

Direct Conversion Process from Syngas to Light Olefins – A Process Design Study

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The scope in this project is the design of a synthesis gas to light olefins (C₂, C₃) process including a technical and economical evaluation. The challenges in this project are to find a catalyst for the direct conversion to light olefins and to implement this in a process. New and promising concepts for reaction and separation are evaluated and compared to proven technologies. An iron catalyst with MnO and K₂O promoters has been selected to catalyze the reaction towards olefins. The CO conversion is sufficiently large (90.4 mole%), but the selectivity towards C₂-C₃ olefins is only 49.7 mole%. The process is designed according to the systematic process synthesis techniques. The design of the reactor and the separators have been developed. An inlet of 500 t/h syngas yields 47 t/h ethylene and 51 t/h propylene. This is in total 98 t of desired product per hour. The rest of the inlet stream is converted to H₂O (226 t/h), CO₂ (67 t/h) CH₄ (52 t/h) and 56 C₄ and alifatics. A large amount of reactant is converted into byproducts. An economic evaluation based on market prices for products and raw materials shows a positive result. Further research can make the process more attractive. The carbon efficiency is too low (CO₂ and CH₄ are produced) and should be increased by improving the catalyst. The available catalyst data such as selectivity, conversion and lifetime is limited and should be subject of further research.

1. Introduction

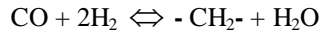
The scope in this project is the design of a synthesis gas to light olefins (ethylene and propylene) process. The challenges in this project are to find a catalyst for the direct conversion and to implement this in the design of a process. New and promising concepts for reaction and separation have to be evaluated and compared to proven technologies. In the design the synthesis gas plant is not considered.

The process is designed according to process synthesis techniques, following systematic stepwise and iterative procedures. In each step several alternatives have to be evaluated. First we consider the process overall, looking at feeds, products, process information found in the literature and boundary conditions. Next we create and evaluate the functions (e.g. reaction, separation) required for the process and set up a preliminary

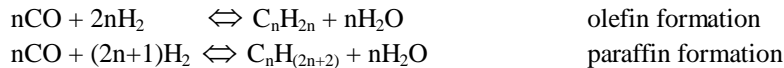
mass balance, before the transition to unit operations is made and final mass and heat balances are prepared.

2. Chemistry and Process overall

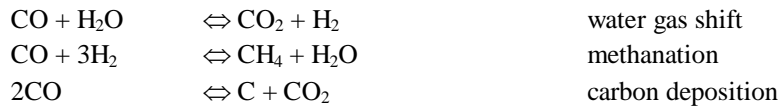
Hydrocarbon chain growth through hydrogenation of CO takes place according to:



This hydrocarbon chain growth leads to the formation of olefins and paraffins:



Side reactions which can take place are:



All reactions have a negative free energy of formation ($\Delta G < 0$) at room temperature, which means that there is a driving force for the reactions to the products at the right hand site. The driving force is reduced if the temperature is increased to temperatures where these reactions usually are carried out to create reasonable conversion rates. On the basis of thermodynamics it is also concluded that the water gas shift, the formation of methane and the formation of alkanes compete with the formation of olefins, the main product.

A catalyst is needed which gives a selective conversion. It is assumed that in the Fischer-Tropsch chain growth mechanism the following steps take place:

- reactant CO and H₂ adsorption on the catalyst surface
- chain initiation, formation of -C-H on the catalyst surface
- chain propagation, extension of the -C-C chain on the catalyst surface
- chain termination and product (viz. olefins) desorption from the catalyst surface
- product re-adsorption and further reaction

The last step will reduce the formation of olefins, the readsorption can be reduced by altering the catalyst surface. Methane is mainly formed when the CO adsorption is strong and the hydrogen adsorption is low on the catalyst surface (Van der Laan, 1999). A balanced ratio CO and H₂ can reduce the CH₄ formation.

Catalyst of group VIII metals have sufficient activity for Fischer-Tropsch synthesis (Steynberg, 2004). Fe and Co catalyst are used in the chemical industry (Dry, 2002). Low concentrations of sodium as a promotor on the catalyst show a good effect on the chain growth mechanism, they increase the dissociation of CO and increase the selectivity towards olefins and decrease the selectivity towards methane.

The process overall consideration is based on a literature search for design data, which includes a catalyst selection. An iron catalyst with MnO and K₂O promoters has been selected to catalyze the reaction towards olefins. The CO conversion is reasonably large (90.4 mole%), but the selectivity towards C₂-C₃ olefins is only 49.7 mole% (XU, 1995,

1998). This performance has consequences for the reaction and separation sections to be designed.

Table 1 Selectivities and conversion/pass for a Fe-MnO catalyst with K₂O promotor

Selectivity, % wt CO converted into product							Conversion %/pass
C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	
23.7	26.0	19.9	22.1	3.2	2.5	2.3	90.4

A molar ratio of H₂/CO=2 in the feed gas is optimal for the conversions to olefins. Syngas can be produced by partial oxidation of methane or catalytic steam reforming. In an autothermal reforming the two methods are combined, so that a H₂/CO ratio close to 2 can be realized.

For the process overall the following is relevant:

- The synthesis gas feed stream is produced from natural gas and has a H₂/CO molar ratio 2
- A 90% CO conversion means that a recycle is needed to achieve 100% conversion
- CO and H₂ combine to larger molecules, so the number of moles is reduced in the process
- In further design steps decisions about the reactor system and the separations are needed.

The assumptions and conclusions can change when we design the process in detail.

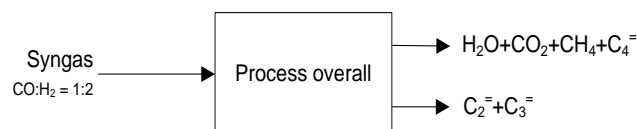


Figure 1 Syngas to olefins process – overall

3. Conceptual design

In the conceptual design the process functions and their connections have been determined. We start with the reaction. For the reaction of H₂ and CO to olefins a ratio H₂/CO = 2 is needed. This ratio has to be 2.1 to account for the formation of paraffins and methane. By introducing a recycle a 100% conversion of CO can be achieved.

The methane formed in the reactor can be treated as follows: (a) Recycled to the reactor until extinction. This can shift the methanation reaction towards the formation of syngas, but might influence the formation of olefins as well; (b) Recovered and converted to syngas outside our process CO₂ can be recycled to the reaction function. It will influence the water gas shift and might influence the formation of olefins as well. Water formed has to be removed. For this and the removal of byproduct hydrocarbons like butylenes, separation functions are needed. The result is a functional diagram as given in Figure 2.

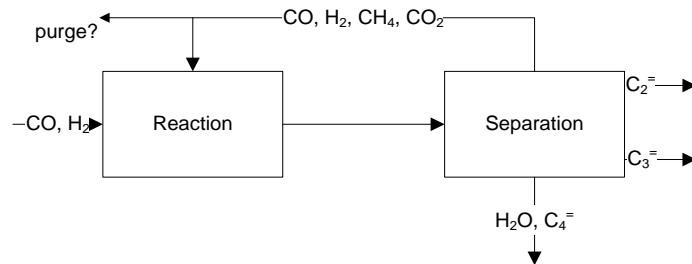


Figure 2 Process functional diagram, recycle (purge?) of reactants CO , H_2 , CH_4 , CO_2 . Still open are issues like the number of separations and potential combinations of separation with reaction.

Three alternative mass balances are created and examined in more detail : (i) recycle of H_2 ; (ii) recycle of H_2 , CO_2 , and CH_4 ; (iii) removal of H_2 , CO_2 , and CH_4 from the reactor effluent. The model for the reactions sections consisted of a conversion reactor for the formations of olefins and parafins according to Table 1, followed by an equilibrium reaction for the water-gas-shift reaction. The water-gas-shift consumes residual CO according to the equilibrium calculations at 350°C and 20 bar (XU, 1995). A purge of 2% of the recycle is assumed. The intention of the recycle is to reduce the formation of CO_2 and CH_4 and to increase the carbon efficiency towards olefins. Comparing the results of the calculations for total recycle with no recycle the maximum incremental yield on ethylene and propylene is 4%. The alternatives and choices are shown in Fig. 3.

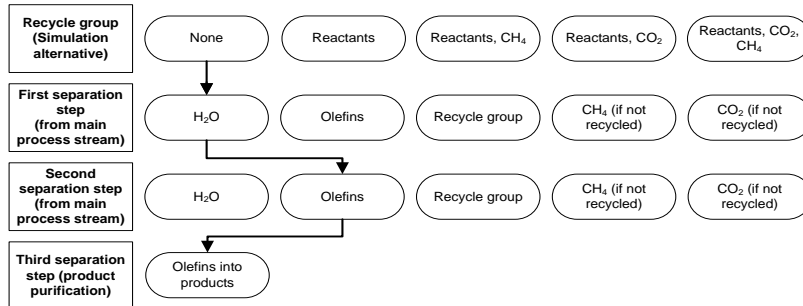


Figure 3 Conceptual design alternatives and choices

In the conceptual design phase reaction and separation functions are defined. First water is separated from the reactor effluent, next raw materials and byproducts are separated from the products. In a third separation the products are separated in the components. Using basic reaction data and alternatives for the separations process set ups have been evaluated and decisions are made. In a next design step unit operations and more detailed mass and energy balance have been created.

4. Process flowsheet and unit operations

In this section potential unit operations and their techniques are selected and evaluated. The performance of the unit operations can change the mass balance which has been created in the conceptual phase. The workdiagram in Figure 4 represents the steps, inputs and decisions.

Reactor system. Following information has to be used in the design:

- the reactor capacity is calculated to be 500 t/h syngas feed
- In the reactor the amount of molecules is reduced from 48,400 kmol/h (reactor inlet) to 23,800 kmol/h (reactor outlet)
- The reactor conditions are 350°C and 20 bar (4)
- In the reactions about 600 MW of heat is produced which makes heat removal essential to control the reactor system
- A solid (heterogeneous) catalyst is used, which means that inside the reactor there is a mixture of a solid and gaseous phase (Xu, 1995)
- Carbon can be deposited on the catalyst particles and regeneration of the catalyst is probably needed.

The reactor characteristics show a high CO conversion, low selectivity and a high heat duty of 600 MW.

Using the methodology of Krishna and Sie (1994) for the selection of a reactor system to fulfill the requirements of our process, a fluidized bed reactor seems a feasible option for our process. For the fluidized bed reactor system, the reactor height is calculated to be 14.6 m with a diameter of 10.5 m. Extra height is needed for additional equipment. Within this system we estimated a catalyst size of 100 μm , a bubble diameter of 0.075 m and a superficial velocity of 0.4 m/s. The reactor is cooled down by generating medium pressure steam (180 °C). This can be achieved by installing about 2000 cooling tubes, with an external diameter of 5 cm. The pitch distance between these tubes is 22.6 cm.

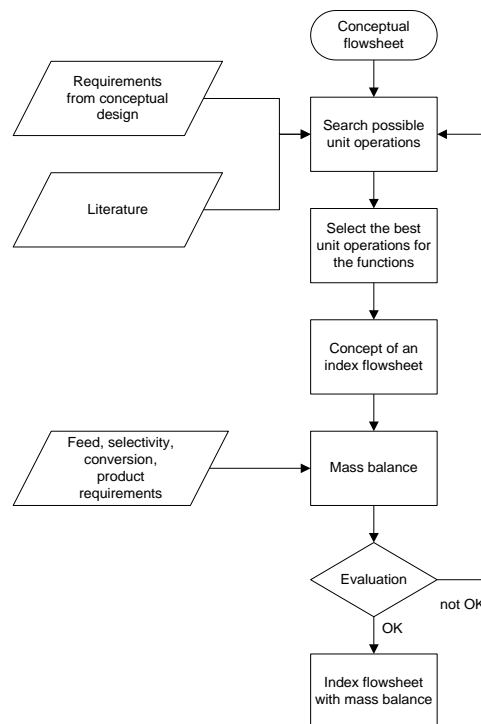


Figure 4: Work diagram from Conceptual to Index flowsheet and mass balance

Separations. In the preliminary mass balance it is calculated that the reactor outlet flow is 23,700 kmol/h of gas with more than half of it water:

Table 2: composition of reactor outlet stream.

component	H ₂	CO	CO ₂	CH ₄	C ₂ H ₂	C ₃ H ₆	C ₄ H ₈	H ₂ O
Mol%	8.4	0	5.0	14.7	8.0	5.5	3.4	55.0

By condensation the major amount of water can be removed and the gas stream left is substantially reduced. The separations of olefins (and paraffins) from CH₄, CO₂ and H₂ are partly based on conventional proven techniques applied in the naphtha process, like adsorbers and distillation columns. CO₂ is best removed by chemical solvents e.g. from the ethanolamines family. A disadvantage of the use of distillation technology for the separation of paraffins and olefins is the low temperatures at which these processes are

being operated. Research shows some promising alternatives like membrane technology, but these are not yet applicable on an industrial scale to fulfill the desired separations. Nevertheless, membrane technology is applied to separate a large part of the hydrogen from the reactor effluent to recycle the hydrogen back to the reactor.

5. Mass & heat balances

From the UniSim® simulation it is concluded that an inlet flow of 500 t/h syngas produces 47 t/h ethylene and 51 t/h propylene produced. This is in total 98 t of desired product per hour. The rest of the inlet stream is converted to H₂O (226 t/h), CO₂ (67 t/h) CH₄ (52 t/h) and 56 C₄ and alifatics. A large amount of reactant is converted into byproducts. Heat management of the process is fairly complex. More than 600 MW of heat is produced in the reactor at 350 °C, streams have to be cooled for separations and cryogenic distillations require cooling. By heat integration cooling and heating duties can be reduced by one third.

6. Economics and evaluation

In the process economics the ethylene, propylene and the syngas prices are the most important drivers. The investment costs for the plant are estimated at about 300 M\$. The feasibility of the project based on technical and economical evaluation is promising. However, there are some items for further research which can make the process more attractive. The carbon efficiency is too low (CO₂ and CH₄ are produced) and should be increased by improving the catalyst. The available catalyst data such as selectivity, conversion and lifetime is limited. The kinetics of the catalyst has to be determined as well. The reaction is highly exothermic which makes temperature control and heat removal a challenge.

Acknowledgement

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