The Shell Higher Olefins Process (SHOP)

The SHOP is a process for the production of olefins C12-C18 via ethylene oligomerization and metathesis. It is made by 3 steps:
1) Oligomerization of ethylene
2) Isomerization of C4-C10 and >C20
3) Metathesis

The scheme of the process is shown below.
Oligomerization of Ethylene

Large-scale industrial process incorporating olefin metathesis for producing linear higher olefins from ethene:

\[
n \text{CH}_2\text{=CH}_2 \xrightarrow{\text{nickel catalyst}} H-\text{(CH}_2\text{=CH}_2)_{n-1}\text{=CH}_2 \quad n = 2 - 38
\]

Catalyst prepared in situ from NiCl\(_2\), Ph\(_2\)PCH\(_2\)COOH, and a reducing agent (NaBH\(_4\)). Three stages:

1. Ethene is oligomerized in the presence of the homogeneous nickel catalyst (at 90 – 100°C and 100 – 110 bar) in a polar solvent (1,4-butanediol) to give a mixture of linear, even-numbered α-olefins (C\(_4\) – C\(_{40}\)) with a Flory-Schultz distribution (immiscible with the catalyst solution):
Oligomerization Mechanism

Generally accepted mechanism: Olefin insertion into a Ni–H bond.

Initiation Step:


Catalytic Cycle
Further Treatment of the C$_{2n}$–Olefins

2. Double bond isomerization over a solid potassium metal catalyst to give an equilibrium mixture of internal alkenes. This step is needed to increase the statistical distribution of the desired C10-C14 fraction:

3. Metathesis step: The isomer mixture is passed over an alumina-supported molybdate catalyst. The cross metathesis gives a mixture of linear internal alkenes with both odd and even numbers of carbon atoms:

$$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH(\text{CH}_2)_9CH}_3 \leftrightarrow \text{CH}_3\text{CH}=\text{CH(\text{CH}_2)_7CH}_3 + \text{CH}_3\text{CH}=\text{CH(\text{CH}_2)_9CH}_3$$

This yields about 10 – 15 wt.% of the desired C$_{11}$ – C$_{14}$ linear internal alkenes per pass, which are the separated by distillation and converted into detergent alcohols (via a hydroformylation process) or into detergent alkylates (see next slide).
Einige Beispiele von verschiedenen Typen von Tensiden

**Aniontenside:**

Carboxylate (Seifen)
\[ R = C_{10} \cdot C_{16} \]

Alkylbenzolsulfonate
\[ R = C_{10} \cdot C_{13} \]

Alkansulfonate
\[ R^1 + R^2 = C_{11} \cdot C_{17} \]

Fettalkoholsulfate
\[ R = C_{11} \cdot C_{17} \]

Ethersulfate
\[ R^1 + R^2 = C_{11} \cdot C_{13} \]
\[ n = 1 \cdot 4 \]

\[ \alpha\text{-Olefinsulfonate} \]
\[ m + n = 9 \cdot 15 \]

**Amphotere Tenside:**

Alkylbetainen
\[ R = C_{12} \cdot C_{18} \]

\[ [N^+R(CH_3)_2(CH_2COO^-)] \]

**Nichtionische Tenside:**

Alkylphenolethoxylate
\[ R = C_8 \cdot C_{12} \]
\[ n = 5 \cdot 10 \]

Alkoholethoxylate
\[ R^1 = C_6 \cdot C_{16}; R^2 = H, C_1, C_2 \]
\[ n = 5 \cdot 10 \]

EO-PO-Blockpolymere
\[ \text{HO-(CH}_2\text{-CH}_2\text{-O)}_m\text{-(CH}_3\text{-CH}_2\text{-O)}_n\text-H} \]
\[ m = 2 \cdot 60; n = 15 \cdot 80 \]

**Kationtenside:**

Quaternäre Ammoniumsalze
\[ R^1, R^2 = C_{16} \cdot C_{16}; R^3, R^4 = C_1 \]
\[ [NR^1R^2R^3R^4]^+Cl^- \]

Mischether
\[ R, R^1 = C_6 \cdot C_{18}; m, n = 3 \cdot 6 \]