Catalyst For The Reformation Of Biomass Pyrolysis Gas And Their Effect On Methanation

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tcbiomass2024

A DCL Technology Group Company


First emissions controls developed
for Underground Mining in 1986.
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40 Years of Energy Efficiency

Trusted by power producers to ensure cost effective, reliable emission reduction solutions for a broad range of industries.

Mobile & Stationary Emissions

Cogeneration Energy Efficiency

Biogas Conditioning & RNG Upgrading

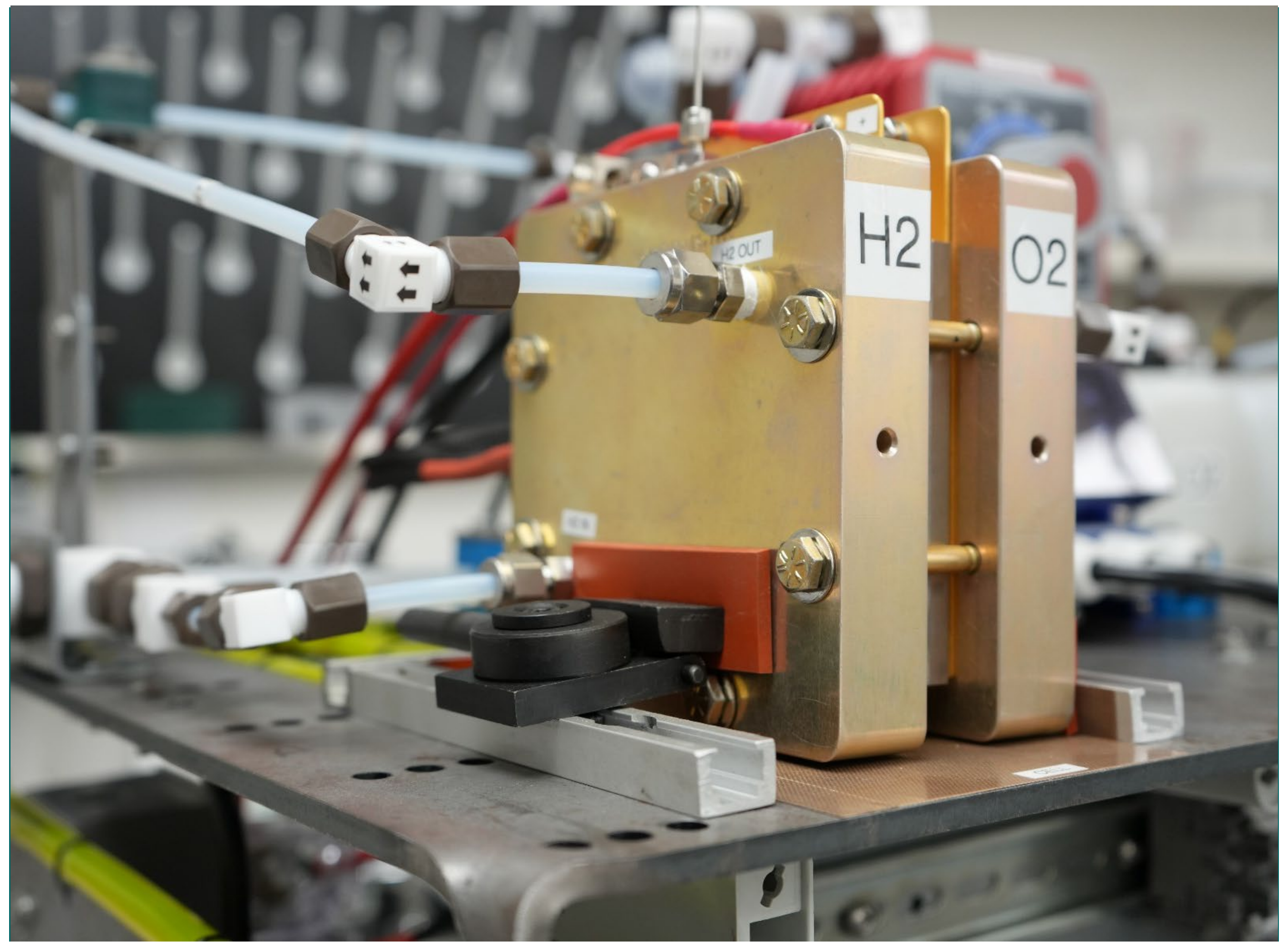
40 Years of
R&D, Engineering, & Manufacturing.

Expertise in emissions controls,
nanomaterials, catalyst & energy efficiency.

Decarbonization Solutions

DCL's expertise in designing & manufacturing high-quality components, for maximum efficiency & performance for clean energy applications, including Hydrogen CHP systems.

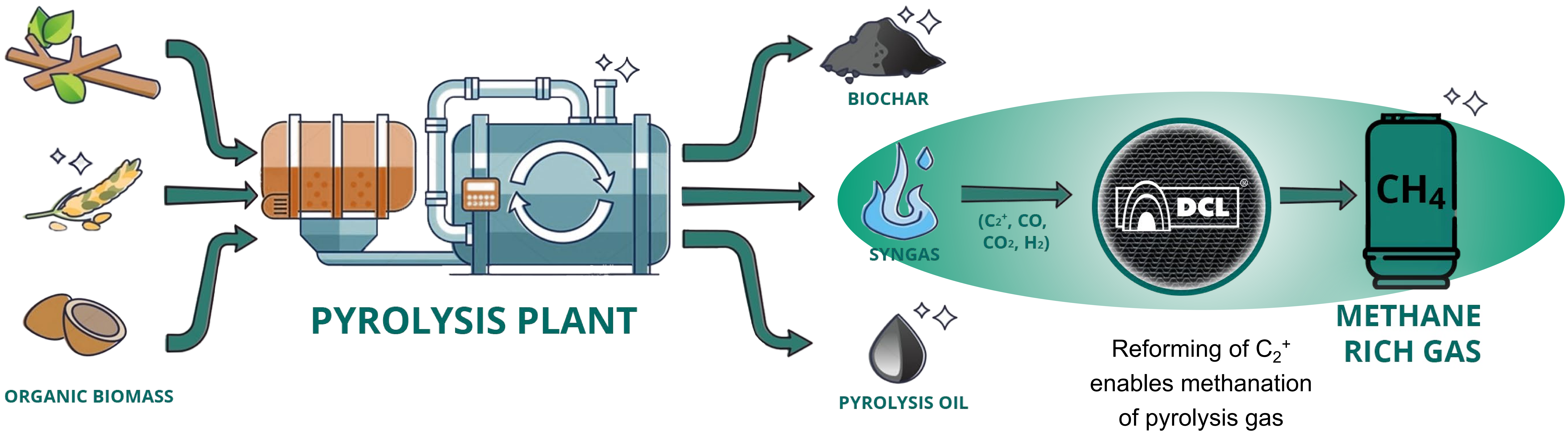
Fuel Cells



Electrolyzers

Reforming & Methanation Catalysts

Pyrolysis Gas – Methanation



Composition & Challenges of Pyrolysis Gas

% Vol	H2	CH4	C2-C4	CO	CO2	N2	LHV [MJ/Nm3]	kWh/tonne inlet
biomass	15%	26%	3%	35%	17%	4%	17.10	2600

Source: *https://www.biogreen-energy.com*

Limited amounts of hydrogen.

Trace hydrocarbons **coke** methanation catalysts and plugs reactor.

CO and CO_2 converted to CH_4 using methanation or WGS to recycle carbon.

CO/CO_2 reacts with H_2 to produce CH_4

***LHV of Methane is 2-3X greater than biomass**

Typical Ni Based Catalyst for Methanation:

- Susceptible to Sulfur poisoning
- Significant Coke accumulation due to HCs
- Max operating temperature 500° - 550°C

Pyrolysis Gas Pre-Treatment

General Composition	
H_2	~15- 40 %
CO_2	~10 - 20 %
CO	~20 - 35 %
CH_4	~10 - 30%
C_2H_4	~3 %
C_2H_6	~0.3 %
C_3H_6	~0.4 %
C_3H_8	~0.4 %
TARS	~0.2 %
DUST	~0.2 %
NH_3	~0.3 %
H_2S	~0.1 %
Temperature >800°C	

DCL Technology Group's gas pre-treatment equipment in operation on W2E and other biogas applications

Treatment Processes For Pyrolysis Gas

Pre-Treatment
eliminates TARS, DUST, NH_3, H_2S

Methanation
converts CO and CO_2 into CH_4

- Limited by hydrogen content in pyrolysis gas.
- Straightforward process if green hydrogen is available.

Pre-Treatment
eliminates TARS, DUST, NH_3, H_2S

Water Gas Shift
(WGS) converts CO to CO_2 + generates H_2

Methanation
converts CO and CO_2 into CH_4

- Increase H_2 concentration using the WGS reaction.
- Requires energy-intensive process with careful energy management.
- Green hydrogen availability boosts CH_4 yield.

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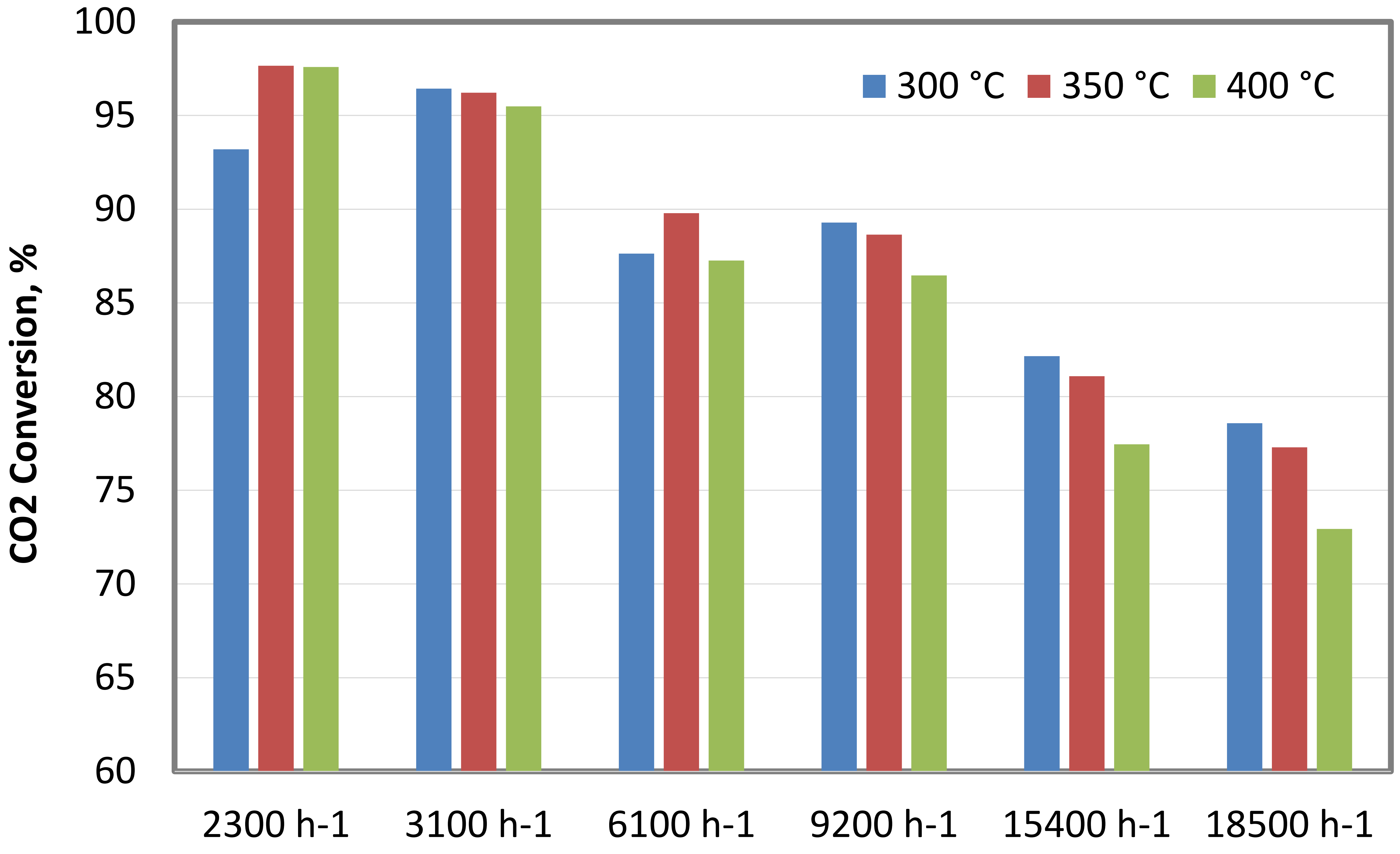
Baseline: CO_2 Methanation



Equilibrium conversion is achieved at 300 - 350°C with a Ni catalyst at 2,000 - 3,000 h^{-1} space velocity.

Ni Based Catalyst for Methanation

$CO_2 + 4H_2 = CH_4 + 2H_2O$

$CO_2 : H_2 = 1:4$

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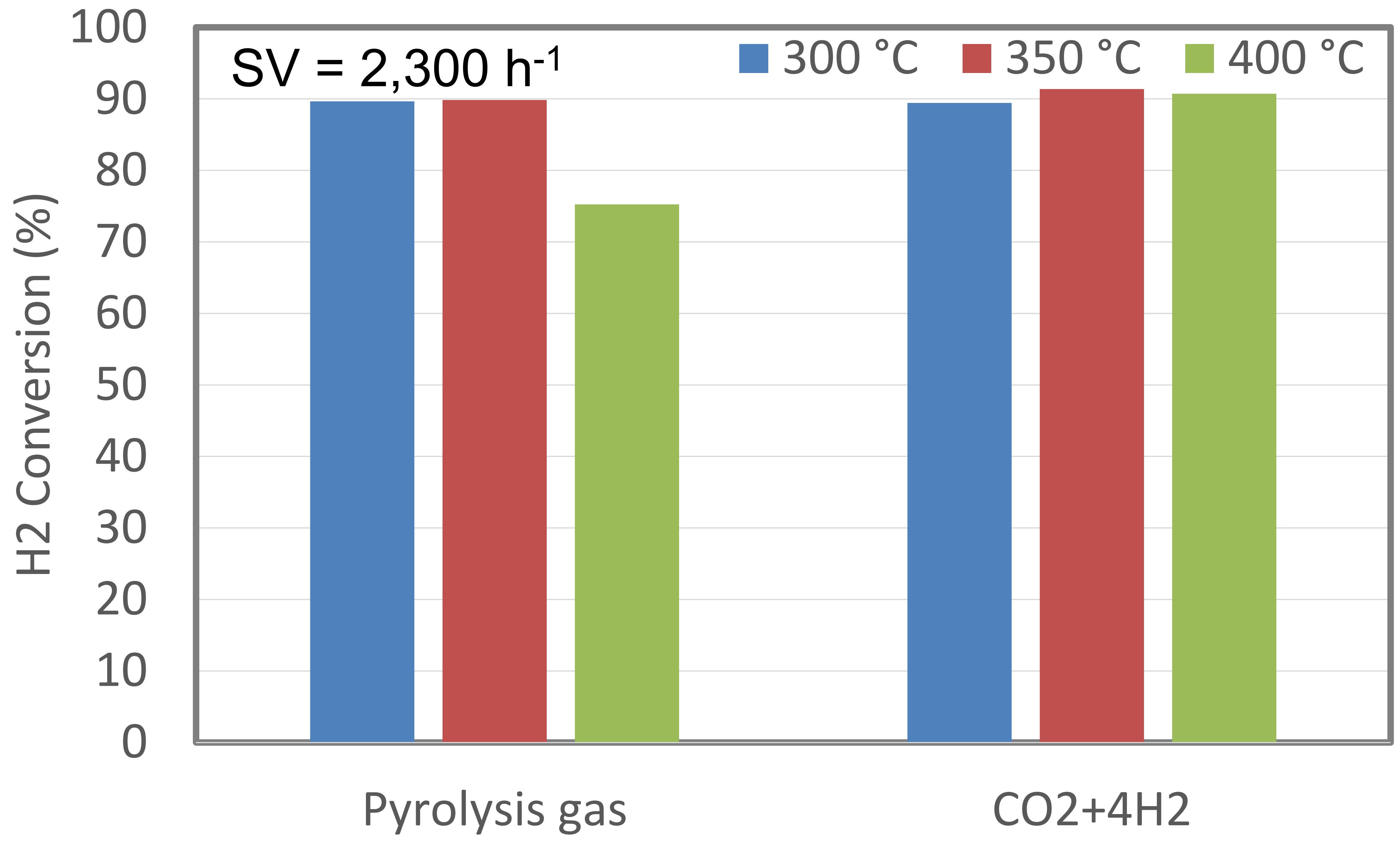
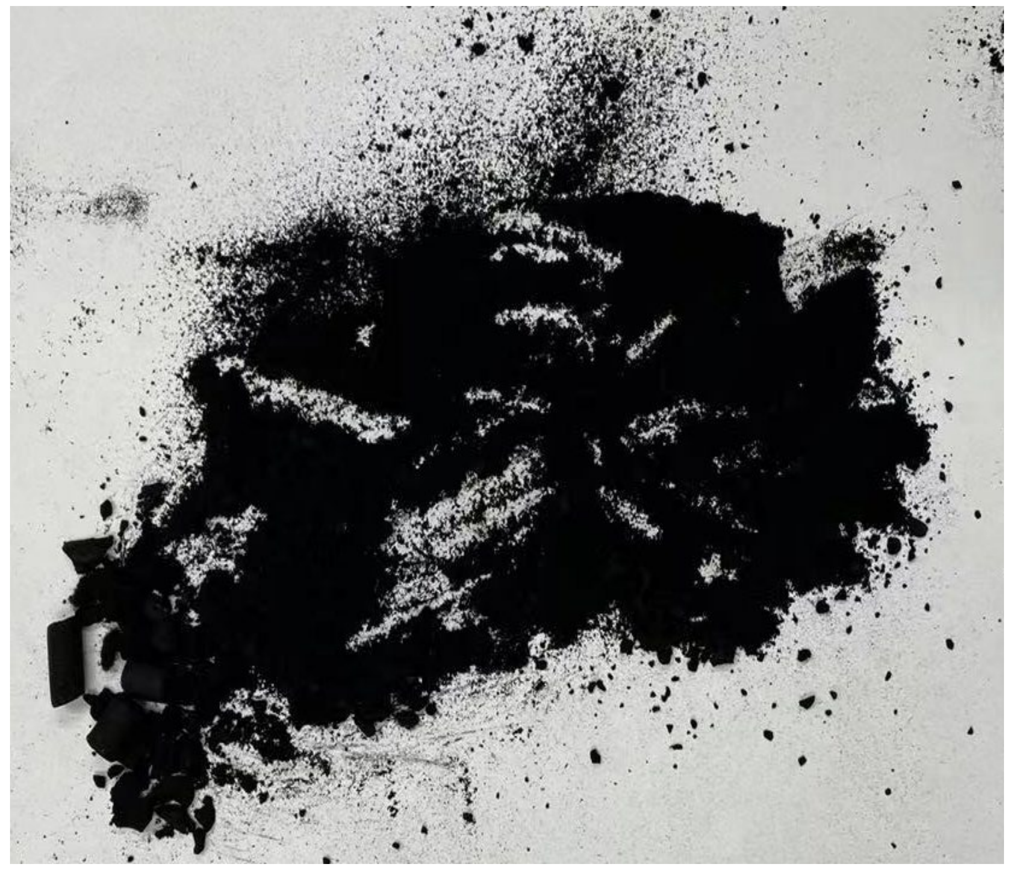
Pyrolysis gas Methanation on Ni based catalyst



***Coke formations block Reactor within 4hrs**

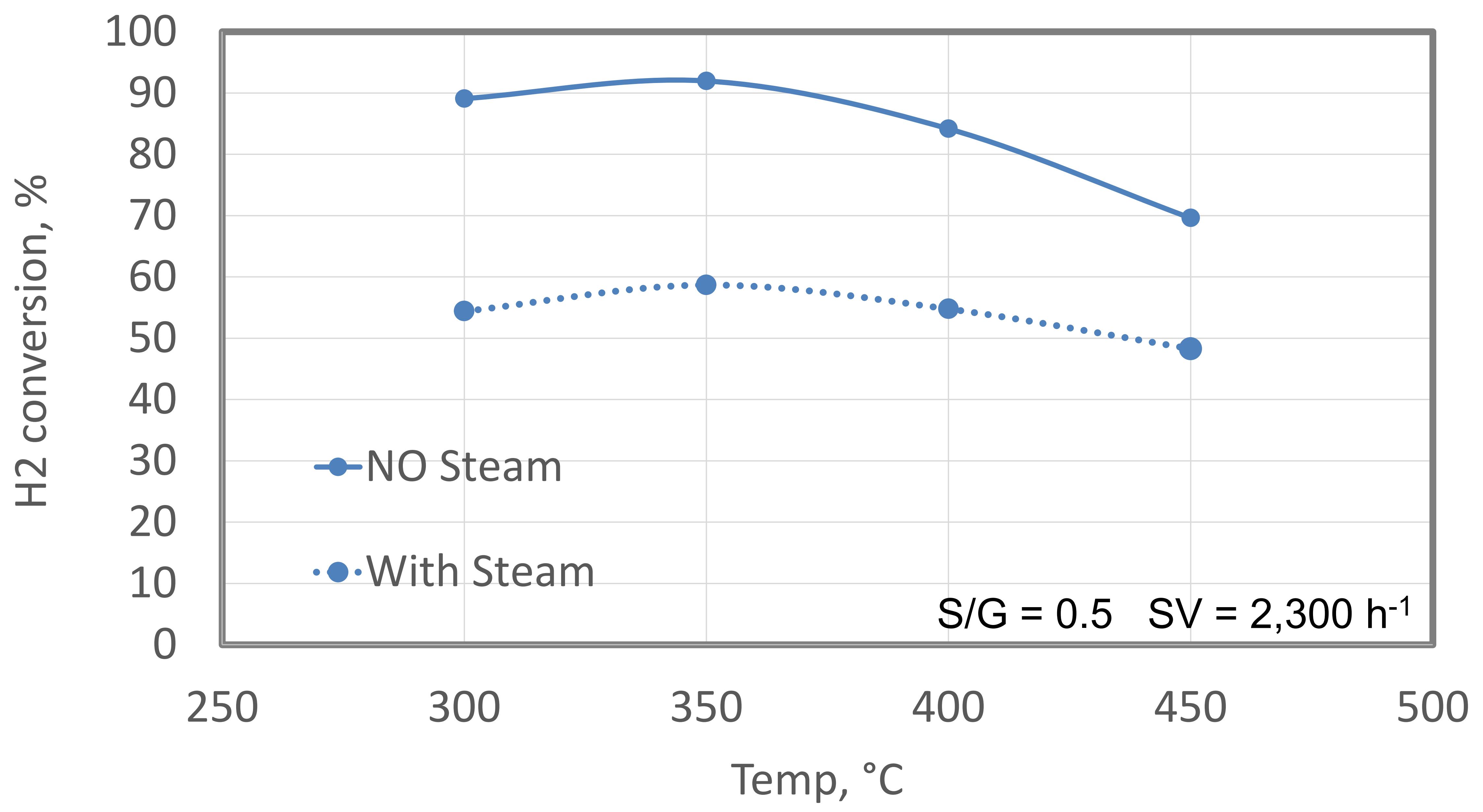


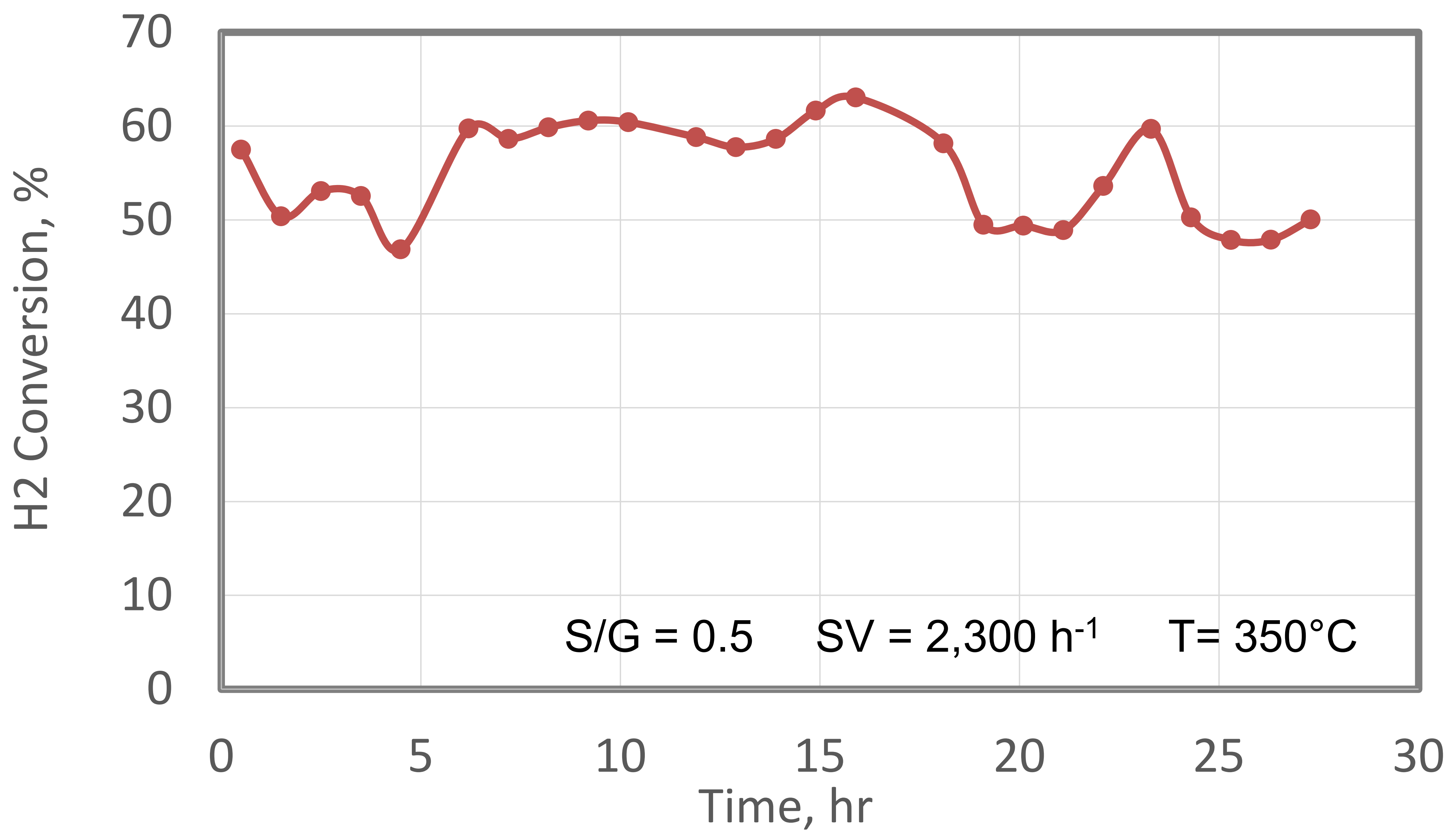
Gas Comp.	Vol, %
H_2	19
CO	35
CO_2	21
CH_4	20
C_2H_6	1.5
C_2H_4	3.5

Lab test gas composition

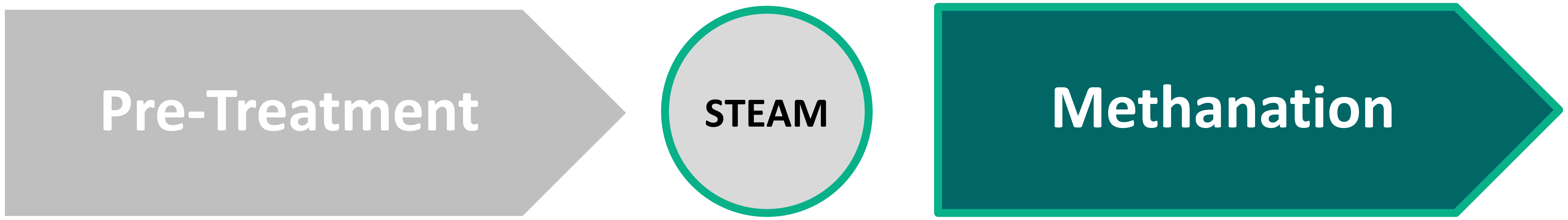
Pre-Treatment → **Methanation**

Steam Reduces Coke But…

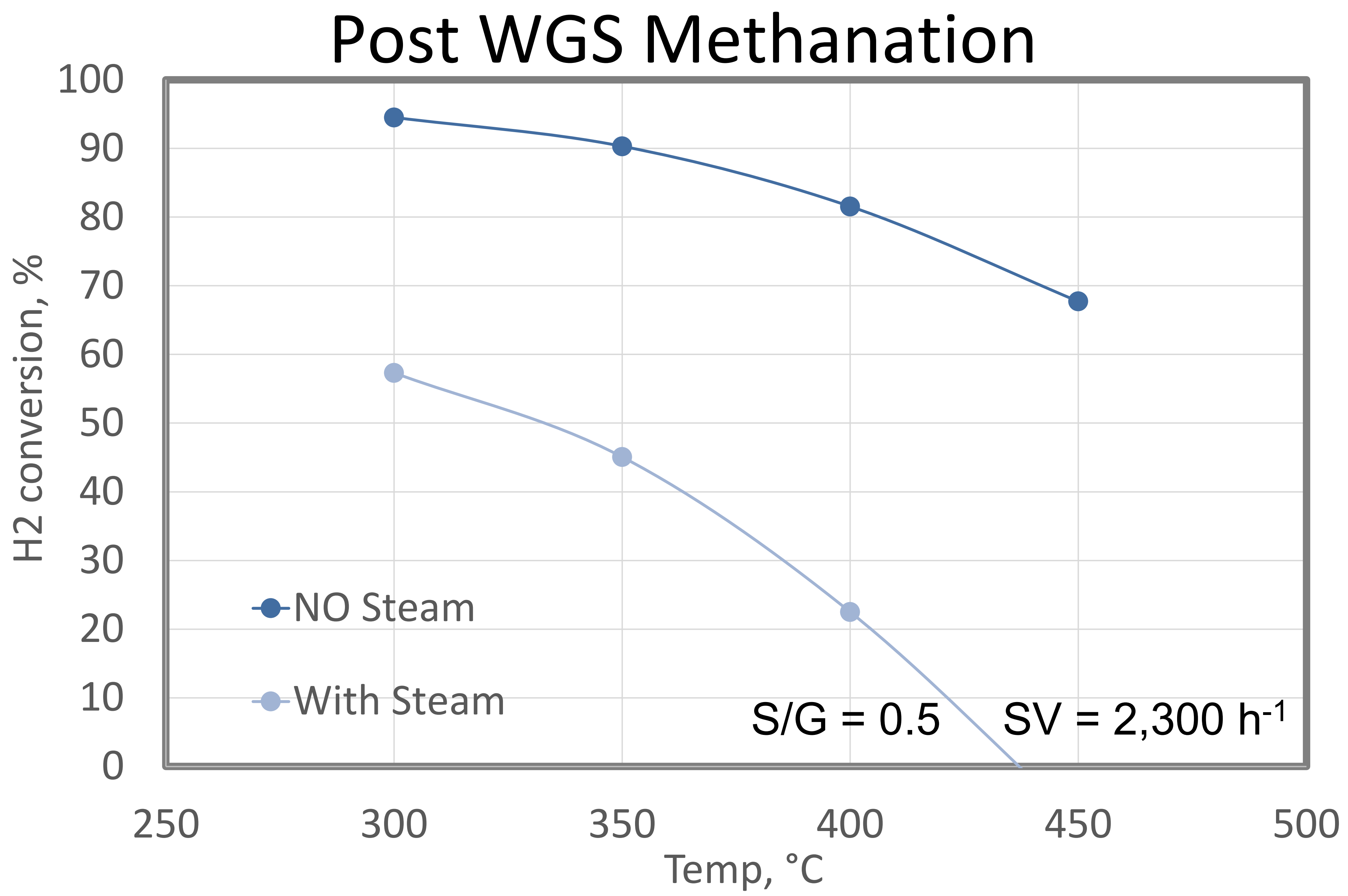




***Coke formations block Reactor after 30hrs**



WGS Yields Greater H_2 & CH_4



Without Steam

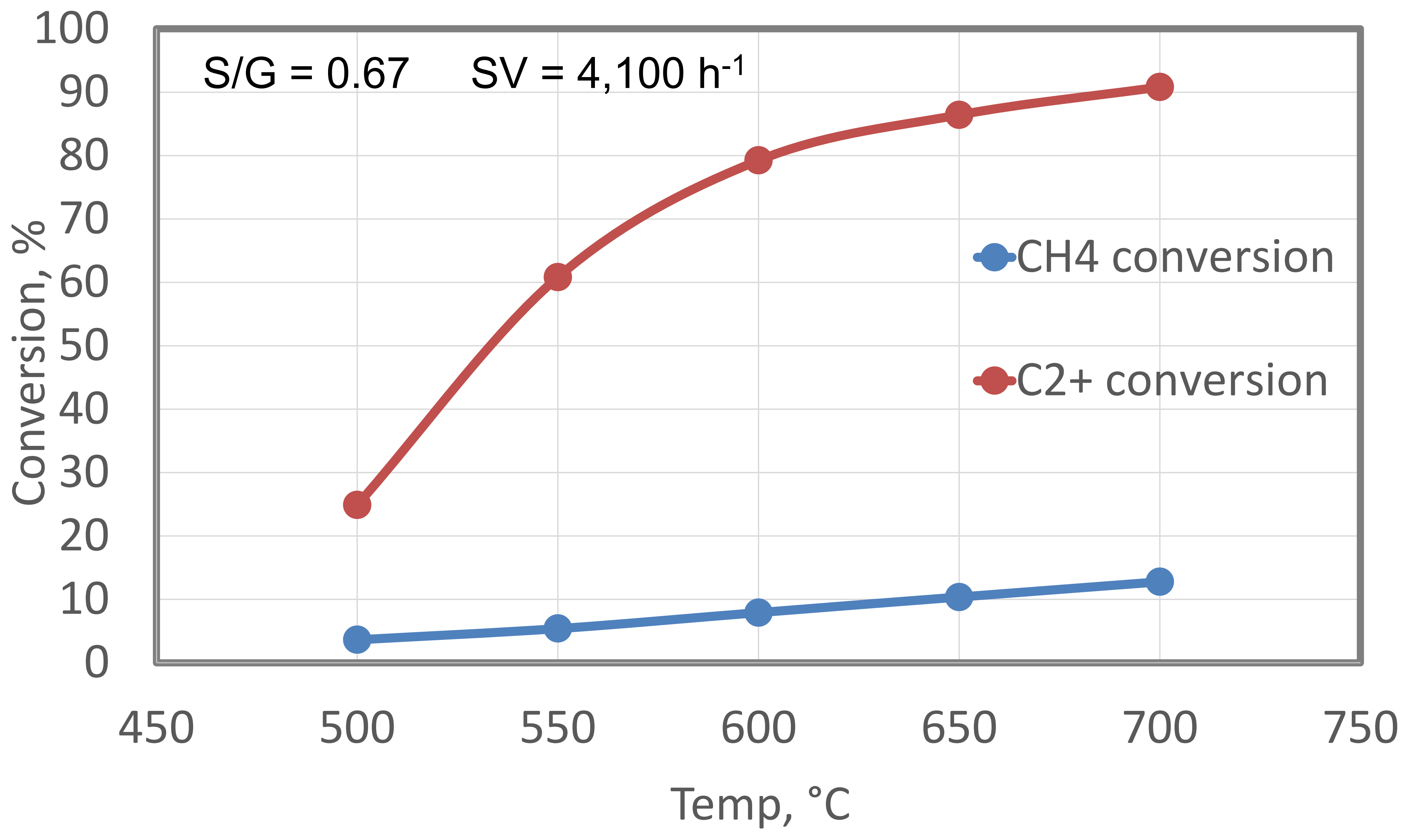
Reactor blocked with coke in less than 60 hrs

With Steam

H_2 conversion is very low

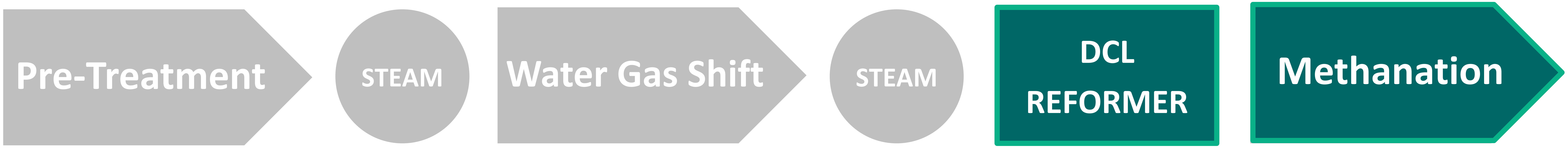
Gas Comp.	Pre-WGS Vol, %	Post-WGS Vol, %
H_2	**19**	**40**
CO	**35**	**5**
CO_2	21	38
CH_4	20	13.5
C_2H_6	1.5	0.5
C_2H_4	3.5	2.5
C_3H_6	0	0.5

Highly Selective Reforming Catalyst

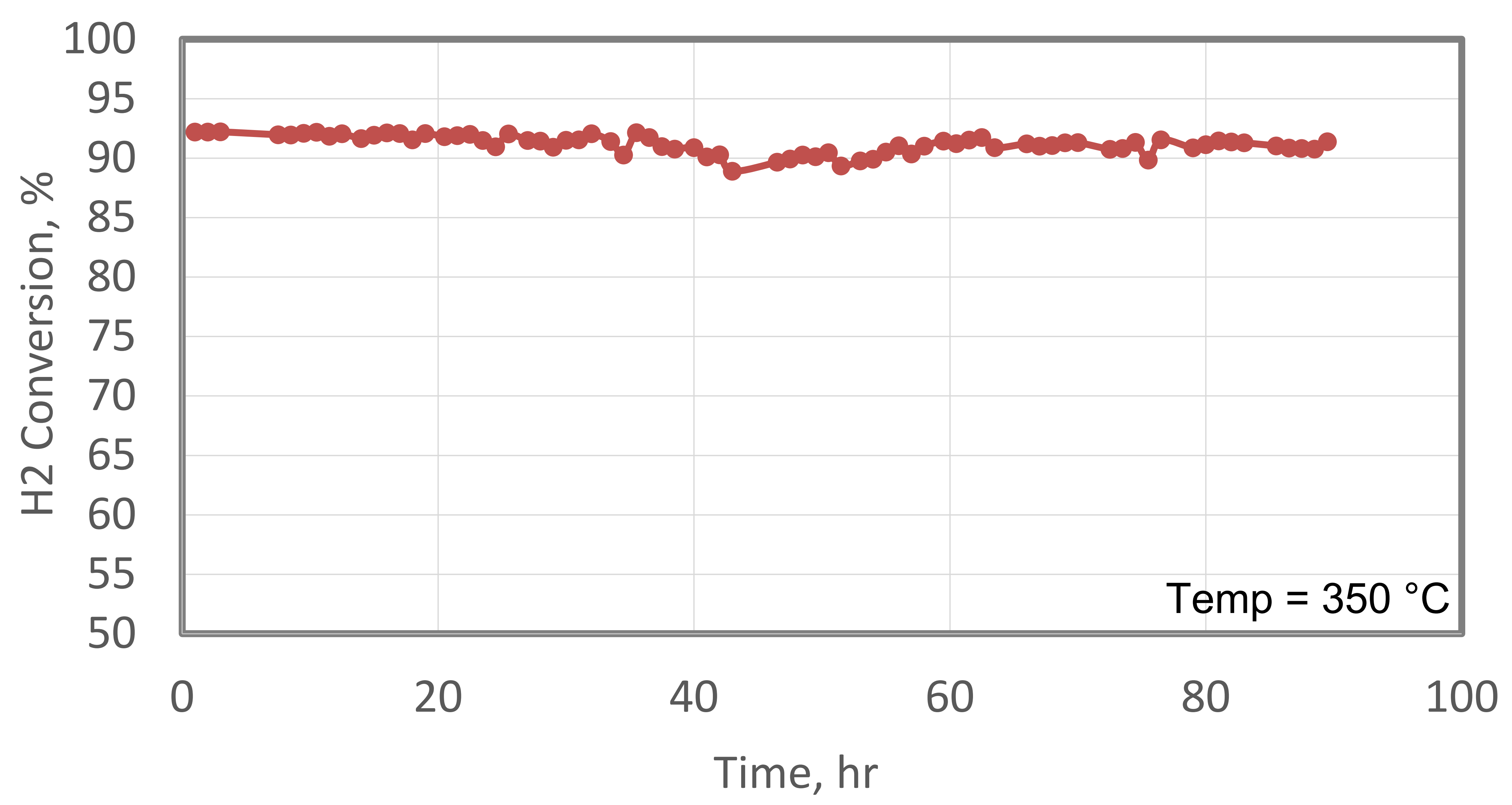


DCL's Proprietary Catalyst can reform C_2^+ without much affecting CH_4 concentration.

Gas Comp.	Post WGS Vol, %	Post Reformer Vol, %
H_2	40	47
CO	5	11
CO_2	38	31
CH_4	13.5	10
C_2H_6	**0.5**	**0.25**
C_2H_4	**2.5**	**0.002**
C_3H_6	**0.5**	**0.001**



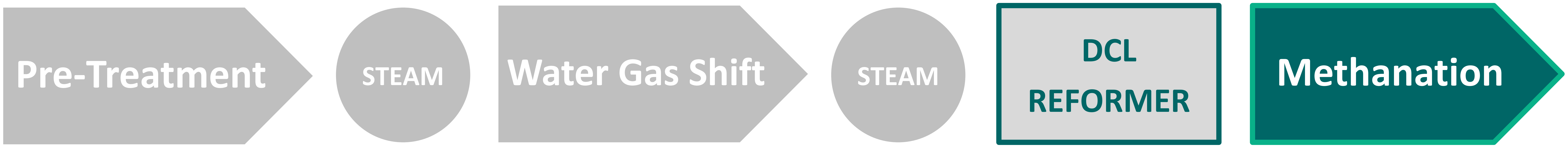
Methanation of Reformed Gas



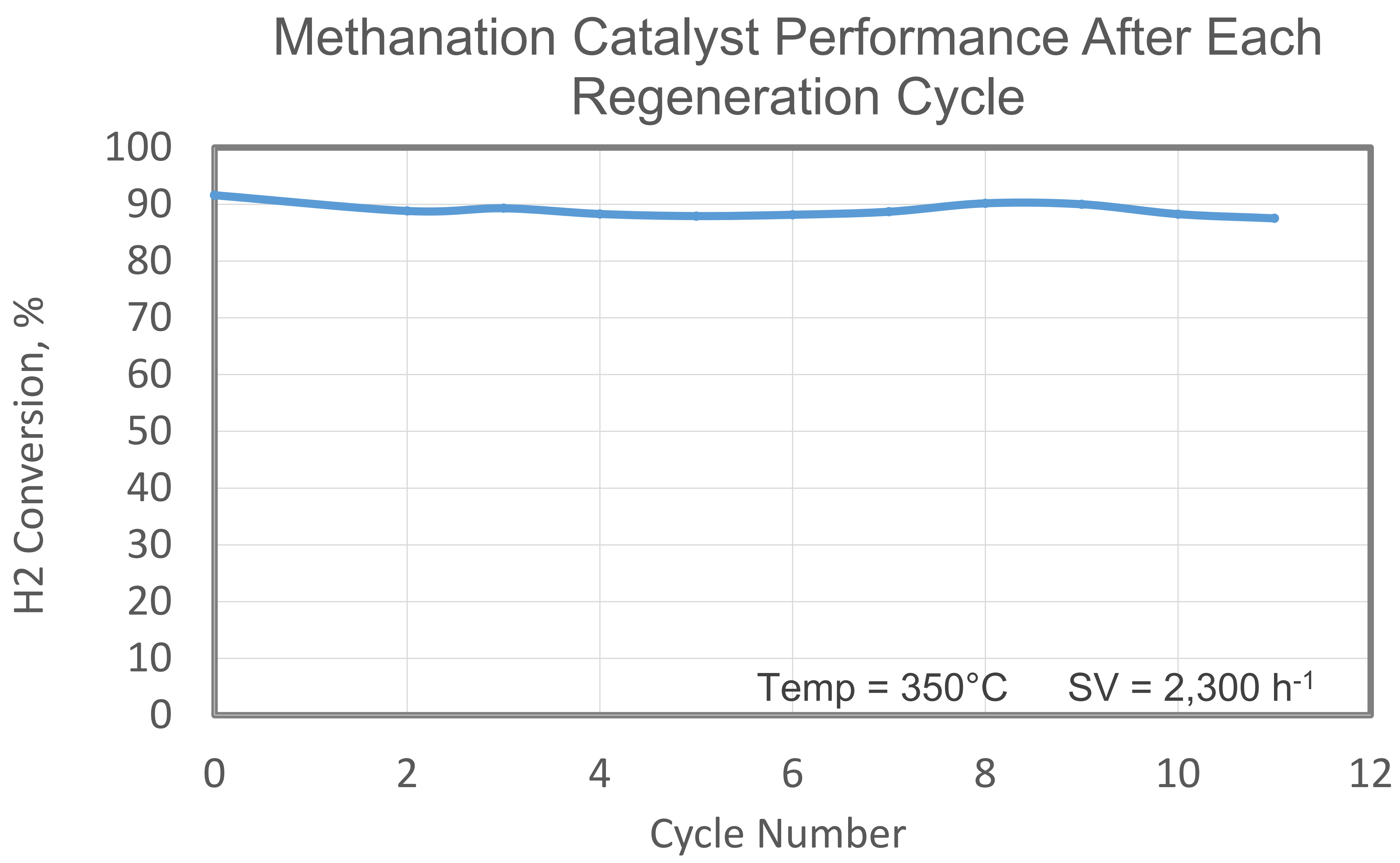
Process	Operating time prior to significant coking
Direct Methanation	4 hours
WGS + Methanation	<60 hours
WGS + **DCL Reformer** + Methanation	>100 hours

Gas Comp.	Post-Reformer Vol, %
H_2	45.5
CO	5
CO_2	44
CH_4	5
C_2H_6	0.4
C_2H_4	0.05
C_3H_6	0.05

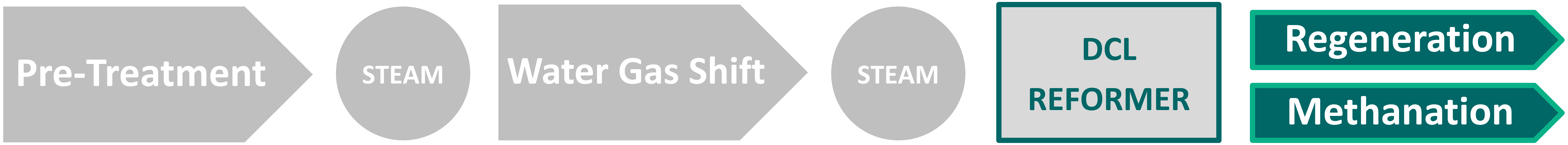
***Coke formations observed after 100 hours of operation.**



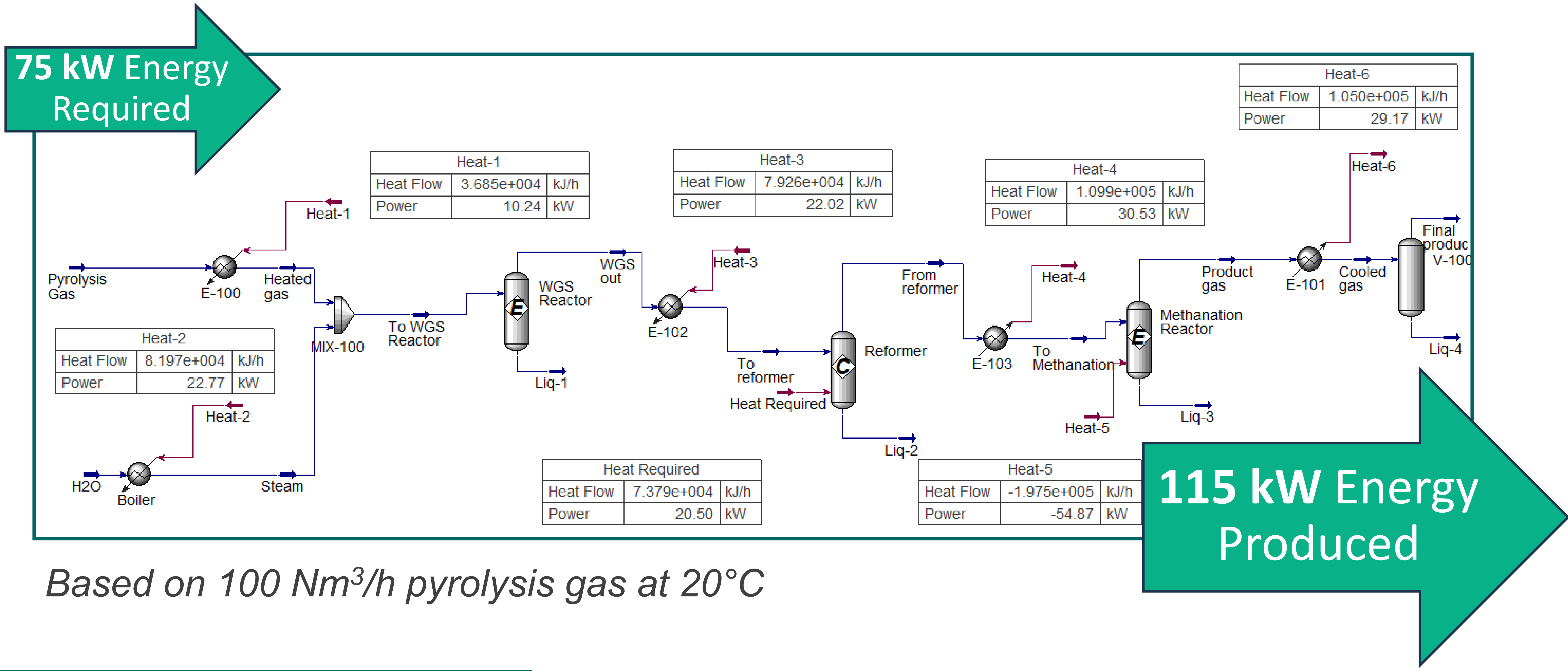
Fewer Regeneration Cycles



DCL Methanation Catalysts can be regenerated every 4-5 days by running reactors in parallel to effectively burn off coke.



Gas Comp.	Inlet pyrolysis gas Vol, %	Final product gas Vol, %
H_2	19	< 5%
CO	35	< 0.5%
CO_2	21	~50%
CH_4	20	~42%
C_2H_6	1.5	< 1.0
C_2H_4	2.5	<0.01
C_3H_6	1.0	<0.001



Based on 100 Nm³/h pyrolysis gas at 20°C

Final Product & System Design

- DCL’s proprietary reforming catalyst enable >90% C2+ hydrocarbon reforming with minimal impact on methane levels.
- DCL reforming catalyst is coke and sulfur resistant.
- DCL reforming catalyst reduces the coke regeneration frequency for the methanation catalyst.

Questions?

Thank You

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