Developing Linear-alpha-Olefins Technology – From Laboratory to a Commercial Plant

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Abstract

Linear α-Olefins (LAOs) are used in several applications in chemical industry. Together with SABIC (Saudi Basic Industries Corporation) Linde jointly developed the α-SABLIN technology for a full range LAO plant as well as a 1-Hexene selective "On Purpose" technology (LAO OP) to cover the rapidly increasing demand for this specific comonomer.

The α-SABLIN as well as the OP technology are both homogenously catalyzed systems. This is raising special challenges concerning process and reactor design compared to much more established heterogeneous systems in chemical industry.
E.g., the reactor concept is a bubble-column which allows efficient mixing as well as cooling of the reaction mixture. The development of the process was based on laboratory experiments which – based on an initial conceptual design for a large scale technical process - were first transformed into a pilot device before the commercial plant was designed, engineered and successfully started up and declared as commercialized. Today the α-SABLIN technology is the only LAO technology with a commercial reference which is free for licensing.

A lot of experience and knowledge from the α-SABLIN development and commercial operation was gained. Although newly developed OP technology is based on a different catalytic system, this experience is now utilized and transformed within the commercialization of this new technological development.

Introduction

Linear α-Olefins (LAO) are used in several applications in chemical industry. Especially 1-Butene and 1-Hexene are highly valuable comonomers for polyolefins. Higher LAOs are processed within the production of Poly-Linear-Alpha-Olefins (PAOs), detergent alcohols and lubricants.

C_2H_4 →	C_4H_8	1-Butene	Comonomer
	C_6H_{12}	1-Hexene	Comonomer
	C_8H_{16}	1-Octene	Comonomer
	$C_{10}H_{20}$	1-Decene	„PAOs“ – Lube Oils
	$C_{12}H_{24}$	1-Dodecene	} Detergent Alcohols, Plasticisers
	$C_{14}H_{28}$ - $C_{18}H_{36}$		
	C_{20+}		Waxes, Lubricants, ...

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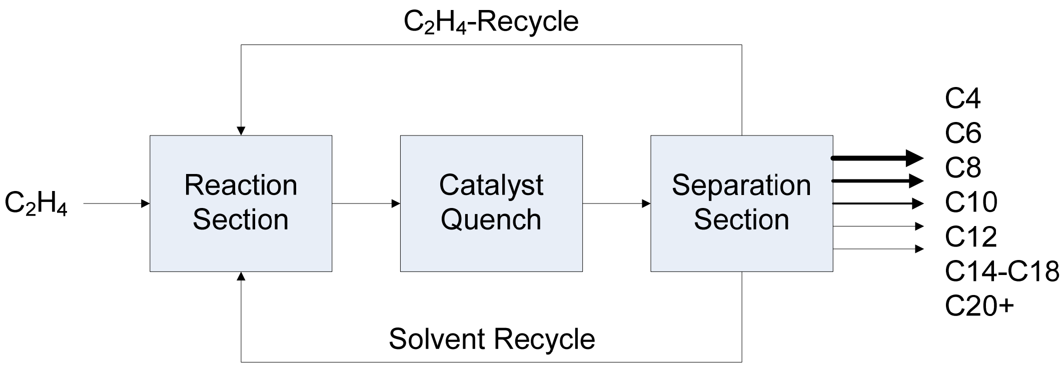
α-SABLIN – Development and Successful Commercialisation of a Full-Range LAO Technology

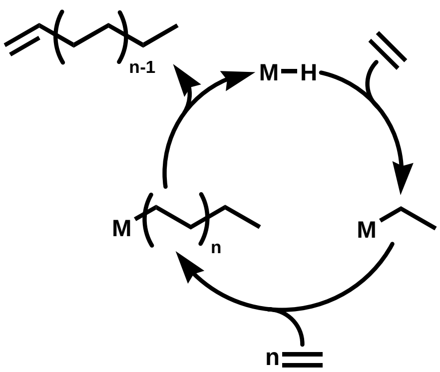
The technology partners SABIC and Linde jointly developed the α-SABLIN technology. Within several stages this technology was growing from first lab scale experiments in the 1990s over pilot plant size up to the commercial plant. The pilot plant was designed and constructed by Linde based on an initial conceptual design for a large scale commercial process. It was put into operation in 2000 at the SABIC Development Centre in Riyadh (Saudi-Arabia). Finally in 2009 the commercial plant in Al Jubail (Saudi-Arabia), after a successful performance test run, was declared as fully commercial by UNITED, which is a SABIC affiliate.
This UNITED plant is the first commercial plant to use the α-SABLIN® technology for the production of linear α-olefins from ethylene and has a name plate capacity of 150.000 t/a total LAO production. Currently further projects utilizing the a-SABLIN technology, which is the only LAO technology with a commercial reference free for licensing, are ongoing.

The major units of an α-SABLIN plant include the Reaction Section, the Catalyst Quench and the Separation Section.



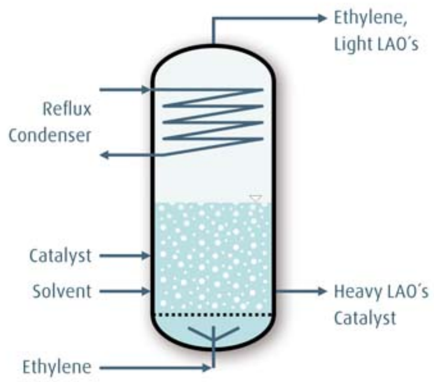
Reaction Section - The α-SABLIN Reactor

The α-SABLIN process is based on a Zr(IV)carboxylate as catalyst and special aluminiumalkyl components as co-catalyst.
The existing technologies for full range production of LAOs are mostly based on ethylene oligomerization routes by an ethylene insertion / β-elimination mechanism. The resulting product distribution is following a Schulz-Flory-distribution.



In case of the α-SABLIN technology, the ratio of catalyst and cocatalyst is strongly affecting this distribution and can be easily controlled in order to tune the desired product distribution. This features allows an enormous flexibility of the process to react to changing market demands for lighter or heavier LAO fractions.

The oligomerization of ethylene into LAOs is performed in a bubble column reactor at 20-35 bar and at temperatures between 50 and 100°C with the solvent toluene and the dissolved catalyst components fed to the liquid phase.

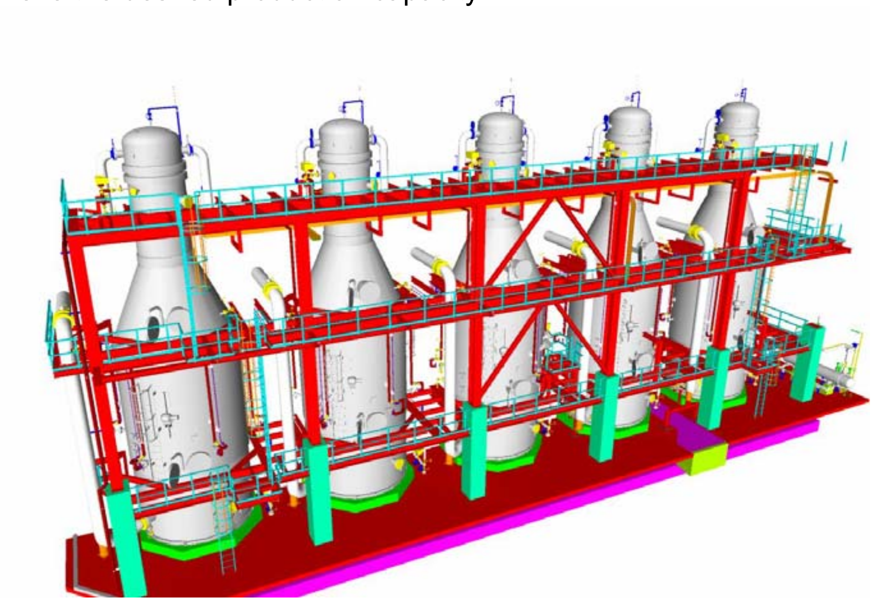


Ethylene is introduced via a gas distribution system to the bottom section, whereas the liquid heavy LAO, together with the solvent and the catalyst, are withdrawn from the bottoms. The LAO reaction is highly exothermic. By removing this heat with the ethylene, heat exchanger surfaces within the reaction area, which would be subject to heavy fouling, are avoided. The function of ethylene as a coolant in the LAO reactor is a unique feature of the α-SABLIN technology.

Thus the ethylene feed to the reactor serves the following three purposes:

- Reaction Feedstock
- Reaction Cooling
- Reaction Mixing

In a modular approach within the commercial plant several of these reactors are placed in parallel to achieve the desired production capacity.



Separation Section - The α-SABLIN Product Separation

Downstream of the catalyst deactivation and removal section, which is realized as a caustic extraction, the LAO products and the solvent are separated in the product separation section (picture on the right).
The separation train applies only standard distillation technology. Due to the high selectivity of the catalyst system, there is no need to install sophisticated superfractionation steps for removal of byproducts or impurities.
By adjusting the co-catalyst to catalyst ratio, the product distribution can be adjusted in a wide range. Depending on client requirements, the production can be shifted either to the lighter LAOs or the production of longer chain LAOs can be maximized. Typical α-SABLIN product distributions are given in the following table.

Product Fraction wt.-%	Low Cat. ratio	High Cat. ratio
C4	10.0	39.1
C6	11.3	26.4
C8	11.3	15.8
C10	10.5	8.9
C12+	balance	balance

Finally, the characteristics and features of the α-SABLIN process can be summarized as follows:

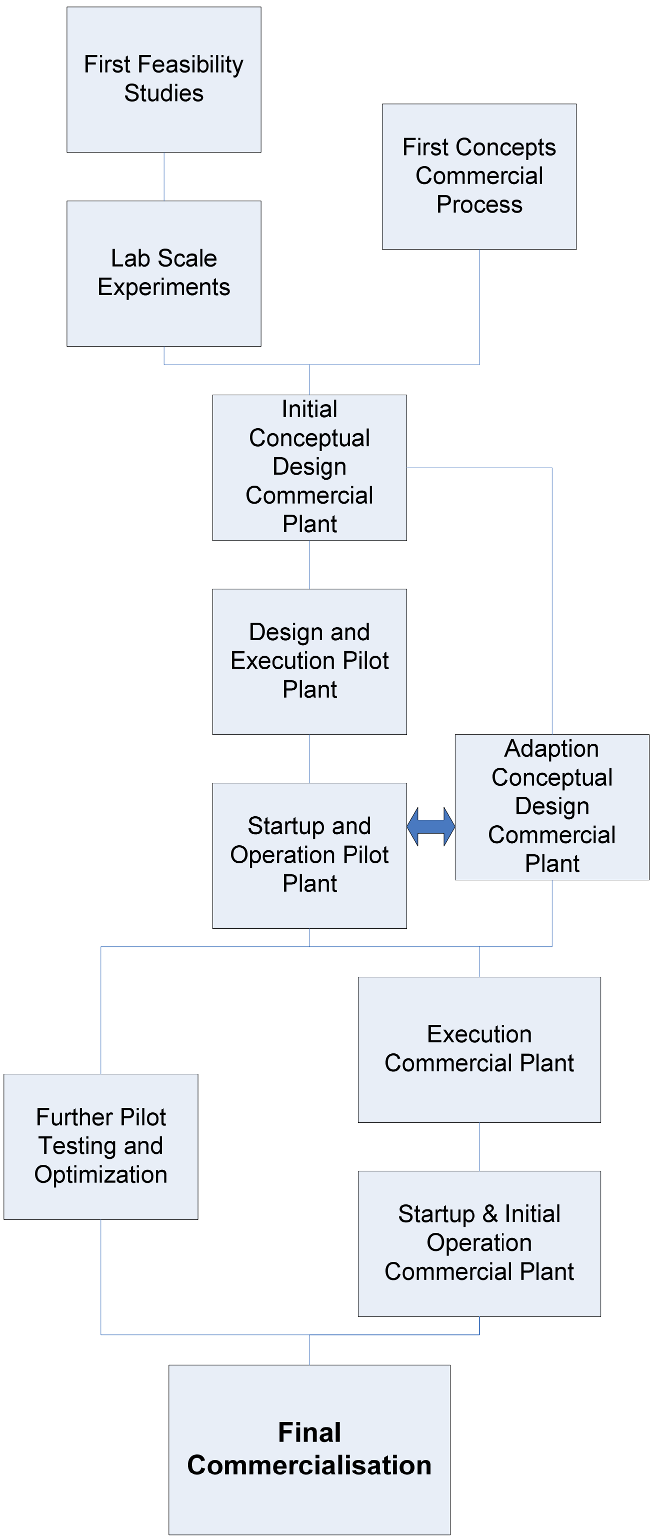
- Moderate reaction conditions
- Single step, homogeneous catalytic reaction
- Runaway-safe reaction system
- High product distribution flexibility
- High selectivities and high product purities without superfractionation
- Attractive economics
- Available for licensing

Development Phase α-SABLIN

The α-SABLIN technology is an excellent example of successful technology development. Starting with laboratory experiments and the implementation and operation of a pilot plant, it has been made ready for marketing by design and realization of a first commercial plant as a reference for the technology. In the technology project it was important that with the development partner or a subsidiary of said partner, a potential customer for the first commercial plant was already very early available.
During the piloting itself it was essential that all relevant new process steps for the later commercial process, i.e. the reaction section, and corresponding loops such as for ethylene or toluene were already implemented. By this it was possible to detect in the pilot plant any possible effects such as e.g. accumulation of trace components or formation of byproducts under realistic conditions. The task of separation was not fully implemented in the pilot plant as this is well known state of the art technology for Linde Engineering. Anyhow, a batch distillation was installed to gain the pure individual fractions and also to recover the solvent toluene.

"Top Down Approach" for Pilot Plant

This approach is based on the long experience within Linde Engineering with the implementation of new technologies. As a key to success the development phases as shown on the right side can be identified for the development of a new (petrochemical) process.



Already during the initial feasibility studies and laboratory experiments first initial ideas and concepts for a potential commercial process have to be developed. It is absolutely mandatory before the planning and construction of a pilot plant to have a first conceptual design for a commercial plant available. Otherwise the pilot plant might be designed in a way which cannot be easily transferred to technical scale or costly modifications and repeated testing might be required. Wherever a final commercial design is deviating from the design of the pilot plant, especially in the case of new processes, there is a high risk of unforeseen challenges and effects which might cause very high costs for corrective measures in the stage of starting up a commercial unit.

During startup and operation of the pilot plant there needs to be a strong inter-action between these piloting trials and the Conceptual Design work which has to be adapted to the findings and experiences gained.

But still during the execution and even after the startup and accompanying the initial operational phase of a first commercial unit additional pilot trials might be required for further testing and optimization purposes.

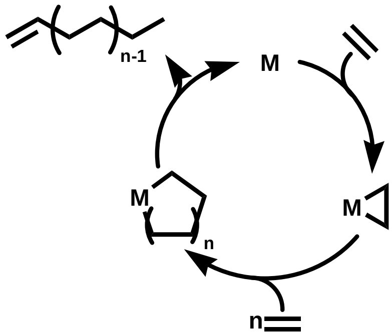
Finally, at least until a first commercial reference plant has successfully passed a performance test run, a pilot plant can be required as well and should be kept available. Experiments in a dedicated pilot plant are much cheaper than modifications and testings in a running commercial unit. Under this aspect also commercial (scale, possible production loss, …) and legal aspects (required authorization, environmental restrictions, …) need to be considered.

Development of a highly selective technology for the production of 1-Hexene

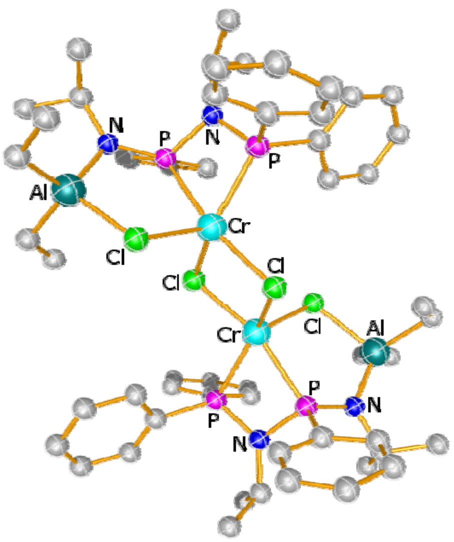
Polyethylene is currently the largest volume polymer in the world. Linear low-density polyethylene (LLDPE) has penetrated almost all the traditional markets for polyethylene but is mainly used for plastic foils, as it allows the use of a lower thickness of the foils. It is a substantially linear polymer with significant numbers of short branches, commonly prepared by copolymerization of ethene with short chain alpha-olefins. This causes a rapidly growing commercial demand especially for comonomer-grade 1-hexene. Therefore and in parallel to the passed commercialisation activities of the α-SABLIN process, both parties Linde and SABIC decided to develop a further technology for the dedicated and selective production of 1-hexene only (LAO OP – LAO On Purpose).

This development was done together with an academic partner (LIKAT Rostock) for the basic research. In the meantime a fully developed catalyst system is available and the commercialisation of this technology is ongoing.

In contrast to the full range LAO technologies with an ethylene insertion / β-elimination mechanism for the selective LAO OP process, a mechanism via metallacycles can be proposed and is explaining the high selectivities:

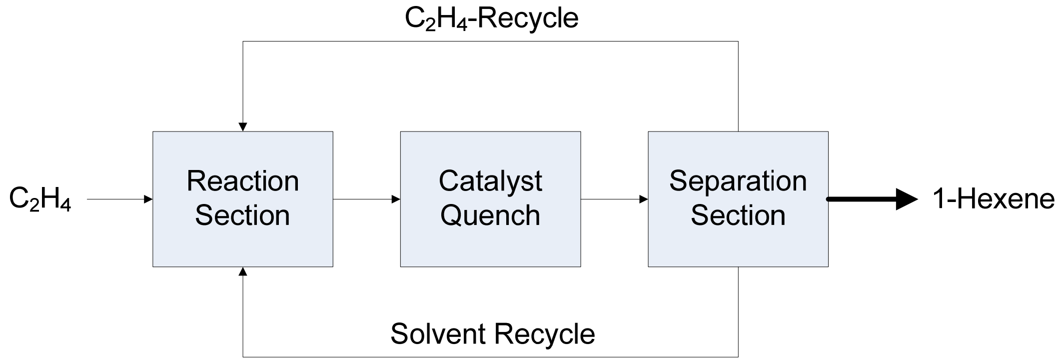


The catalytic system is based on $[CrCl_3(thf)_3]$ as a chromium source, the ligand $Ph_2PN(iPr)P(Ph)N(iPr)H$ and triethylaluminium as co-catalyst in toluene. By testing chlorine-free alternative chromium sources and by the addition of ammonium or phosphonium chlorides as modifiers it became obvious that chlorine must be an essential part of the catalytically active species. Furthermore, a screening of different aluminium alkyls revealed the outstanding relevance of triethylaluminium for activity and selectivity of the described catalytic system. The crystallographic structure of the proposed precatalyst species which is shown on the right side is giving an indication of the active species itself.



Actually the commercialisation process according to the schemes and principles described above is ongoing. Off course the Know-How and expertise from α-SABLIN development and commercialisation is utilized also for the commercialisation of the selective LAO OP technology. Valuable experiences and insights from α-SABLIN commercialisation are significantly reducing the time to market for the selective LAO OP technology.

Reviewing the principal block flow diagram, the principal setup is quite similar to the α-SABLIN process. But as there is only one product fraction the separation section can be simplified to a high extent.



Nevertheless the 1-Hexene selective LAO OP process is utilizing a new catalyst system and therefore it was and still is essential to perform the complete pilot plant testing for this process with an appropriate setup.

Summary

Linear α-Olefins (LAO) are used in several applications in chemical industry. Together with SABIC Linde developed the α-SABLIN technology for a full range LAO production as well as a 1-Hexene selective "On Purpose" technology (LAO OP) to cover the rapidly increasing commercial demand for this specific comonomer.

Within these development and commercialisation activities, scale up from laboratory over pilot plant size up to commercial plant size was performed. During these activities the initial conceptual design for a commercial plant was done already on a very early stage. This allows to build and to operate a pilot plant with the same features and characteristics as the later commercial process. All new process steps need to be considered and potential recycles need to be closed. The successful development activities and final commercialisation of α-SABLIN in 2009 has proven that carefully following up on this approach is minimizing the risks, the costs and the time demand for the commercialisation of a new (petrochemical) technology. The total time demand between first lab experiments and final commercialisation was less than 15 years. Actually on the same basis the commercialisation of the selective LAO OP technology is on-going.