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:

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

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 \(\alpha\)-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:


Further Treatment of the C\textsubscript{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 C\textsubscript{10}–C\textsubscript{14} fraction:

![Chemical structure](image)

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

\[
\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_9\text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 + \text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_9\text{CH}_3
\]

This yields about 10 – 15 wt.% of the desired C\textsubscript{11} – C\textsubscript{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)
\[
\text{R} = \text{C}_{10} - \text{C}_{16}
\]

Alkylbenzolsulfonate
\[
\text{R} = \text{C}_{10} - \text{C}_{13}
\]

Alkansulfonate
\[
\text{R}^1 + \text{R}^2 = \text{C}_{11} - \text{C}_{17}
\]

Fettalkoholsulfate
\[
\text{R} = \text{C}_{11} - \text{C}_{17}
\]

Ethersulfate
\[
\text{R}^1 + \text{R}^2 = \text{C}_{11} - \text{C}_{13}
\]
\[
\text{n} = 1 - 4
\]

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

**Kationtenside:**

Quaternäre Ammoniumsalze
\[
\text{R}^1, \text{R}^2 = \text{C}_{16} - \text{C}_{16}; \text{R}^3, \text{R}^4 = \text{C}_{1}
\]

\[
[\text{NR}^1\text{R}^2\text{R}^3\text{R}^4]^+\text{Cl}^-
\]

**Amphotere Tenside:**

Alkylbetainen
\[
\text{R} = \text{C}_{12} - \text{C}_{18}
\]

\[
[\text{N}^+\text{R}(\text{CH}_3)_{2}(\text{CH}_2\text{COO})^-]
\]

**Nichtionische Tenside:**

Alkylphenolethoxylate
\[
\text{R} = \text{C}_{6} - \text{C}_{12}
\]
\[
\text{n} = 5 - 10
\]

Alkoholethoxylate
\[
\text{R}^1 = \text{C}_{6} - \text{C}_{16}; \text{R}^2 = \text{H}, \text{C}_{1}, \text{C}_{2}
\]
\[
\text{n} = 5 - 10
\]

EO-PO-Blockpolymere
\[
\text{m} = 2 - 60; \text{n} = 15 - 80
\]

Mischether
\[
\text{R}, \text{R}^1 = \text{C}_{6} - \text{C}_{16}; \text{m,n} = 3 - 6
\]

\[
[\text{RO}(\text{CH}_2\text{CH}_2\text{O})_{\text{m}}\text{H}]^+\text{Cl}^-
\]