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# An industrial perspective on the impact of Haldor Topsøe on research and development in synthesis gas production

# Jens R. Rostrup-Nielsen

Furesøvej 27, 2830 Virum, Denmark

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#### ABSTRACT

Haldor Topsøe was a fast follower in syngas technology and soon became a major player in the field. This was based on a development effort supported by fundamental studies of the key problems. This paper summarizes the science behind this parallel approach stressing the collaboration with academia. It was a result of Haldor Topsøe's attitude that this should be a two-way process to the benefit of both parties. It required that his company was active in basic research as well.

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#### 1. Introduction: The history

After the successful introduction of the ammonia synthesis catalyst and reactor technology to industry during the 1950s it was natural for Haldor Topsøe to expand into technologies for the manufacture of synthesis gas (syngas) [1–3]. The main principles of catalytic partial oxidation and steam reforming processes converting hydrocarbons to syngas had been described in an early patent by Mittasch et al. [4] and a later patent [5] claimed a big fraction of the Periodic Table as catalyst components.

Low pressure processes for catalytic partial oxidation were developed in the 1930s, but low pressure meant high compression costs for the synthesis. Thermal processes for partial oxidation at high pressure had been developed around 1945 [6,7], but Topsøe pioneered a hybrid version using partial combustion in a flame followed by catalytic reaction, called autothermal reforming (ATR). This was done at first with the Belgian SBA company [8] during the 1950s, and later alone, first for ammonia plants and later for methanol and gas-to-liquids Plants [3,9,10].

The first industrial steam reforming plants were installed in 1930 [11] based on natural gas as feedstock, but the commercial breakthrough of the technology took place when ICI succeeded in starting two tubular reformers operating at 15 bar pressure in 1962 [12]. Haldor Topsøe was a fast follower [13]. The first Topsøe reformer (operating at low pressure) was started in 1956 and high pressure reformers followed from 1962 onward, with

ble to take advantage of the availability of better tube materials. As a result the reformers of today are designed for average heat fluxes that are about twice of what was industrial practice 30 years ago. This means a smaller number of reformer tubes and hence a cheaper plant. The limits of the reforming process with respect to heat flux,

one operating at 42 bar in 1966 [3]. The introduction of high pressure reforming meant that the energy consumption of the ammonia plants could be decreased significantly [14]. The catalysts

consisted of supported nickel, able to withstand the high temper-

ature and partial pressures of steam. Topsøe focused on a ceramic

magnesium aluminium spinel support fired at high temperatures

[15]. During the first decades, reforming plants of Topsøe design

were mainly built in Europe, Japan and India, where naphtha was then the available feedstock [16,17]. This required special

alkali-promoted catalysts to deal with carbon formation

[13,18,19]. Another approach was the use of an alkali-free catalyst

based on active magnesia [17,19,20], which could handle heavier

feedstocks (kerosene, light gas oil) owing to its higher activity. An alternative solution was to use low-temperature adiabatic

reforming, as pioneered by the British Gas Council [21] and later

applied by Topsøe [22,23], as pre-reforming for tubular reactors.

This not only avoided the complications of tubular reforming of

higher hydrocarbons, but also allowed steam reforming at more

economic conditions, with lower steam to carbon ratios and higher

inlet/outlet temperatures of the reformer [24]. This, and a better

understanding of mechanical stress problems [1,15], made it possi-

The limits of the reforming process with respect to heat flux, carbon limits and activity were explored in a full-size monotube







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E-mail address: rostrup-nielsen@mail.tele.dk

pilot plant [1,25]. This led to more advanced design models [25] and development of processes working at almost stoichiometric reforming and with the presence of  $CO_2$  [1,26]. One result was a process for reducing gas for direct reduction of iron ore [27]. Haldor Topsøe himself was actively involved in the development work and engaged in discussions mainly with the Swedish steel industry. Another process (SPARG) [28] utilized sulphur passivation of the nickel catalyst, allowing operation with high contents of  $CO_2$  in the feed gas at conditions which would otherwise result in carbon formation. This was applied for the manufacture of CO-rich syngas [29].

Fuel cells became a new opportunity for reforming technology during the 1970s. Topsøe was involved early by supplying catalyst for naphtha-based phosphoric acid fuel cell (PAFC) plants. This was followed up by development of a convective reformer in collaboration with EPRI [30,31], resulting in the supply of reforming units to a number of PAFC plants primarily in Japan. Haldor Topsøe was attracted by the thermodynamic potential of the high temperature fuel cells for high electric efficiency. This resulted in close contacts to Bernie Baker (founder of Energy Research Corporation (ERC)) [32], who was a pioneer in internal reforming, seen as the key for high performance. Topsøe's system for internal reforming including catalysed hardware in the anode chamber was demonstrated in an ERC molten carbonate fuel cell (MCFC) plant at a Danish Utility [33]. The interest in fuel cells led to a close collaboration with the Danish Risø National Laboratory on solid oxide fuel cells (SOFC) and the formation of the Topsøe Fuel Cells (TOFC) company [34].

The convective reformer was further developed and optimized for small hydrogen units [35,36] and later for chemical recuperation in large gas-to-liquids (GTL) [37] and hydrogen plants [38]. Haldor Topsøe himself was deeply engaged with ideas for new reactor designs, see for example Fig. 1.

Autothermal reforming (ATR) became the preferred technology for large-scale Fischer–Tropsch plants based on natural gas [1,37,39]. The presence of a catalyst allows a decrease of the maximum temperature compared with the thermal partial oxidation, which means a lower oxygen consumption and less  $CO_2$  in the syngas ( $CO_2$  being inert for low-temperature FT synthesis). On the other hand, the thermal process results in less  $CH_4$  in the syngas. The application of ATR for FT synthesis required further development of the technology to minimize the addition of steam. This required extensive pilot work with burner optimization before a scale-up from 400 Nm<sup>3</sup> syngas/h to 500,000 Nm<sup>3</sup> syngas/h in the Sasol Oryx plant in Qatar [35]. ATR was also introduced to large-scale methanol plants [1,40], mainly driven by a more favourable economy of scale compared to tubular reforming.

Catalytic partial oxidation (CPO) was considered for large-scale syngas, but was not feasible due to higher oxygen consumption (lower preheat temperature) and other problems. Haldor Topsøe did some work in collaboration with Snamprogetti [41]. However, CPO may be the preferred technology for small-scale fuel cell plants due to the compactness of the reactor [34].

The reforming technology still faces challenges [1]. One is to decouple the heat transfer from the catalytic reaction. Another is to take advantage of the high catalyst activity by membrane reforming at low temperature [42].

The development of processes for syngas production was not based on an initial understanding of the catalysis. In contrast to ammonia synthesis, progress was mainly driven by feedback from industry and pilot plants. The conventional testing of catalysts in laboratory units simulating industrial conditions was replaced by scale-up to semi-industrial pilot plants operating at industrial mass velocity and heat transfer rates, and a scale-down to dedicated equipment allowing study of the catalyst at defined conditions in *in-situ* studies [43]. Samples from the pilot plants (and from industrial units) are then examined by the fundamental characterization methods, which give feedback to the catalyst development work. In this way, the circle is closed, making catalyst development a learning process [43].

Already from the beginning [13,44], Haldor Topsøe initiated research projects in parallel to the developments to understand the science behind the work. This multiple approach gave strength to cope with problems and to make a more rational scale-up. This type of research depends strongly on fundamental methods to characterize the catalyst structure, part of which can be published. Needless to say that this type of research is an ideal theme for collaboration with universities. In the following, we review the main scientific results of this work that supported the development of syngas catalysts and technology. Other examples of the approach are given in several articles of this special issue.

## 2. The science behind steam reforming

# 2.1. Understanding the nickel catalyst

The initial vague ideas of the science behind the reforming process were mainly formulated by industrial groups [19,45,46]. Input

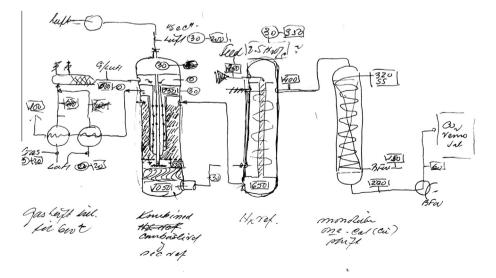


Fig. 1. Process scheme for syngas production, hand-drawn sketch by Haldor Topsøe from the 1990s.

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