

## The new HPPO Process for Propylene Oxide: From Joint Development to Worldscale Production

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BASF and DOW Chemicals independent starts and joining the development of the innovative and environmentally-benign first world scale HPPO process for the production of Propylene Oxide using Hydrogenperoxide with a capacity of 300 kt/a and its first successful implementation in Antwerp, Belgium, is described.

### 1. Introduction

With global capacities of 7.5 Mt/a Propylene Oxide belongs to the top 50 immortal chemical intermediates. The molecule is an essential building block for a wide range of industrial chemicals and products including polyurethanes, propylene glycols and glycol ethers. It's part in automotive bumpers, car seats, inline-skate wheels, refrigerator insulations, mattresses, diving suits and detergents.

### 2. Established Technologies and Alternative HPPO Process

As propylene till today refuses against direct epoxidation with Oxygen or Air in high yields like e.g. Ethylene allows, chemical mediators are necessary for economic PO production processes. Using Oxygen or air means, electronegative charged oxygen will preferred bind to the terminal allylic carbon, creating acrolein and acrylic acid finally. With mediators, which have to be used in stoichiometric, not in catalytical amounts only, electropositive oxygen-species are generated binding at the electronegative doublebond and ending up in significant stoichiometric coproduct or recycling product streams.

As precursors for technical PO production processes Chlorine and water, Ethylbenzene, Isobutene and Cumene are established. For 1 ton of Propylene Oxide wanted 42 tons of salty water, 2.2 tons of Styrene or 2.4 tons of tertiary Butanol or 1.5 tons of Cumyl alcohol are coproduced and have to be handled, sold or recycled.

An alternative commercial epoxidation reaction for Propylene Oxide based on Hydrogen peroxide as mediator, using TS-1 catalyst was invented by ENI in Italy 25 years ago. Independent process developments were started then by several companies in the last decade with different approaches and success: DOW Chemical and BASF were among them independently from each another first.

The promise of this route was that based on low cost Hydrogen peroxide as mediator only stoichiometric amounts of 300 kg of water would contribute to the coproduct mass balance at reasonable raw material costs.

process	precursors	intermediate	Coproducts / recycle t / t PO
PCH PO	Cl <sub>2</sub> , H <sub>2</sub> O	HOCl, PCH	≥ 2 t Chloride salts ≥ 40 t H <sub>2</sub> O
SM PO	Ethylbenzene	EB-hydroperoxide	≥ 2.2 t Styrene
MTBE PO	Isobutane	t-Butylhydroperoxid	≥ 2.4 t t-Butanol
Cumene PO	Cumene	Cumene-hydroperoxide	~ 1.5 t Cumyl-alcohol
<b>HPPO</b>	<b>H<sub>2</sub>, O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>≥ 0.3 t H<sub>2</sub>O</b>

Figure 1: HPPO coproduction fingerprint

### 3. Catalyst, Kinetics, Reactor and Process

BASF started about 10 years ago the development of an epoxidation process of propylene with hydrogen peroxide, HP referred to as HPPO process with a solid catalyst in a tubular reactor (Figure 1).

Reaction in Methanol as essential solvent is catalyzed by a proprietary TS-1 zeolite arranged in fixed bed. The technical TS-1 catalyst we developed is shown on the Figure 2. The electron microscopic and atomistic model enlargements illustrate how educt molecules and solvent fit into the zeolite cavities of the lattice. Hydroperoxotitanium stabilized by Methanol is assumed to do the catalytic epoxidation job with Propylene giving Propylene Oxide and water.

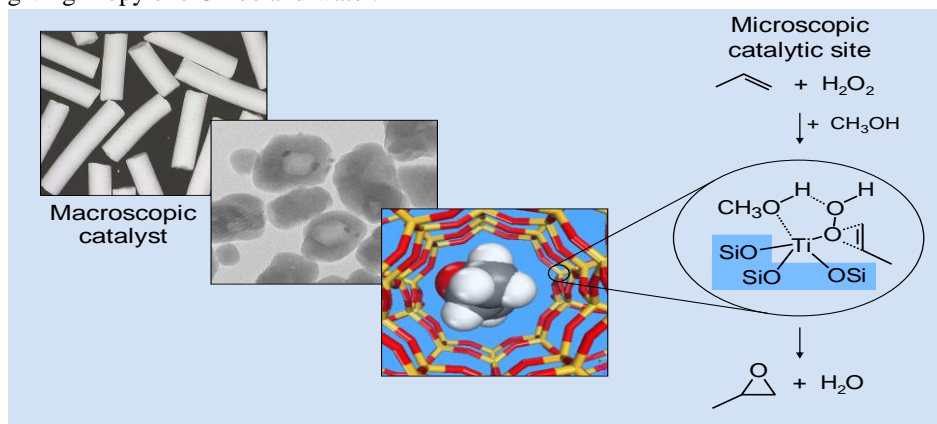


Figure 2: Proprietary TS-1 Ti-zeolite catalyst – HPPO epoxidation mechanism

Transforming this simple epoxidation reaction mechanism to a technical reactor needs detailed looks and studies of possible parallel and consecutive reactions in the reaction mixture. Essential details of the experimental HPPO reaction scheme studies are summarize in Figure 3. PO production rate and its yield are maximized, if consecutive reactions with water, Methanol and Hydrogenperoxide can be limited and parallel HP decomposition to Oxygen and water is mostly avoided.

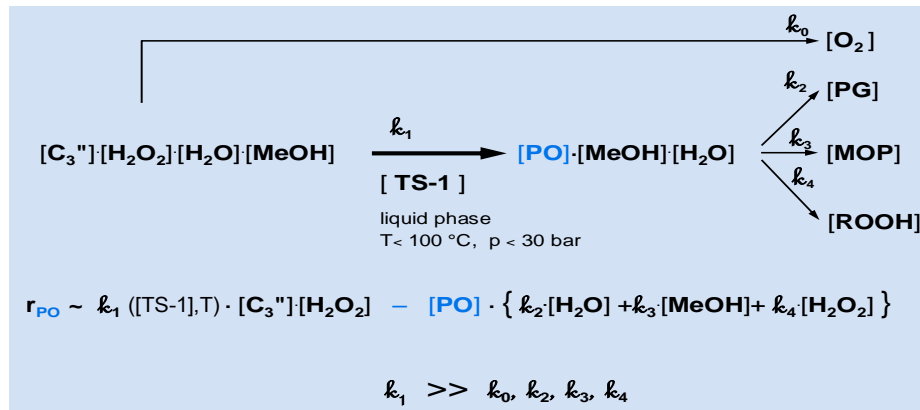


Figure 3: HPPO reaction scheme details

The differences in temperature dependent rate constants in our system help to achieve this target. If high conversion of HP for example is wanted, increasing HP conversion gives increased PO concentration which reduces PO selectivity by increased consecutive byproduct formation.

Measured PO selectivity – HP conversion data of our reaction system confirms this kinetic based relation in the picture using enlarged scales for illustration (Figure 4).

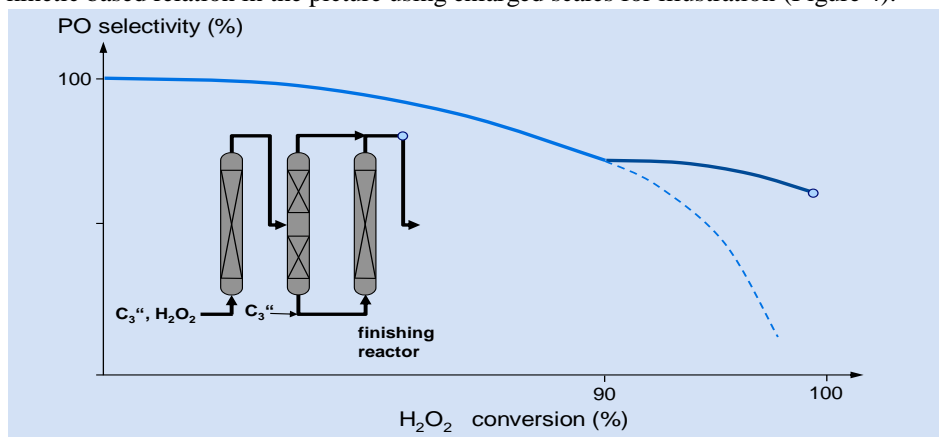


Figure 4: Reactor concept for  $H_2O_2$  conversion and PO selectivity

To reach high HP conversions at high PO selectivity in a production process without violating kinetic laws, we select a 2 step reactor concept with a design point of about 90

% HP conversion in the first step at below 90 °C and 30 bar in liquid phase using Methanol as solvent. In a following separation step produced PO is removed from the reaction mixture by distillation. After feeding additional olefin, final HP conversion realized in a finishing reactor is above 99 %. With optimized process parameters and TS-1 catalyst, total PO selectivity can exceed 94 %.

#### 4. Joint HPPO Process Development With Examples

As mentioned several companies worked on HPPO process developments last years. DOW chemical approached in a parallel development similar process targets as BASF did. DOW based on Enichem's TS-1 catalyst in suspension.

After comprehensive technology, development, potentials and risk benchmarks between both companies we decided in 2003 to combine both of our development efforts in the final process development phase and focus on a joint HPPO process combining best of each company's process contributions in every step for further on joined world scale realizations.

Some of the best process contribution examples are shown for the reactor feed ratios finally optimized together in the joint development and design phase: Optimal MeOH / Propylene / H<sub>2</sub>O<sub>2</sub> ratios are studied for reliable and safe single liquid phase epoxidation operation due to kinetic and economic reasons (Figure 5).

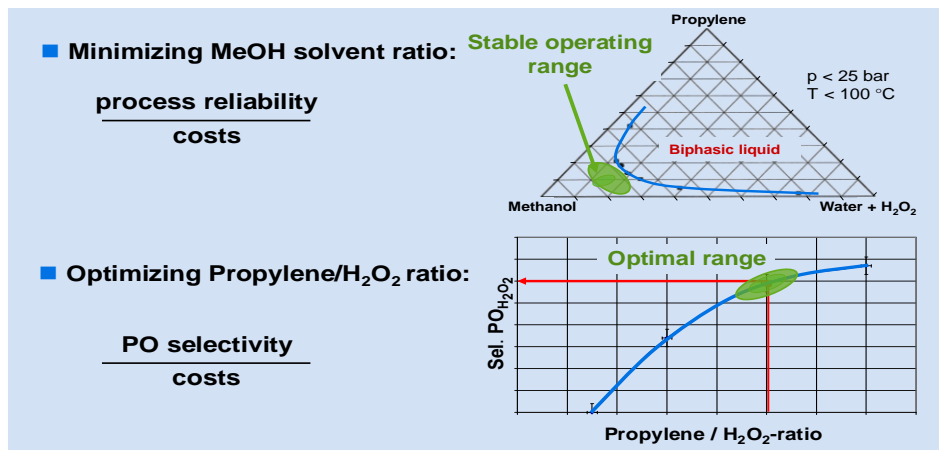


Figure 5: Reaction optimisation in pilot plant

Minimal Methanol solvent concentration is wanted to avoid educt concentration dilution and liquid phase separation between hydrophobic propylene and aqueous Hydrogen peroxide. Sufficient propylene surplus at each conversion level is needed to avoid reaction rate decreases at reasonable process effort and hold high PO selectivity without blowing up recycle loops and its costs.

We remember our mentioned two step reactor concept and the outcomes of joint optimized feed ratios in the reaction section as core part of the process scheme (Figure 6) and complete it now.

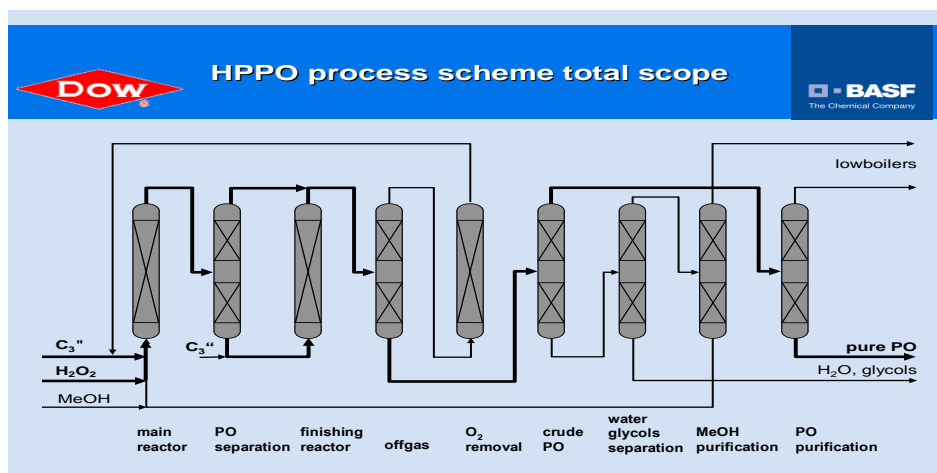


Figure 6: HPPO process scheme total scope

Around reaction and reactors, total HPPO process scope also has to take care of discussed Propylene surplus, solvent recycle and product purification for a technical realization. The small Propylene surplus off-gas stream is recycled to the main reactor after removal of Oxygen traces – for safety reasons. Hydrogen peroxide is converted completely and the propylene conversion in the process is nearly quantitative. The crude PO product from each reaction step is purified by distillation. The Methanol is recycled. The final water stream is tested for traces of glycols and Methoxipropanols prior to being discharged to the wastewater treatment unit.

Our final HPPO process by combining best process contributions examples shown stands for high raw material conversions and high selectivity to PO. Compared to established PO processes using organic hydro peroxides for epoxidation, the overall propylene excess required for HPPO is significant below 50 %. Material integration for the HPPO process is simple – hydrogen peroxide and propylene are the only raw materials. Polymer grade or chemical grade Propylene fulfil the process needs. HP concentration and quality needs are reached with the HP product out of the extraction steps of commercial Antraquinone working solution processes. There is no need for additional infrastructure or markets for co-products.

HPPO has significant environmental benefits versus the conventional processes:

- wastewater is reduced by up to 80%.
- Energy use is reduced by 35%.
- The simple raw material integration and avoidance of co-products reduces the infrastructure and physical footprint of the plant significantly.

The HPPO jv plant in Antwerp started operation last quarter of 2008 very smoothly representing the first successful commercial world scale application of this novel technology with 300 kt/a PO capacity. Project venture partner beside BASF and DOW for HP supply on Antwerp is Solvay S.A. with a new world scale 230 kt/a HP plant.

Investigation and construction of additional HPPO plants also with project partners in Middle East, and Asia are ongoing. A large number of patent applications have been filed globally for this process by BASF and DOW.

## 5. Conclusions

The joint developed HPPO process and its first successful implementation in Antwerp is an innovative and environmentally-benign step to PO production with smaller footprints. Public recognition like IChemE award 2009 (Chemeurope, 2010), the Kirkpatrick honor award 2009 (Chemdigital, 2010) and US EPA's Presidential Green Chemistry Challenge Award 2010 ad-hoc confirmed our HPPO jointly developed technology in Europe and in the US.

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