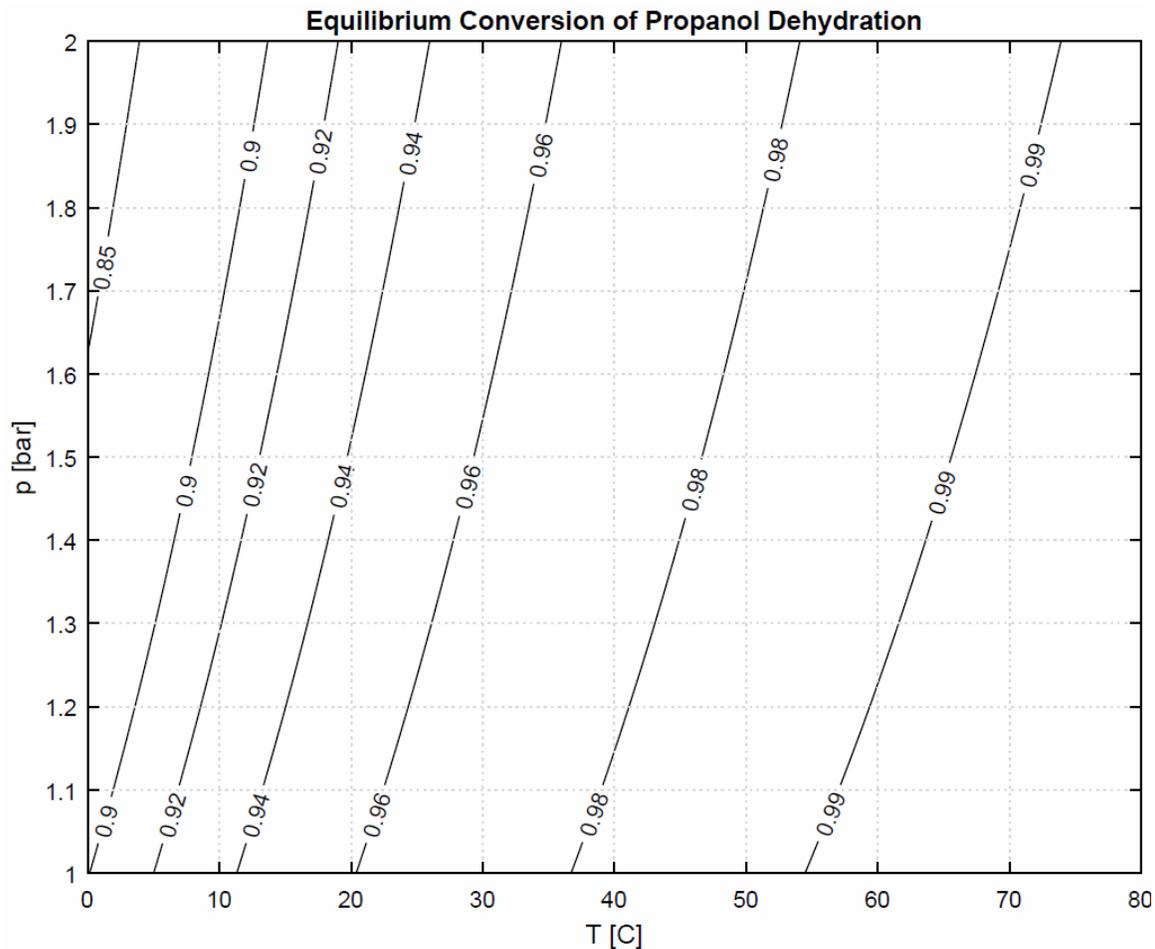


Fig. 13: Equilibrium conversion of the dehydration reaction

Although the intention of the C123 project is to minimize the intermediate separation and purification effort, a minimum set of such process operations will be required (e.g. separation, drying). Due to different temperatures of the specific reactions, heat exchangers need especially to be implemented accompanied by the respective pressure drop.

The light unconverted gases H_2 , CO and ethylene, but also by-products such as ethane, need to be separated from the HF product. a. Cryogenic separations themselves already require significant technical effort and equipment and are therefore expensive. If cryogenic separation can not be avoided the effective removal

of water and CO₂ using e.g. adsorptive removal and drying over molecular sieves are mandatory and further increase the technical and financial effort. Accordingly low temperatures are preferably avoided to maintain the process efficiency. Further, to minimize the cryogenic effort a minimum pressure is also required for these steps."The column design requires the detailed knowledge of the column feed stream and therefore of the performance of all reactors. Again, the separation efficiency also defines the reactor feed streams. The C₂/C₃ separation gives a C₃ product stream with low gas impurities. The overhead fraction contains different light molecules including some uncondensed C₃. At this point of the process an extractive distillation can for example be used to separate a gas recycle from the C₃ product, avoiding a cryogenic process step. A further separation of this gas recycle stream is not possible without a cryogenic process. Again, the OCoM selectivities highly impact the process design: if this stream cannot be sent to combustion or if some species shall be recovered due to other reasons, this stream could be either recycled to an existing petrochemical plant or the cryogenic separation needs to be implemented as its own process unit.

Due to numerous feedbacks and interferences between reactor performance, separation efficiency and the overall process due to operating conditions, heat integration and the influence of trace components, none of these designs can be done separately. Specialized solutions need to be identified and combined in an optimal manner to ensure high efficiency and sustainability of the overall process.

Accordingly, this task requires special expertise not only in the basic principles of all individual process units – including especially reaction and separation steps – but also in the technical implementation on industrial scale. Only a few companies specialized

on Engineering, Procurement and Construction (EPC) of world scale petrochemical plants such as Linde Engineering have the appropriate knowledge and experience to develop and provide a reliable and sustainable technical solution.

Conclusions

The C123 project aims to develop new technology for the upgrading of stranded natural gas or biogas to the easy-to-transport C3 commodities propanal and propanol, which can thereafter be transformed to propylene for the growing polypropylene market. The technology development aims to improve upon OCM technology by encouraging the production of CO in addition to ethene in the OCoM process and to develop a heterogeneous HF catalyst that provides comparable activity and selectivity to the well-known homogenous process.

There are many challenges ahead for this idea as the OCoM and HF processes are very different in nature and need to be united in an efficient overall process as possible. Specific issues that impact the direction of OCoM and heterogeneous HF catalyst development and the overall process include the following:

1. Should OCoM catalyst development emphasize ethene production and accept a stoichiometric deficiency of CO, or should a 1:1 mixture of ethene and CO be targeted? Does this ultimately depend on the methane feedstock and the location and size of the C123 process?
2. What is the best process design to merge the disparate pressure and temperature regimes for OCoM and HF?
3. How do the by-products from each of the two process steps affect the other? Can extensive purification steps and large recycle streams be avoided?

Fortunately, the C123 project has an experienced consortium team that is tackling these issues in a unified catalyst and process development strategy, to bring this potentially disruptive technology to TRL 5.

C123 will also evaluate the process market viability and end the user requirements for the different final product opportunities that can be derived from C3 commodities. The methane sources and the challenges presented by stranded gas such as infrastructure and transport will also be reviewed.

Acknowledgements

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