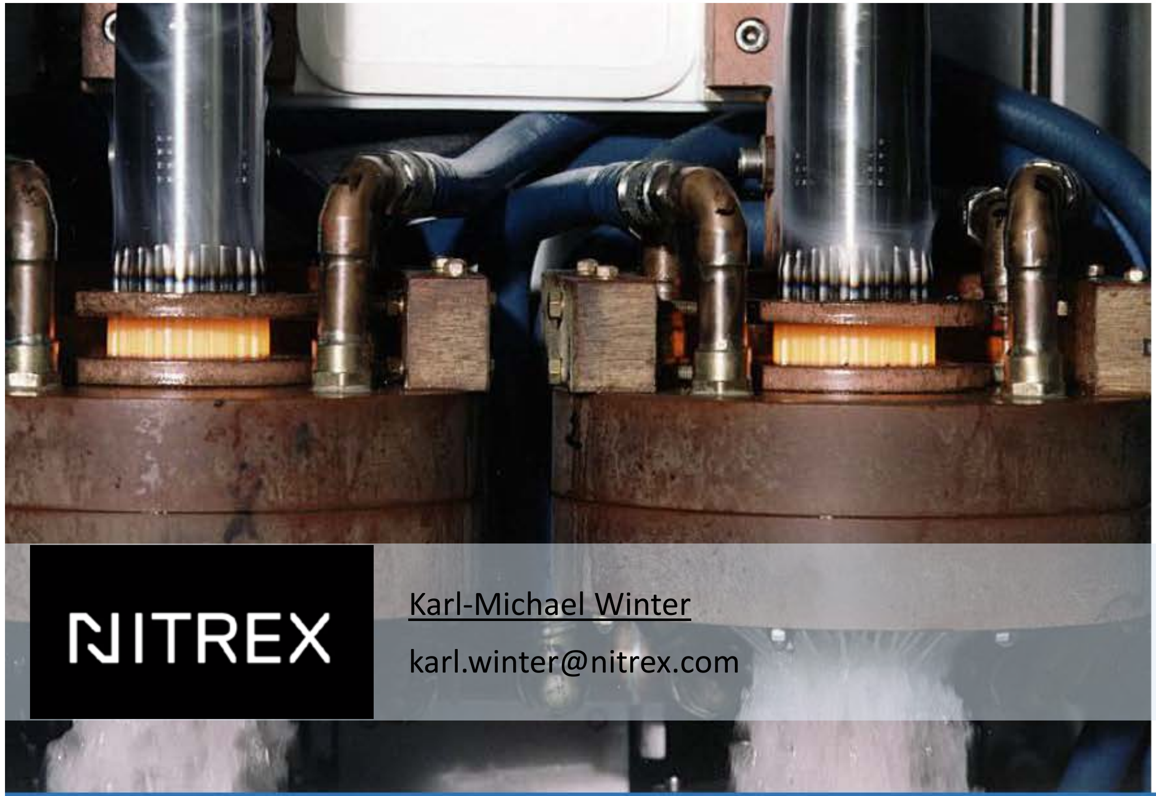
Variable CO content in heat treatments

Cutting cost –
reducing carbon footprint



NITREX

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Värmebehandlingskonferensen, 4 – 5 maj 2022 på Aronsborg Konferens i Bålsta

Making our world more productive

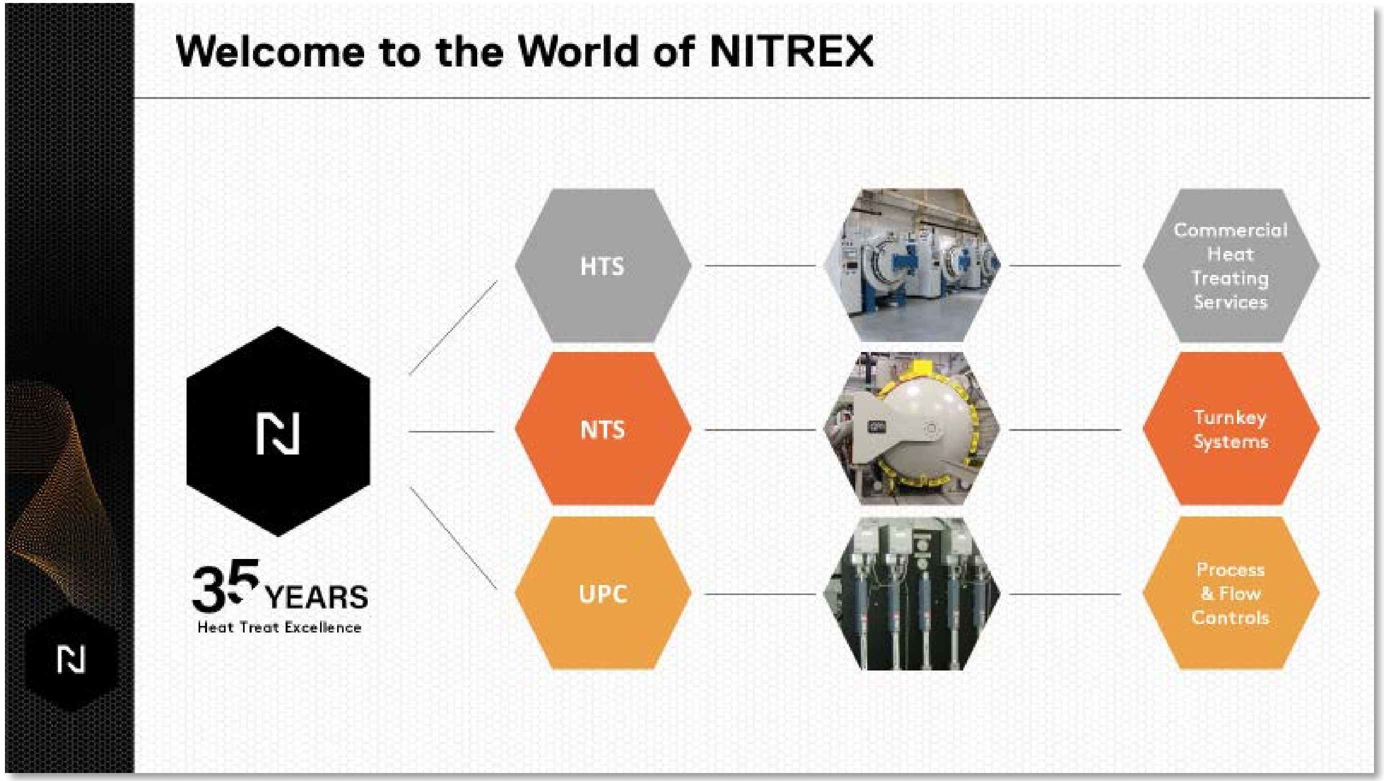
Michael Graf

Joined Linde in 1998.

Since 2006 focusing on heat treatment applications in several functions (R&D and application sales).

Current position (2022):
Global Commercialization Manager
Heat Treatment & Additive Manufacturing

Karl-Michael Winter



Joined Process-Electronic GmbH, now United Process Controls, in 1989. Starting off in software and controls development, he later served as managing director in Germany and France.

In 2019, he took on the position of VP Global Engineering and R&D for the entire Nitrex Group.

He is an active member of the AWT, the German Society for Heat-Treating and Materials.

Agenda

- Motivation
- Nitrogen-Methanol Systems
- Cutting Cost Examples
- Summary
- Q & A

Motivation

- Technical
  - Adjusting oxidation throughout a process enhances products and furnace lifetime
  - About 50% of IGO is created at the very beginning of the process
  - Adjusting carbon transfer throughout carburizing will shorten the cycle and save methanol
  - Reducing carbon transfer allows for easy neutral processes

- Ecological
  - In the next years heat treaters will have to quantify but also reduce their carbon footprint
  - Soon, natural gas pipelines will also be used to transport green hydrogen and biogas to consumers. This will impact endogas generators and disqualify natural gas for enrichment

- Economical
  - Shorten process time and reducing process gas cost will increase efficiency

- Political
  - Russian natural gas will eventually be banned

Agenda

✓ Motivation

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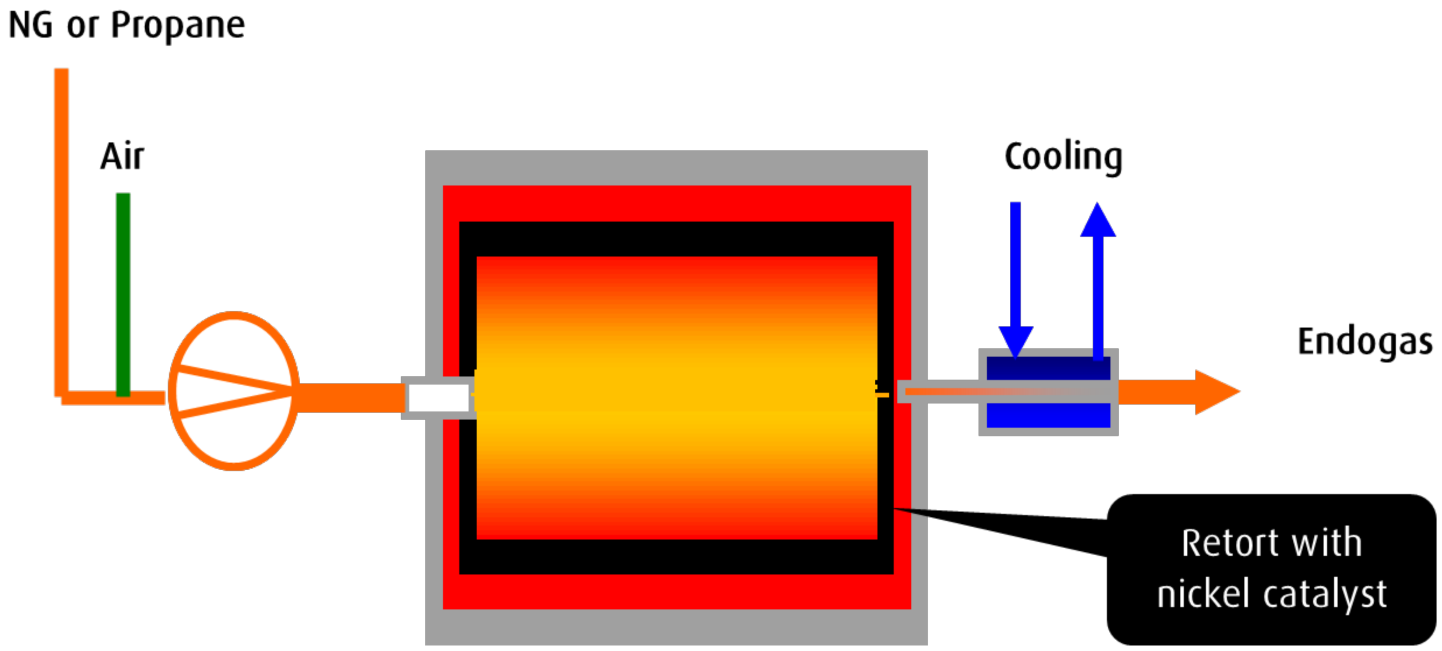
N_2 – CH_3OH Technology

	In-situ atmospheres									Generator solutions					Vacuum
Process	N_2/H_2, % H_2			N_2/CH_3OH		$N_2/NH_3/CO_2$			Ar/He	Exo	Mono	Endo		Cracked NH_3	
	<10	10-99	100		$+NH_3$	N_2/NH_3	$N_2/NH_3/CO_2$	N_2O or H_2O add.					$+NH_3$		
Steel Annealing	Usable			Optimal						Usable	Optimal				
Stainless Annealing		Usable	Optimal						Usable					Optimal	Optimal
Carburizing				Optimal								Optimal			
Carbo-nitriding					Optimal								Optimal		
Nitriding						Optimal									
Nitrocarb.							Optimal	Optimal					Optimal		

Optimal atmosphere — Usable atmosphere

N_2 – CH_3OH Technology



Propane: C_3H_8 + 7.2 parts air → 3CO + $4H_2$ + $5.7N_2$

NG (Methane): CH_4 + 2.4 parts air → CO +$2H_2$ + $1.9N_2$

N_2 – CH_3OH Technology

Endogas (Natural Gas + Air)

$CH_4 + ½\,O_2 + 2N_2 \rightleftarrows CO + 2H_2 + 2N_2$

1m³ CH_4 → 5m³ Endogas

Endogas (Propane + Air)

$C_3H_8 + 3O_2 + 12N_2 \rightleftarrows 6CO + 8H_2 + 12N_2$

1m³ C_3H_8 → 13m³ Endogas

CARBOTHAN® (Methanol + Nitrogen)

$CH_3OH + 2N_2 \rightleftarrows CO + 2H_2 + 2N_2$

1l CH_3OH → 1.7m³ Cracked gas

Ideal case!

N_2 – CH_3OH Technology

Linde NITREX

Endogas (Natural Gas + Air)

$$CH_4 + ½\,O_2 + 2N_2 \rightleftharpoons 2N_2 + A\,H_2 + B\,CO + C\,CO_2 + D\,H_2O + E\,C + F\,CH_4 + \ldots$$

Endogas (Propane + Air)

$$C_3H_8 + 3O_2 + 12N_2 \rightleftharpoons 12N_2 + A\,H_2 + B\,CO + C\,CO_2 + D\,H_2O + E\,C + F\,CH_4 + \ldots$$

CARBOTHAN® (Methanol + Nitrogen)

$$CH_3OH + 2N_2 \rightleftharpoons 2N_2 + A\,H_2 + B\,CO + C\,CO_2 + D\,H_2O + E\,C + F\,CH_4 + \ldots$$

Real case!

N_2 – CH_3OH Technology

$CH_3OH \longrightarrow CO + 2H_2$

100% 33.3% + 66.7%

Reaction takes heat so this is also endothermic

Heat is usually supplied by the furnace

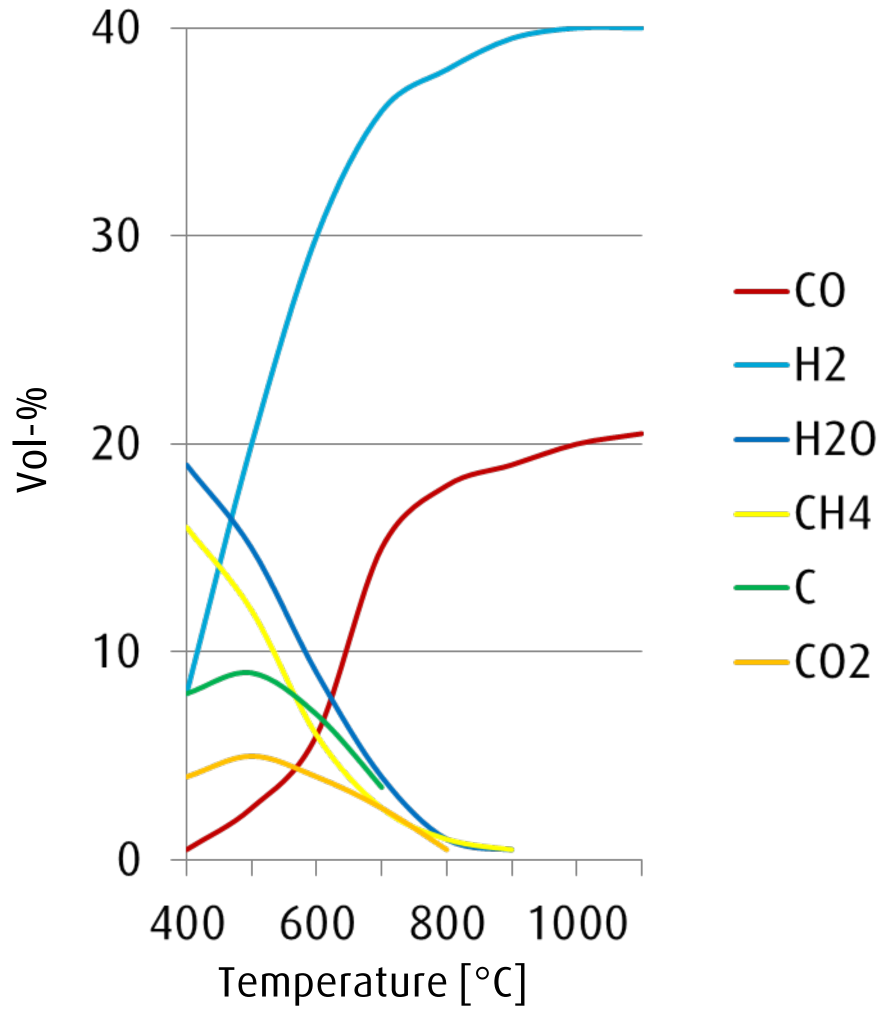
The methanol **cracks** on entering the furnace.

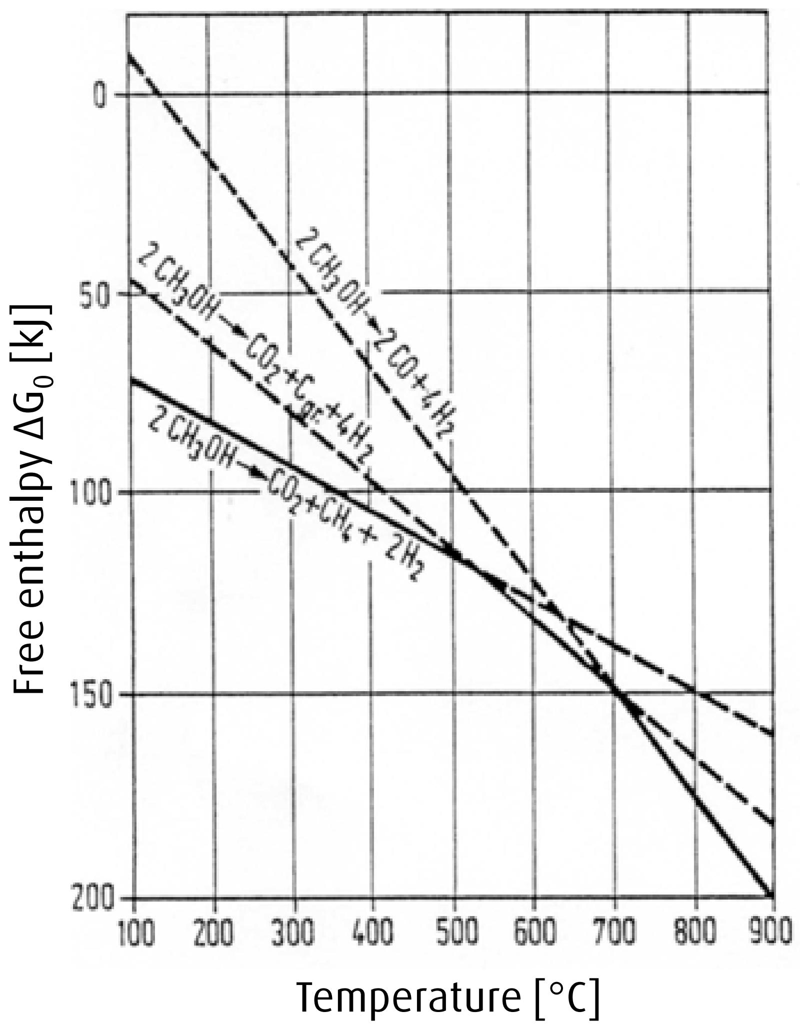
For every liters of methanol that is added, **1.67 m3 of gas** is formed.

Different gas compositions are obtained by **varying the mixing ratio** between nitrogen and methanol.

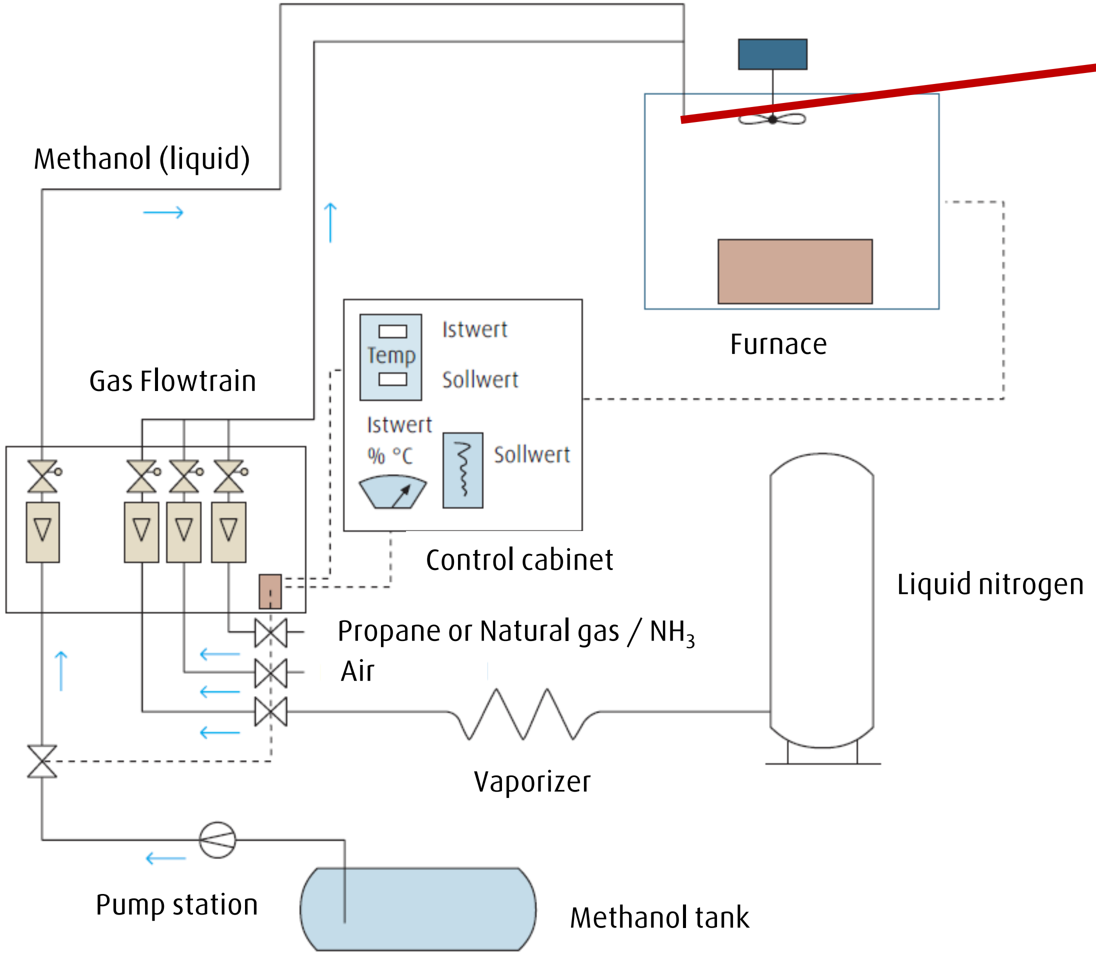
N_2	+	CH_3OH	→	CO	+	$2H_2$	+	N_2
40%	+	60%	→	20%	+	40%	+	40%
70%	+	30%	→	10%	+	20%	+	70%
85%	+	15%	→	5%	+	10%	+	85%

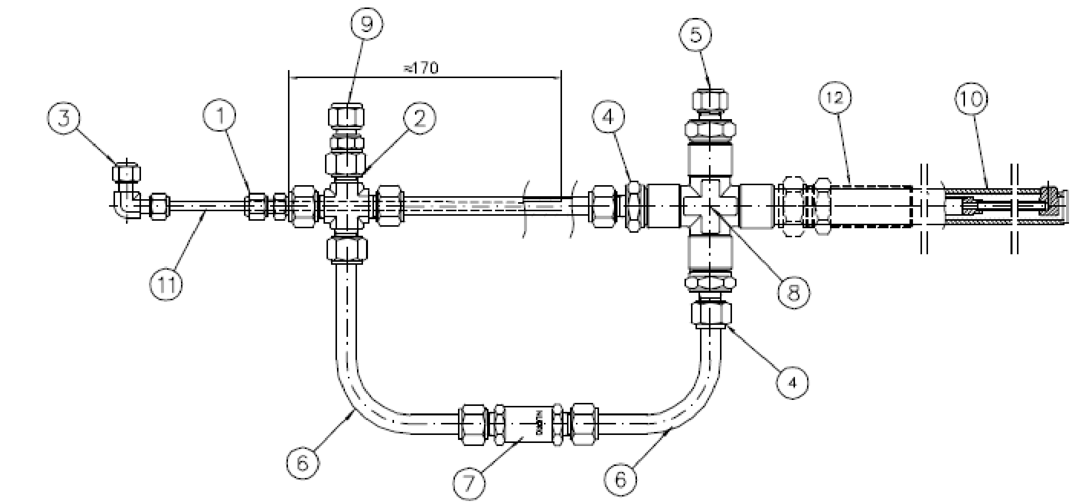
N_2 – CH_3OH Technology





N_2 – CH_3OH Technology





„AGA“ Version

Agenda

NITREX

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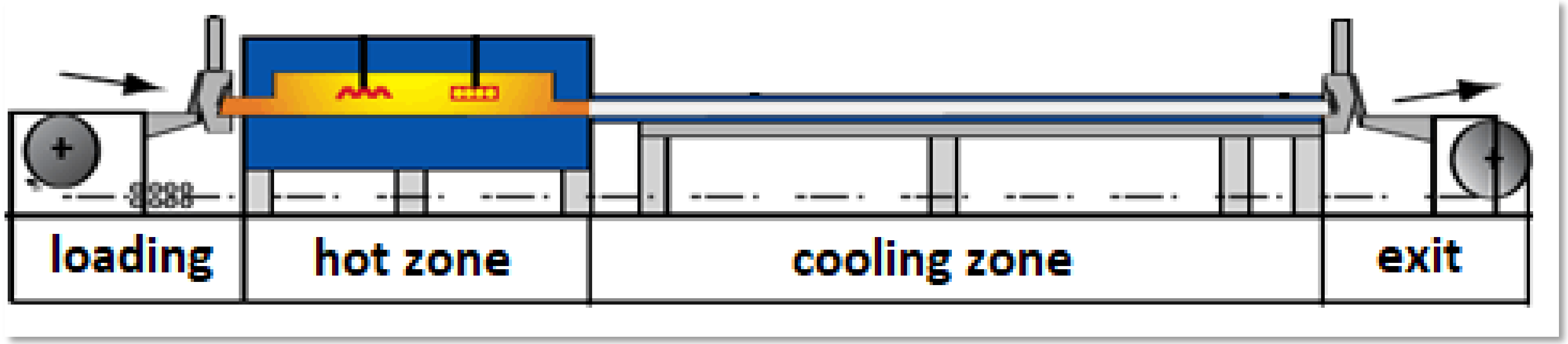
Cutting Cost Examples

Adjusting oxidation

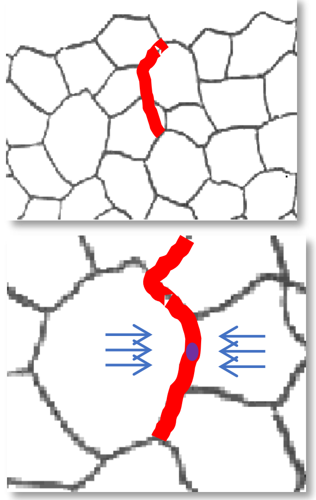
When treating parts at neutral carbon potential in an endogas atmosphere, also the belt material (e.g., 1.4841)will be exposed to degradation related to tension, oxidation, carburization and nitridation. Using Nitrogen-Hydrogen / Nitrogen-Hydrocarbon blends in the hot zone and re-oxidizing the belt in the cooling zone will increase belt material lifetime.

Thus, reducing the replacement costs (belt, labor, down time)



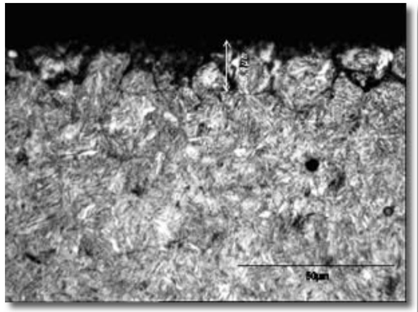
Cutting Cost Examples

Reducing IGO



- Steel has very little solubility for Oxygen (< 0.0002 wt-% @ 900°C)
- Diffusion will take place on grain boundaries.
- Oxygen on grain boundaries will attract alloys such as Chromium.
- Alloy oxides will settle between the grains.
- The grains no longer having the desired hardenability.

This results in an insufficient hardened surface layer of up to 100 microns, depending on the aimed for case depth.



Cutting Cost Examples

NITREX

Reducing IGO

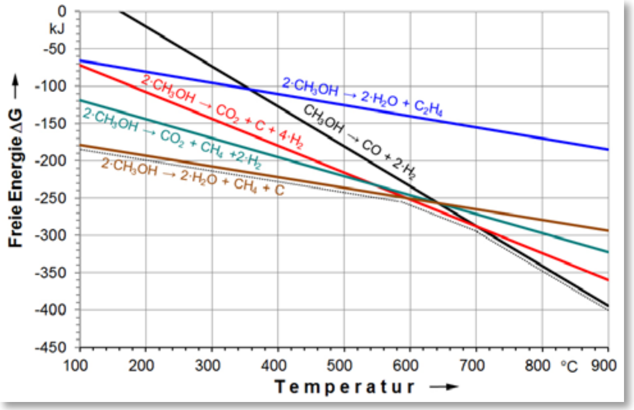
While heating the parts there are two effects:

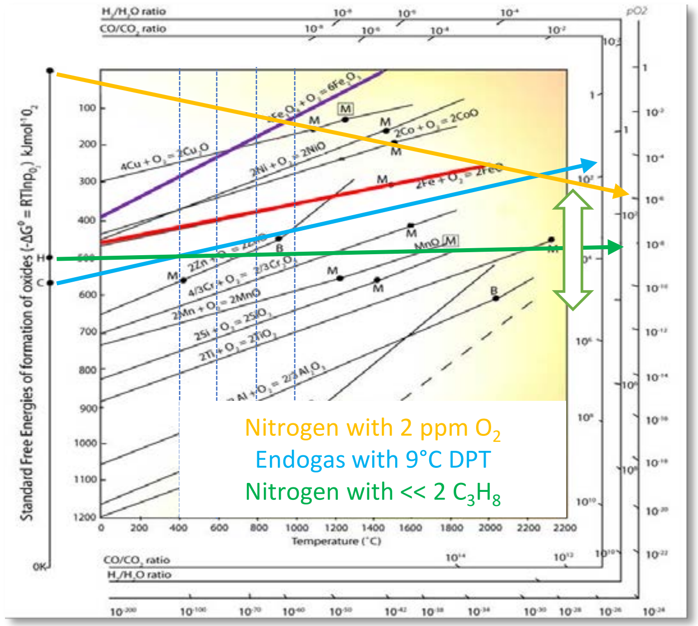
1) Below ~ 880°C a part of Methanol will crack into soot, carbon dioxide and water vapor.

2) Moreover, with the parts still being on a low temperature, the oxidation potential in the atmosphere is sufficient to form iron oxides.

Starting the process with Nitrogen blended with very little hydrocarbon before injecting methanol eliminates this effect.

Saving rejection cost



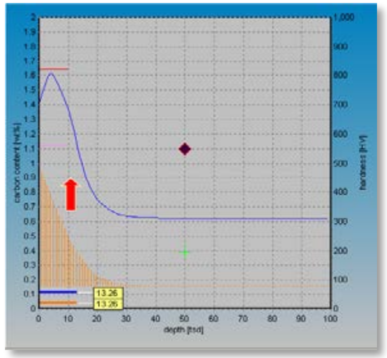


Ellingham-Diagram: © 2010 University of Cambridge, www.doitpoms.ac.uk

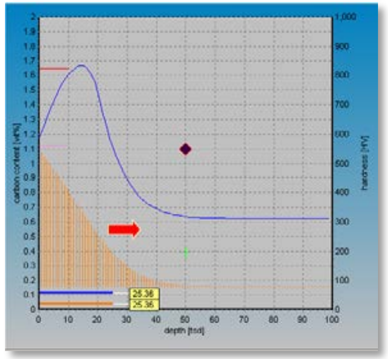
Cutting Cost Examples

Adjusting carbon transfer throughout carburizing

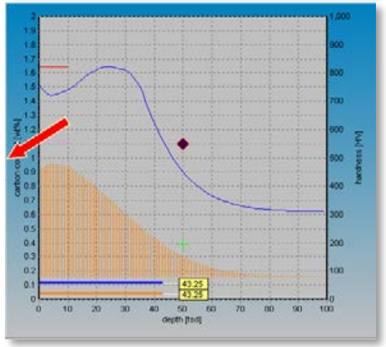
1) When starting the boost stage, the parts need to take up carbon as fast as possible to reach the maximum solubility before starting to create cementite in a short time



2) Once the surface is saturated, the carbon pickup will gradually slow down as the carbon flow is now limited by diffusion



3) Once we switch to the diffusion stage, the parts do no longer need carbon from the process atmosphere, on the contrary, carbon will effuse from the surface



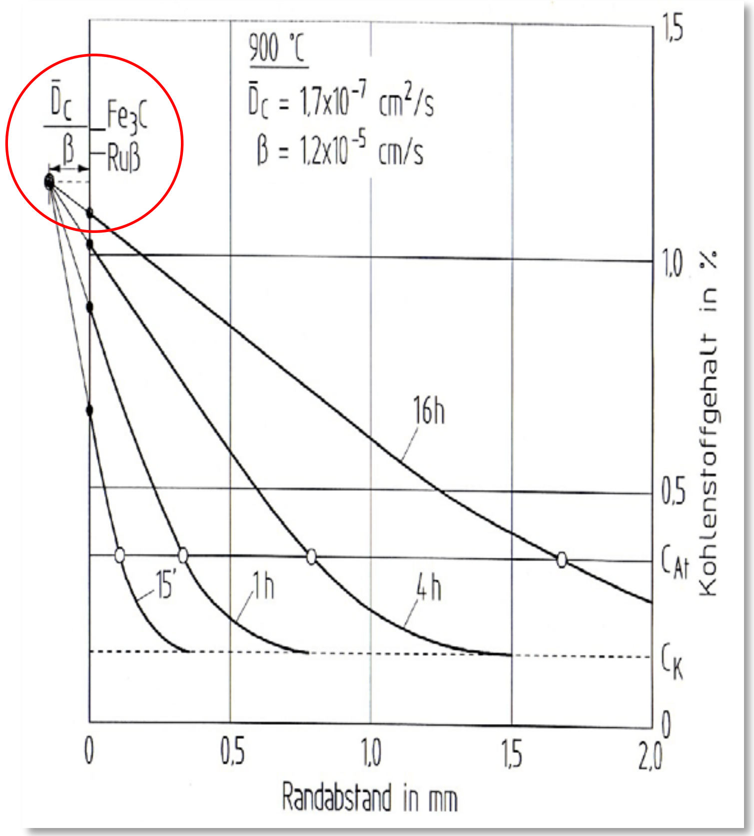
Cutting Cost Examples

Adjusting carbon transfer throughout carburizing

1) The uptake of carbon from atmosphere to surface is given by the temperature having the biggest impact on carbon diffusion and the so-called carbon transfer coefficient β

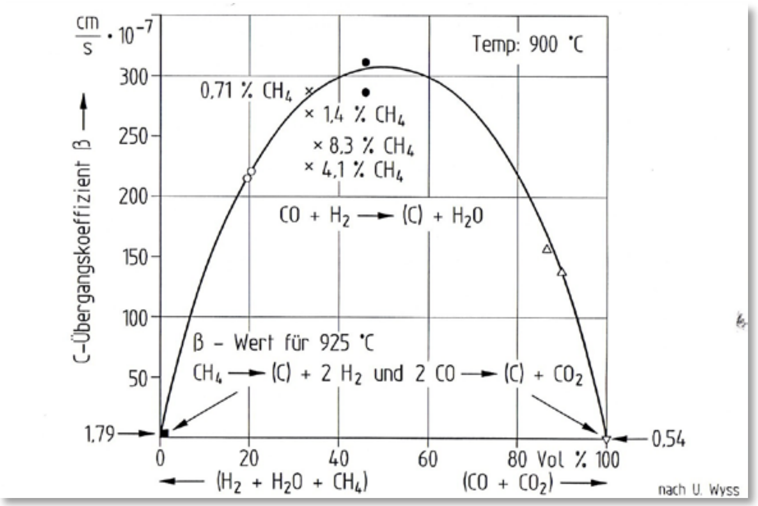
2) Modelling is using an imagined transfer layer between the parts' surface and the process gas atmosphere. The thickness of this layer is defined as s = D / β

3) Appling a high coefficient at constant diffusion speed reduces the thickness of this layer, accelerating the increase of surface carbon and vice versa



Cutting Cost Examples

Adjusting carbon transfer throughout carburizing



1) As β is proportional to the product of partial pressures of Carbon Monoxide and Hydrogen it can be controlled by adjusting the ratio of Methanol to Nitrogen

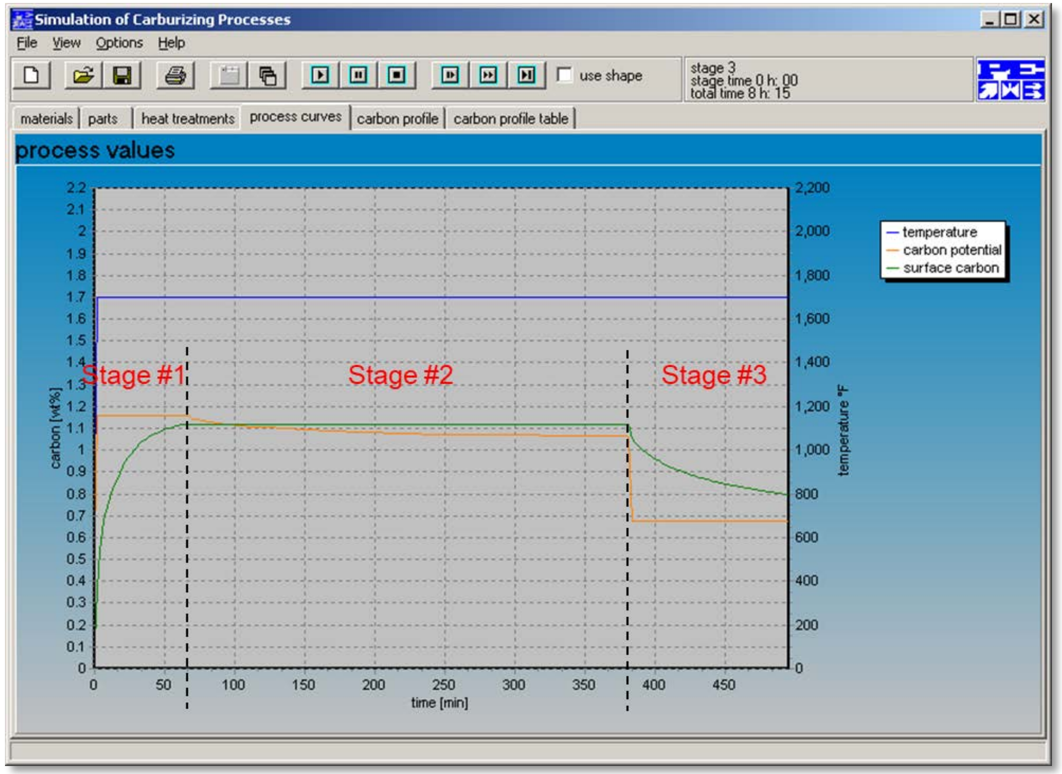
2) Assuming constant temperature of 930°C and CP of 1.25 a part made from 16MnCr5 will reach 1 C in the surface after

Carrier	rel. Beta	time (depth)
Endogas from nat. gas (20 CO, 40 H_2)	1.0	50 min (0.3 mm)*
Nitrogen – Methanol (20 CO, 40 H_2)	1.0	50 min (0.3 mm)
Endogas from Propane (23 CO, 31 H_2)	0.9	60 min (0.33 mm)
Pure Methanol (33 CO, 67 H_2)	2.7	22 min (0.2 mm)
technical carrier (50 CO, 50H_2)	3.1	20 min (0.2 mm)

*) in brackets: carbon depth$_{0.35}$ after given time

Cutting Cost Examples

Setting up the process



We are using 2 model driven approaches:

1) Carbon potential control automatically adjusting to the evaluation of the surface carbon content in order to allow for maximum saturation during the boost phase

2) Automatically adjusting beta to optimally support carbon transfer from atmosphere to steel surface

Cutting Cost Examples

Benefits

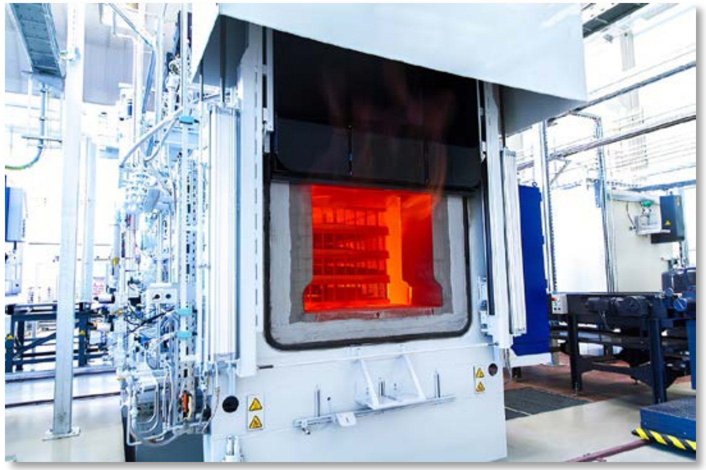
Required case depth [mm]	Savings in process time [%]	Savings in Methanol/Cost [%]	Savings in Methanol/Cost [%]
0.5	25	19 / 12	27 / 19
1.0	12	29 / 16	46 / 31
1.5	6	34 / 19	55 / 38
2.0	3	36 / 20	59 / 40
2.5	1.8	37 / 21	60 / 41
3.0	1.5	41 / 25	67 / 48
4.0	0.75	44 / 28	73 / 54

Compared to an optimized 2 stage process (close to the carbide limit !)

Compared to N_2 / CH_3OH 20/40, pure CH_3OH at a given prize ratio of 2/1 for Methanol/Nitrogen

Cutting Cost Examples

Benefits in
process time
@ 0.8 mm
typical CHD



Batch/IQ: Ipsen

	Annual Sales (estimated)		$ 400,000 to $ 500,000		
	Before		**Upgrade**	**Additional Sales**	**Final**
Sales	$ 450,000			+ $ 79,400 →	$ 529,000
Hours	7,200	-15 % * →	6,120 →	1,080	
Sales/Hr	$ 62.50		$ 73.53		$ 73.53
Direct Cost	$ 225,000	→		** →	$ 250,000
Direct Profit	$ 225,000				$ 279,400
				Gain +24 %	$ 54,400

* 15 reduction in time

** more work through furnace will not increase annual cost in energy or gas, but there will be more people to process the work (washing, racking etc.) and there will be a higher usage of other equipment (forklifts, washers, drawers etc.)

Cutting Cost Examples

Benefits in
process gas
@ 2.5 mm
typical CHD

Pit furnace installation: IVA Schmetz

Assuming big pity type furnace using a fixed nitrogen - methanol flow of 3.5l/h all the way through the process
giving a CO percentage of ~ 20%.

Applying variable carrier gas composition by automatically
adjusting the methanol-nitrogen ratio by maintaining the
same total flow will reduce the methanol consumption by
37% and the total carrier gas cost by 21%.

Cutting Cost Examples

Additional benefits @ neutral hardening

Processing parts with varying carbon contents

0.8 %C

0.2 %C

1: carburizing no quench
2: mechanical work
3: neutral hardening

CO=5%, H_2=10%, 60 min
0.80 %C controlled
0.20 %C raises to 0.25 %C max.

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Summary

Applying variable CO / carrier gas composition in heat treating processes opens a wide field of benefits

- Enhancing lifetime of furnace components
- Reducing IGO significantly
- Increasing capacity of short processes
- Reducing cost at long processes
- Allowing for true neutral processes

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Thank you for your attention!

Are there any questions?