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Benefits of new generation methanol synthesis catalyst in existing methanol plants

Madhan Janardhanan

Principal Process Engineer

Agenda

Methanol synthesis

Reactions

Methanol is mainly produced from CO_2 and H_2

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

$$\Delta H^o_{298K} = -49.5 \text{ kJ/mol}$$

CO is shifted to CO_2 and then to methanol

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$\Delta H^o_{298K} = -41.2 \text{ kJ/mol}$$

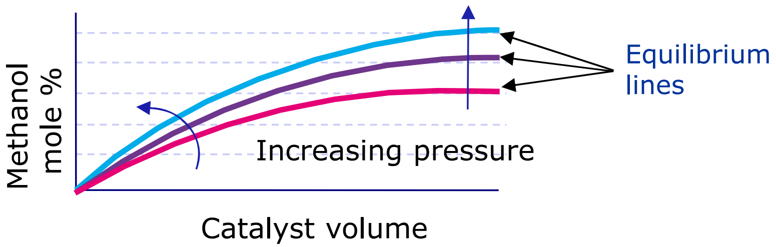
Some methanol is synthesised from CO and H_2

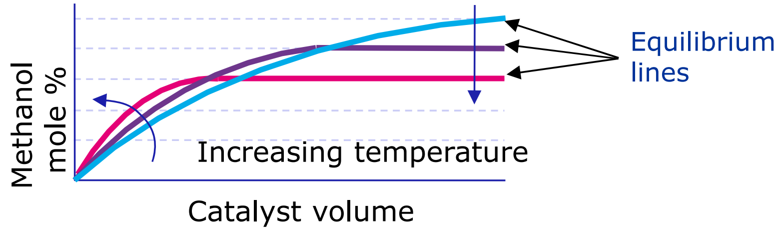
$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$\Delta H^o_{298K} = -90.6 \text{ kJ/mol}$$

Methanol synthesis

Kinetic and thermodynamic considerations





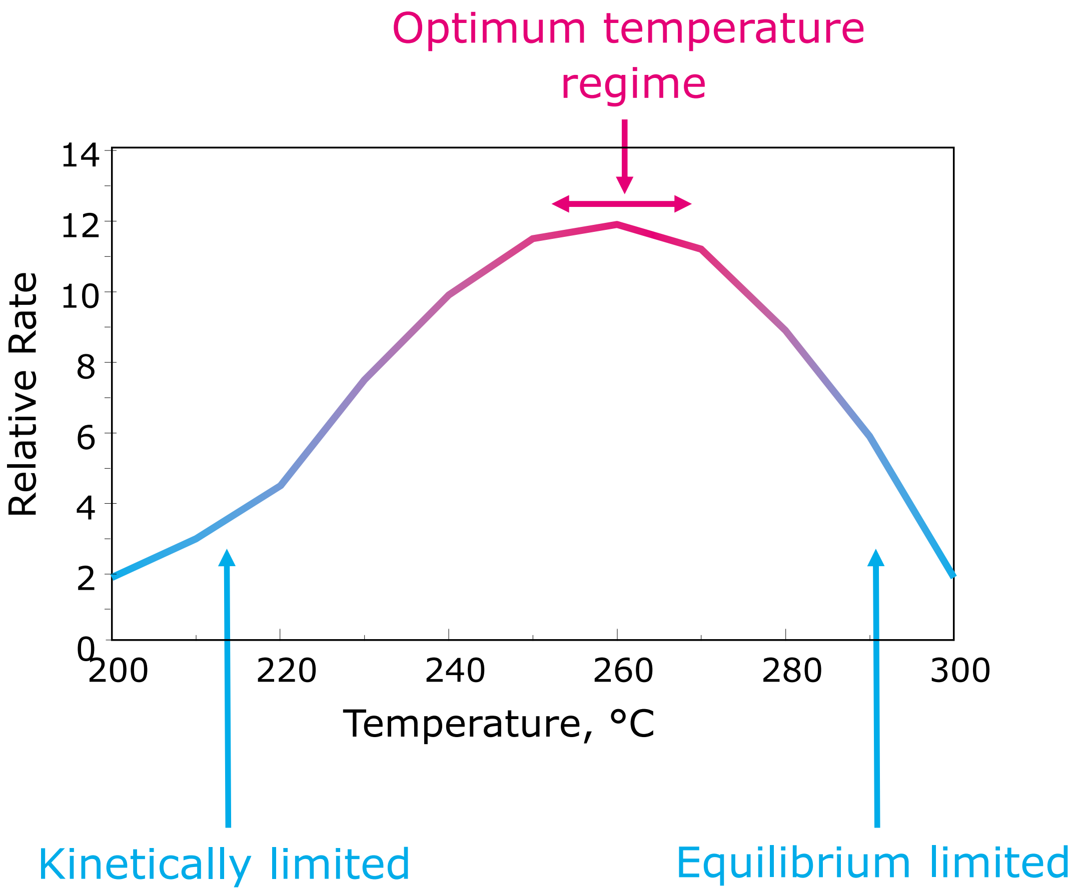
For good conversion what conditions are required?

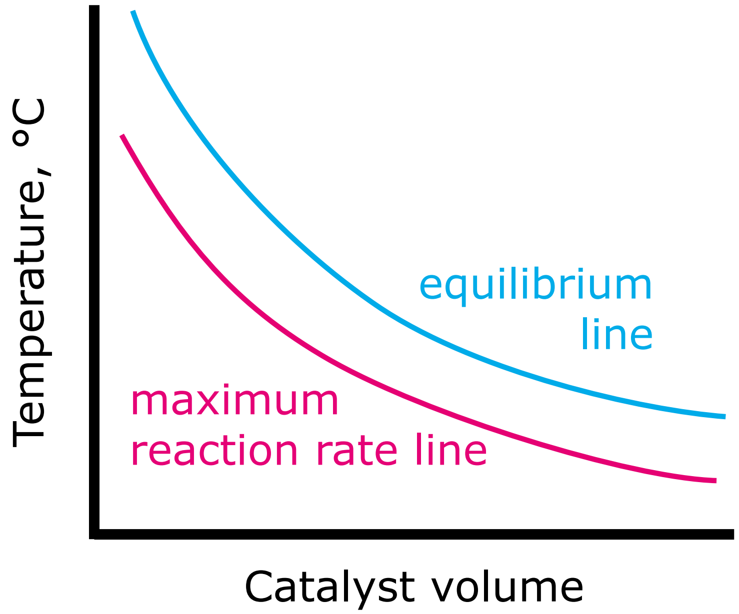
	Equilibrium	Kinetics
Temperature	Low	High
Pressure	High	High
Catalyst activity		High

So there is a conflict for temperature!

Methanol synthesis

Kinetic and equilibrium considerations - effect of temperature





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Catalyst deactivation

Thermal sintering

Causes for catalyst deactivation

- poisoning (sulphur, carbonyl & chloride)
- thermal sintering

Reaction rate is dependent on temperature

- hot loop gas increases the rate of reaction as well as sintering
- cool loop gas slows the rate of reaction as well as sintering
- thermal sintering of catalysts is inevitable

Impact of catalyst deactivation

- loss of production
- excess loop purge gas to fuel
- rate limiting in plants with combined reforming front end and low circulation methanol synthesis loop

Methanol synthesis loop designs

The methanol synthesis loop designs falls within one of the two categories listed below:

High circulation loops

will have a circulation ratio of about 6.

methanol concentration exiting the converter will be between 5 and 6 mole %

will contain one of the following converters

- advanced reactor concept (ARC)
- **radial steam raising converter (rSRC)**
- **tube cooled converter (TCC)**
- isothermal methanol converter (IMC), both steam raising and gas cooled
- variobar

Low circulation loops

will have a circulation ratio of about 2.

methanol concentration exiting the converter will be between 10 and 12 mole %

will contain one of the following converters

- **axial steam raising converter (aSRC)** or
- gas cooled converter (GCC) installed in tandem with aSRC

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Examples

Basis

Syngas generation	SMR + CO2 injection		Combined reforming	
Makeup syngas composition	Inerts	3.2 mol%	Inerts	1.6 mol%
	CO_2	9.5 mol%	CO_2	8.1 mol%
	CO	18.7 mol%	CO	22.0 mol%
	H_2	68.6 mol%	H_2	68.3 mol%
Circulation ratio	≈ 6		≈ 2	
Converter type	radial steam rising converter (rSRC)		a gas cooled converter (GCC) installed in tandem with axial steam rising converter aSRC	

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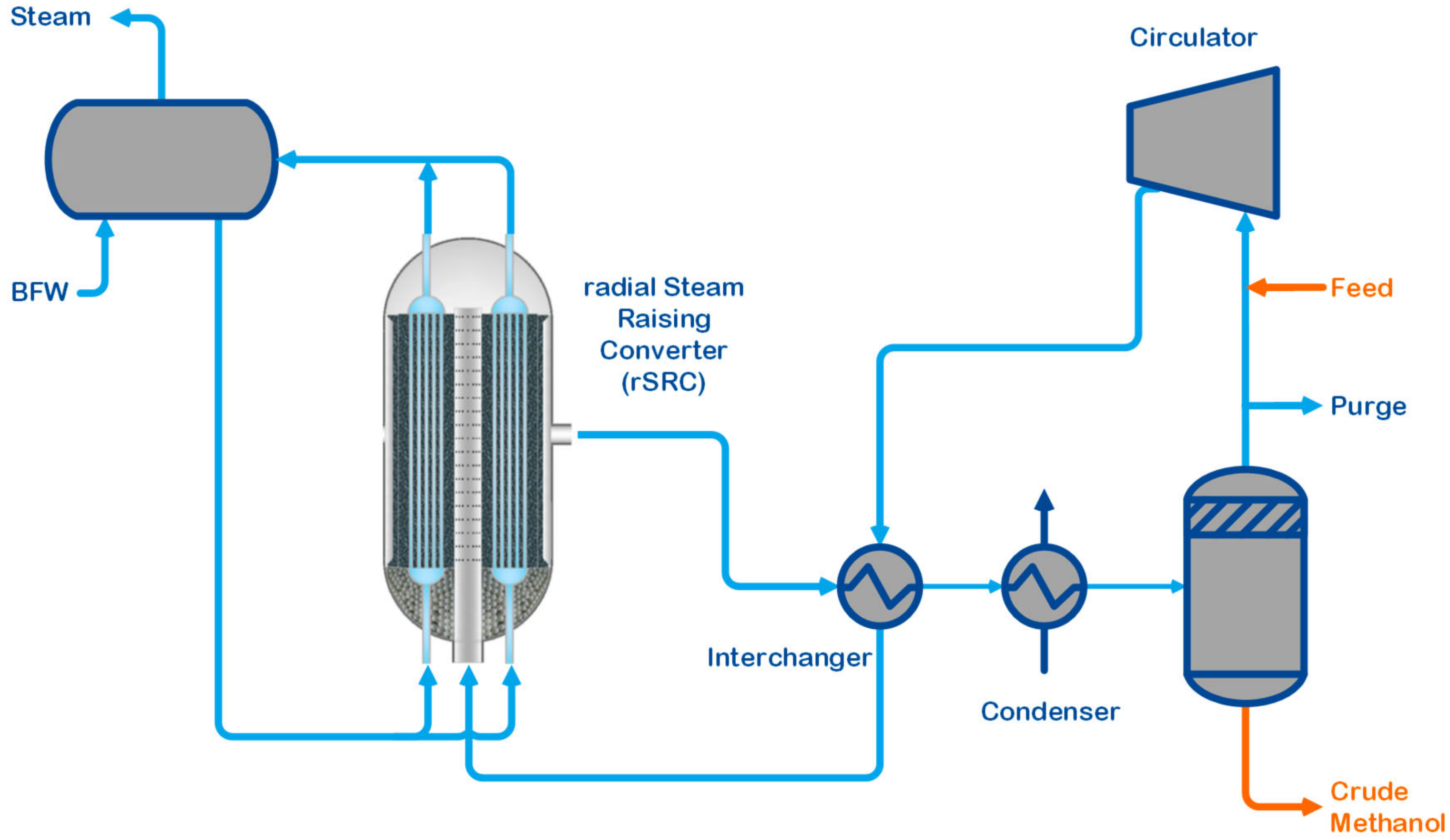
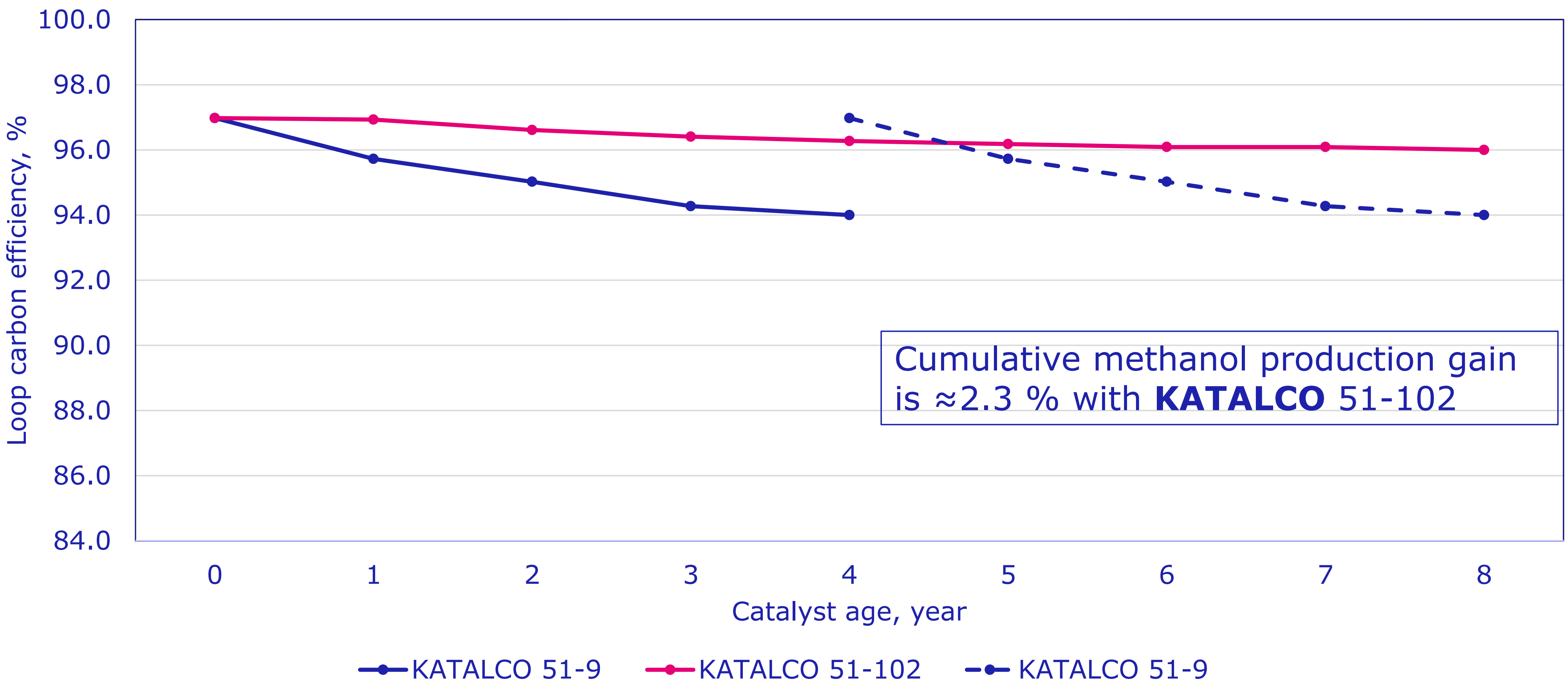
JM licensed high circulation loop with radial steam raising converter



High circulation loop

Loop carbon efficiency



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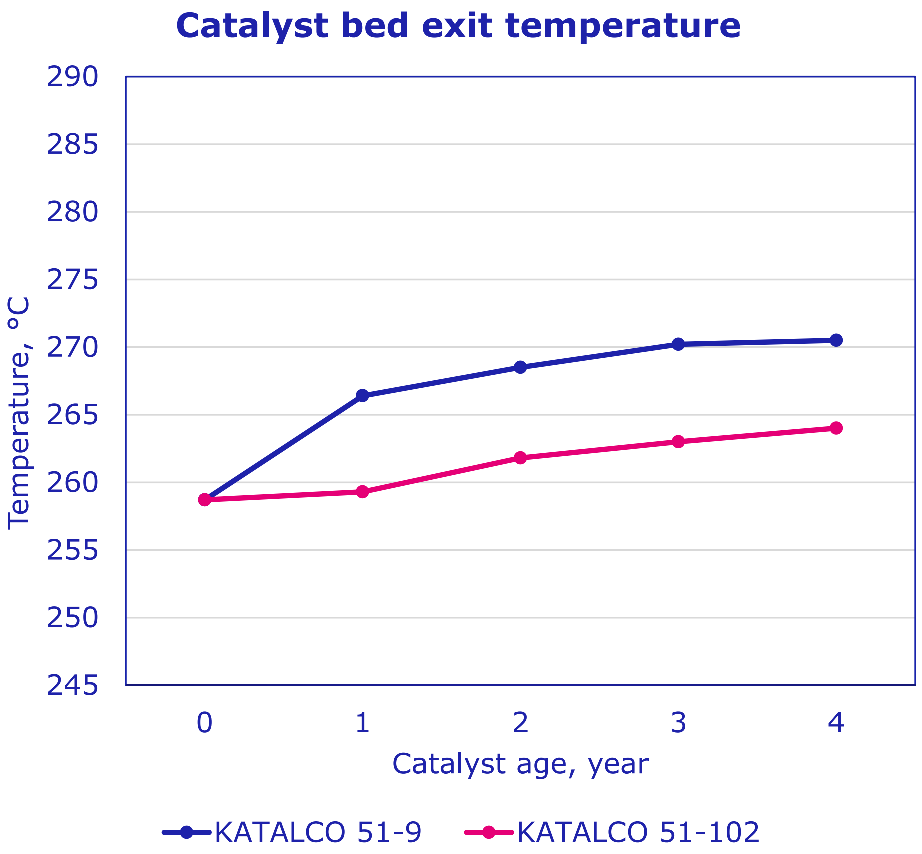
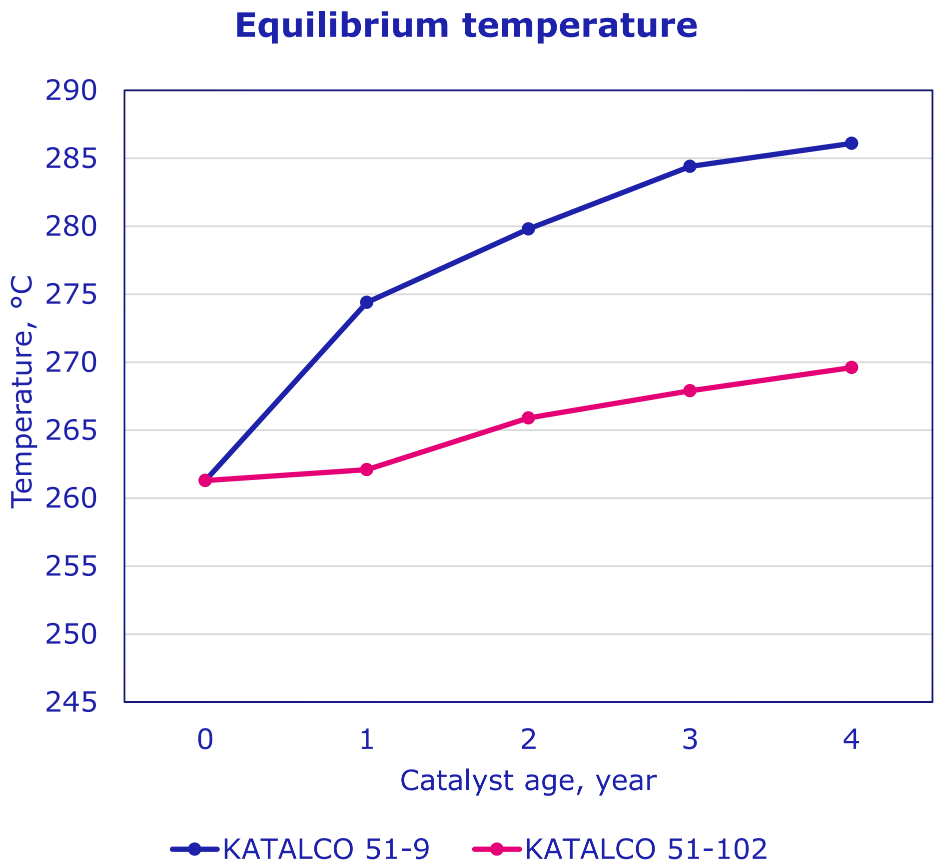
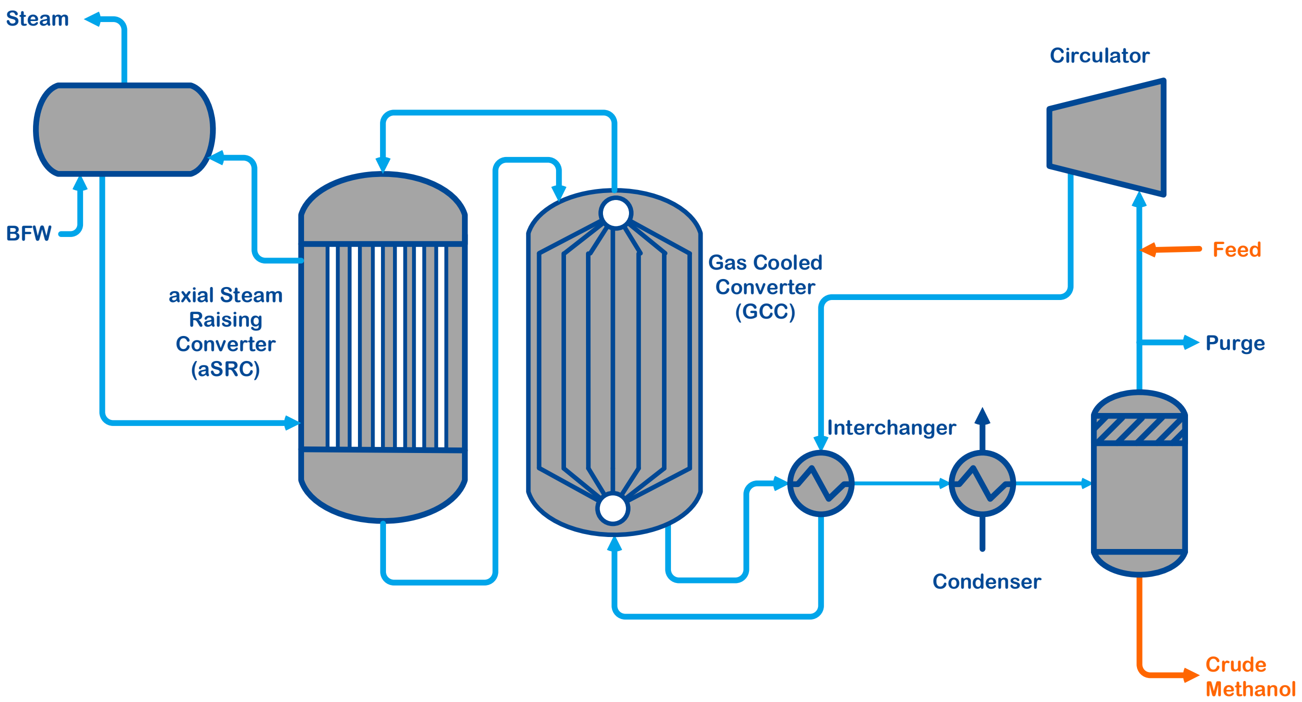
High circulation loop





Low circulation loop with axial steam raising converter (aSRC) and gas cooled converter (GCC)



At **BOL** the **aSRC** is doing more work

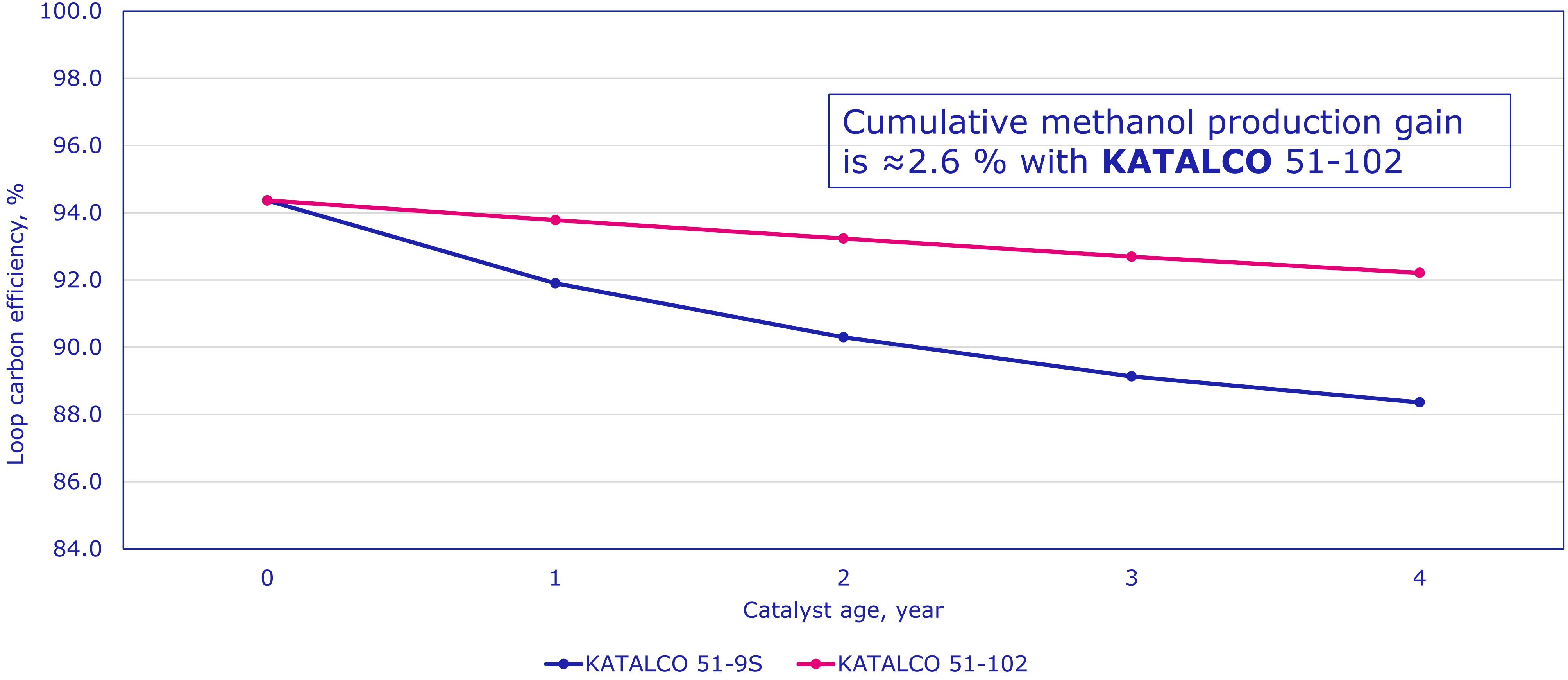
- High peak temperature
- Catalyst activity falls quickly

At **EOL** the **GCC** is doing more work

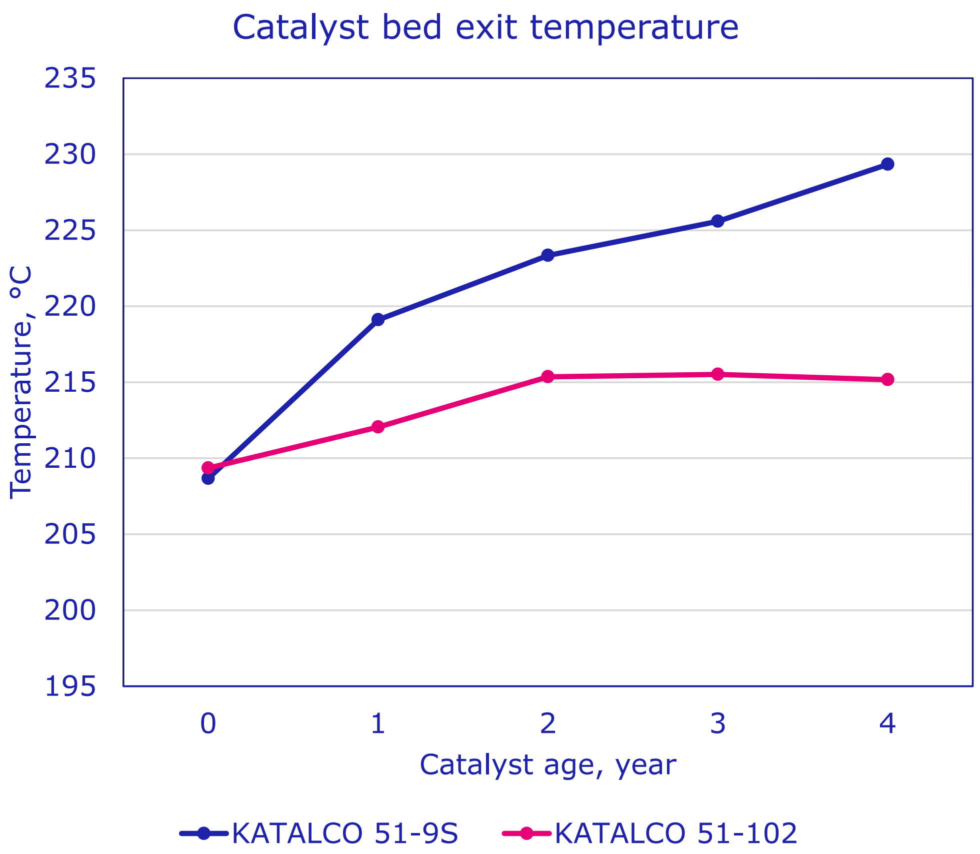
- High exit temperature
- High equilibrium temperature

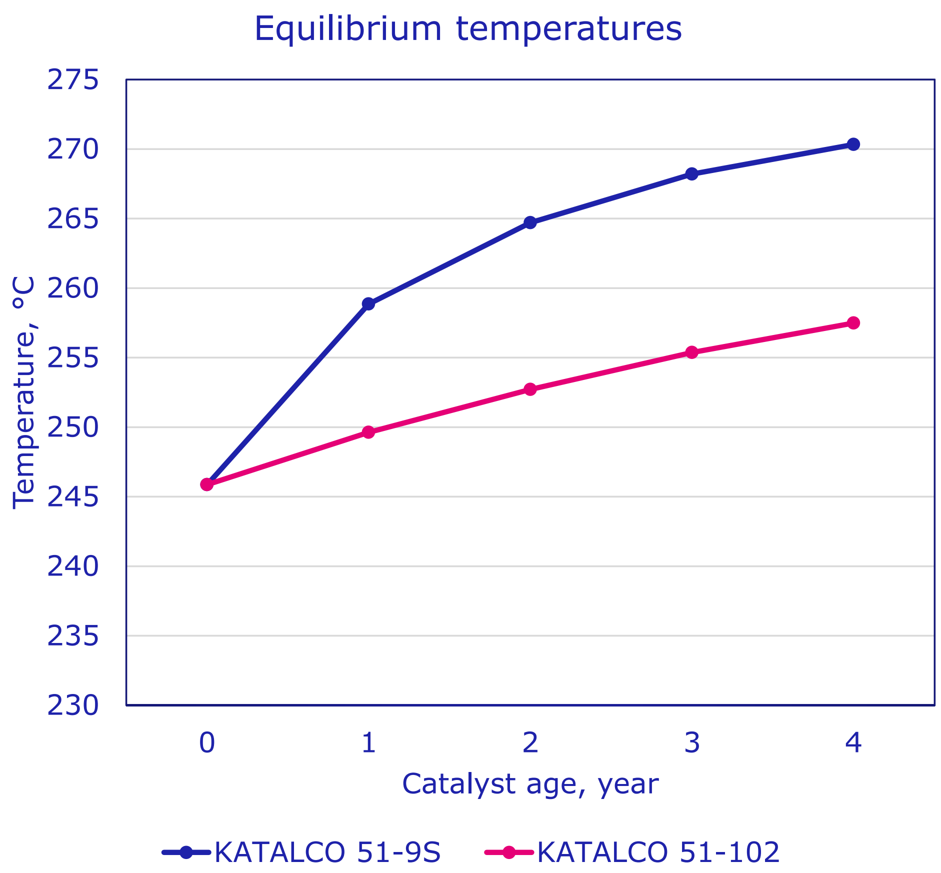
Low circulation loop

Loop carbon efficiency



Low circulation loop





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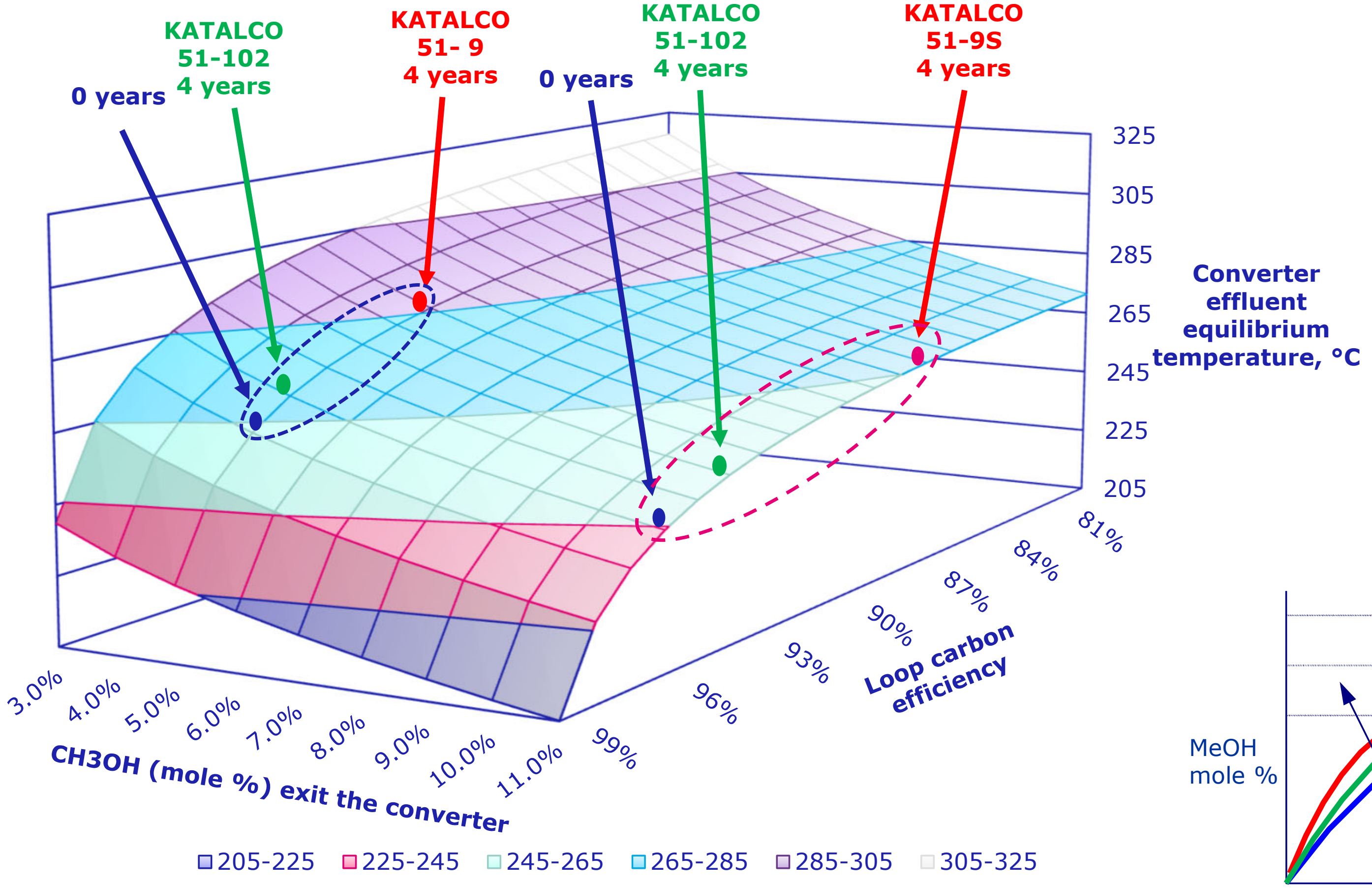
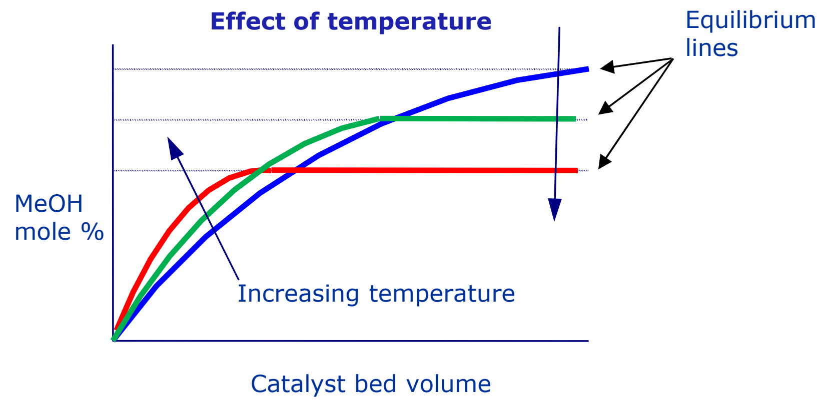
Methanol equilibrium vs loop efficiency and methanol exit the converter

3D surface graph representation



- At 5% MeOH exit the converter 1% efficiency loss for a 6 °C temperature rise.
- At 11% MeOH exit the converter 1% efficiency loss for a 3 °C temperature rise



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Conclusion

- JM has allowed customers to **increase production** and/or **extend catalyst lives** by slowing the rate of sintering in its new **KATALCO 51-102** catalyst
- The slow deactivation of **KATALCO 51-102** allows the catalyst bed to operate at consistently lower temperatures, which maintains good equilibrium conversion at favourable reaction rate
- The low equilibrium temperatures helps to
  - Keep the carbon efficiency high in low circulation loops so the **fuel balance is closed for longer without flaring**, allowing for at least 4 year catalyst change over cycles
  - Maintain the high loop carbon efficiency for longer, achieving **8 years catalyst life**, which maximises methanol production in high circulation loops
- Consistent low temperature operation will also reduce the formation of by-products.

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