HYDROGEN PRODUCTION BY AQUEOUS-PHASE REFORMING

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Bioenergy - II:
Fuels and Chemicals
From Renewable Resources, March, 2009

instituto de investigación en ingeniería de Aragón
Universidad de Zaragoza

Grupo de Procesos Termoquímicos

OUTLINE

1. INTRODUCTION
2. EXPERIMENTAL METHOD
3. RESULTS
4. CONCLUSIONS

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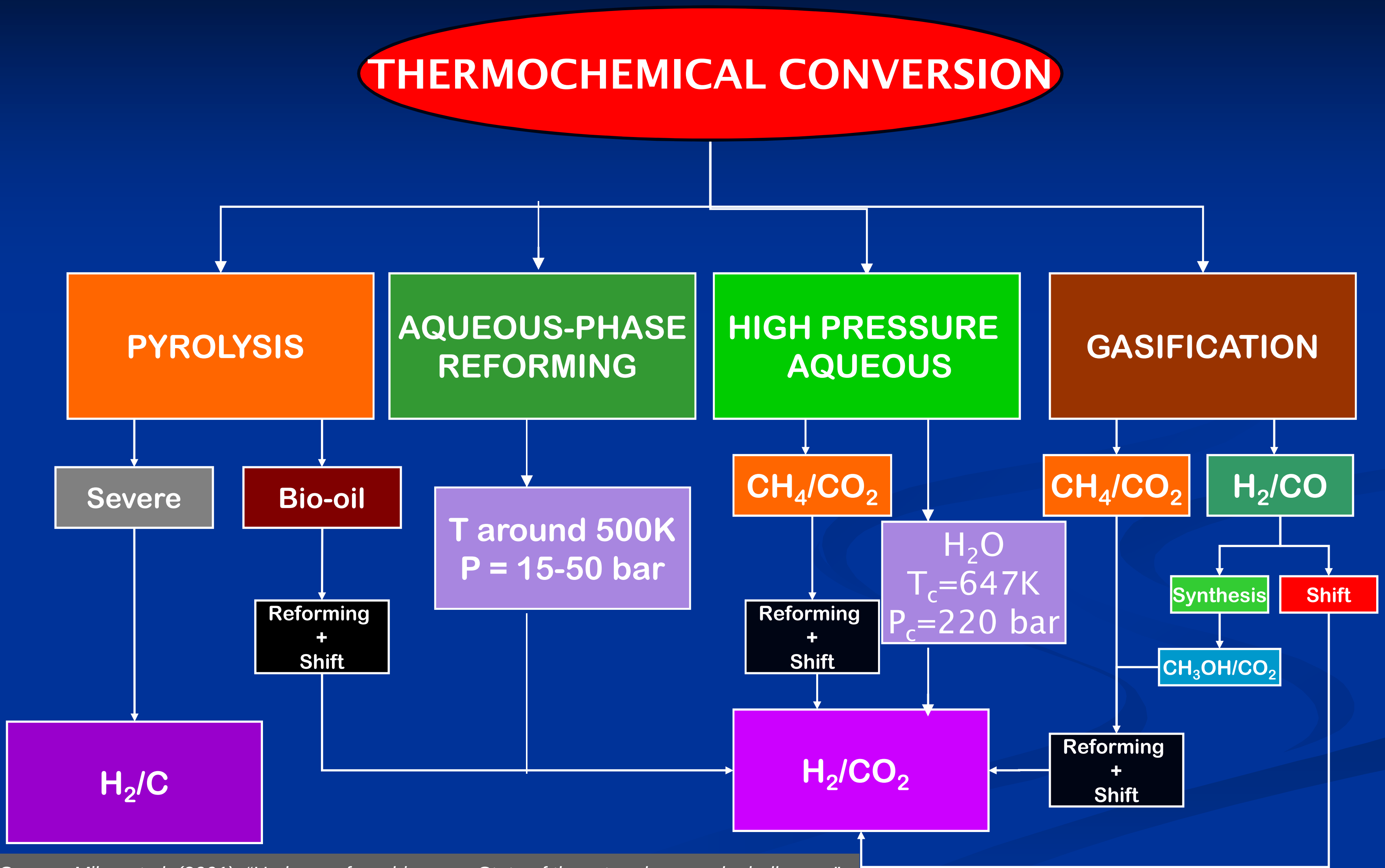
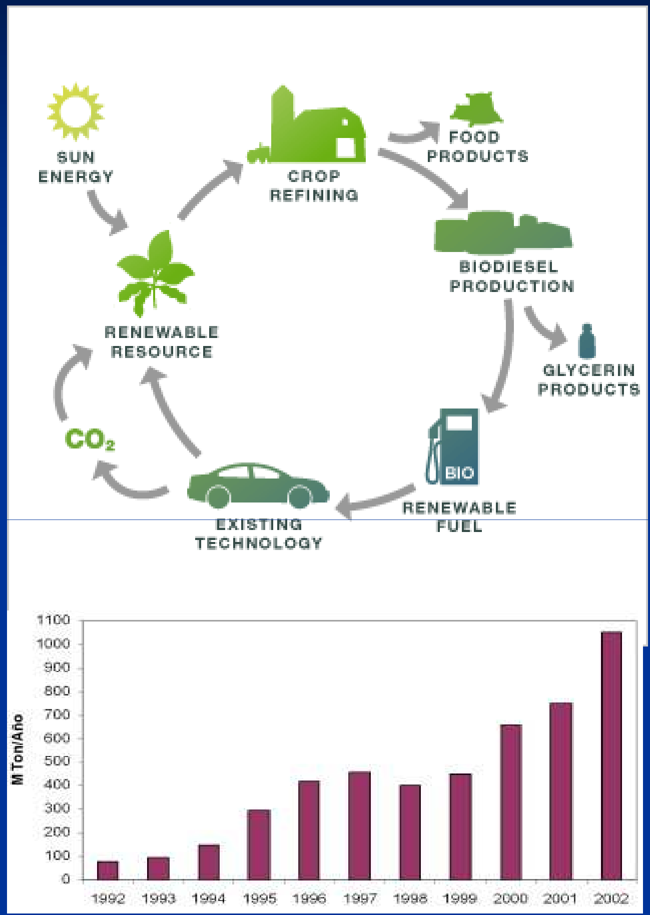
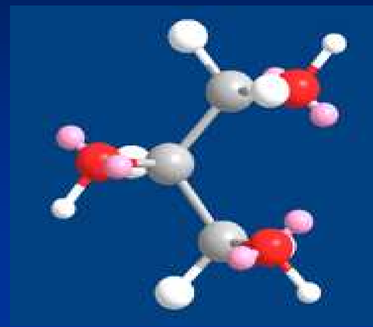


Source: Milne et al. (2001). "Hydrogen from biomass. State of the art and research challenges".
A report for the International Energy Agency. ref. IEA/H2/TR-02/001

- Important increasing in biodiesel production





- Glycerol

Glycerol prices decrease, so it is necessary to find new ways to convert glycerol into valuable added products → H_2

- Waste treatment - WHEY

ADVANTAGES OVER STEAM REFORMING PROCESS

1. APR eliminates the need to vaporize both water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen.

2. APR occurs at temperatures and pressures where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor.

Davda, R.R.; Shabaker, J.W.; Huber, G.W.; Cortright; Dumesic J.A. Appl. Catal B 56 (2005) 171-186

ADVANTAGES OVER STEAM REFORMING PROCESS

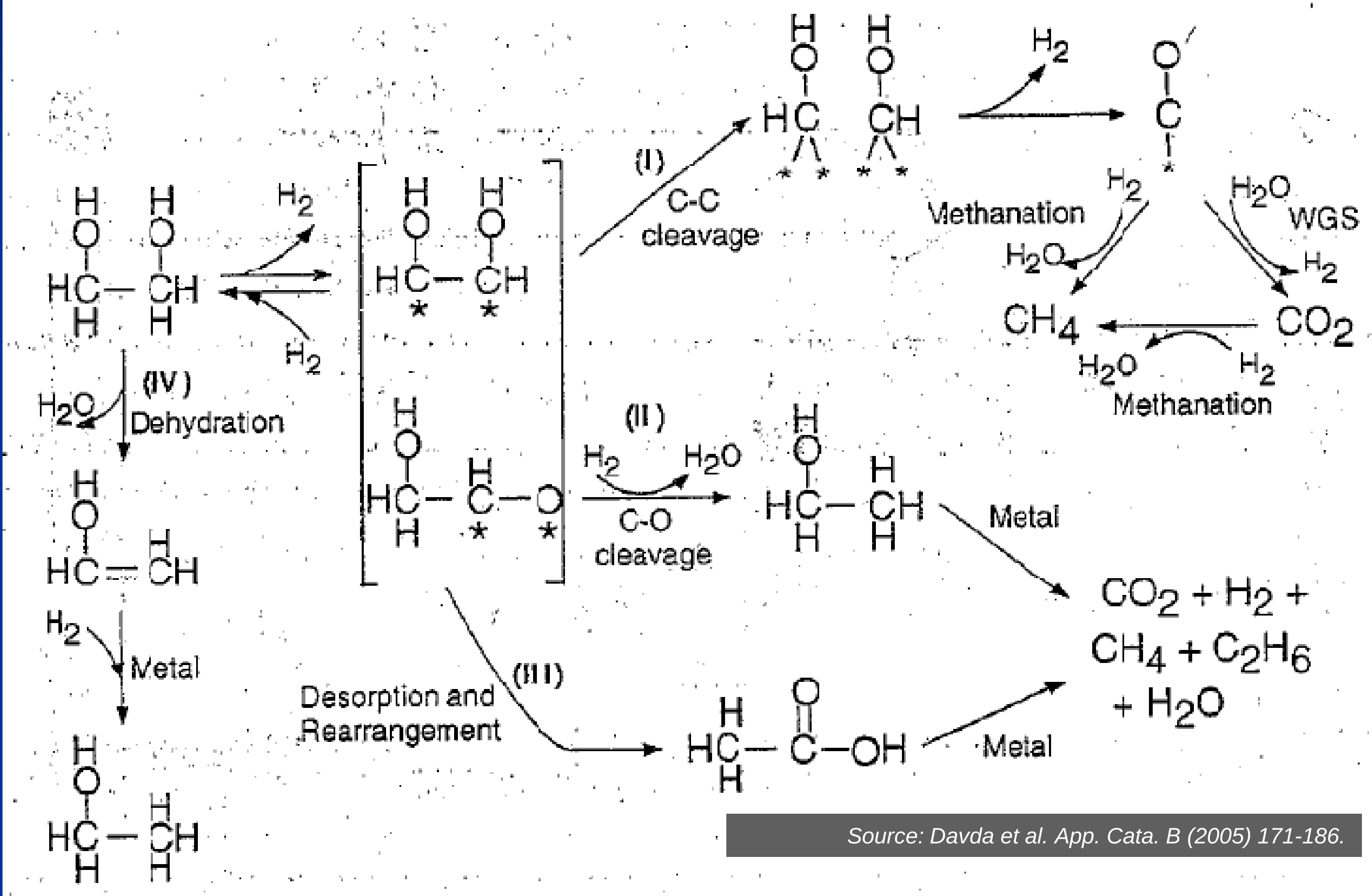
3. APR is conducted at pressures (typically 15-50 bar) where the hydrogen-rich effluent can be effectively purified using pressure-swing adsorption or membrane technologies, and the carbon dioxide can also be effectively separated for either sequestration or use as a chemical.

4. APR occurs at low temperatures that minimize undesirable decomposition reactions typically encountered at elevated temperatures.

5. Production of H2 and CO2 may be accomplished in a single-step, low temperature process, in contrast to the multi-reactor steam reforming system.

Davda, R.R.; Shabaker, J.W.; Huber, G.W.; Cortright; Dumesic J.A. Appl. Catal B 56 (2005) 171-186

REACTION PATHWAYS



Source: Davda et al. App. Cata. B (2005) 171-186.

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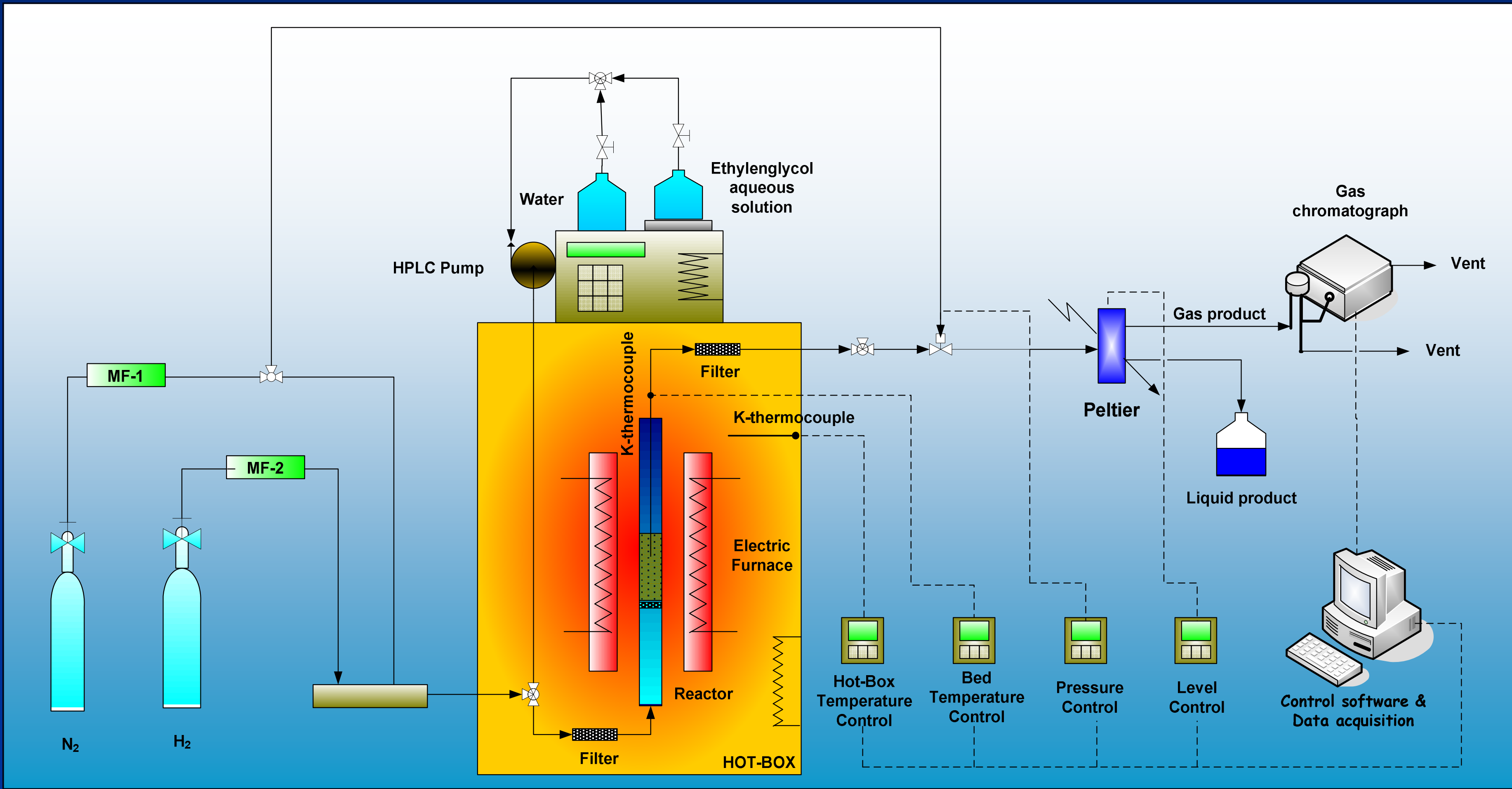
EXPERIMENTAL SYSTEM



EXPERIMENTAL SYSTEM

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EXPERIMENTAL CONDITIONS

P = 27 - 36 bar

T = 500 K

Liquid flow rate: 1 mL/min (5 wt% ethylene glycol aqueous solution)

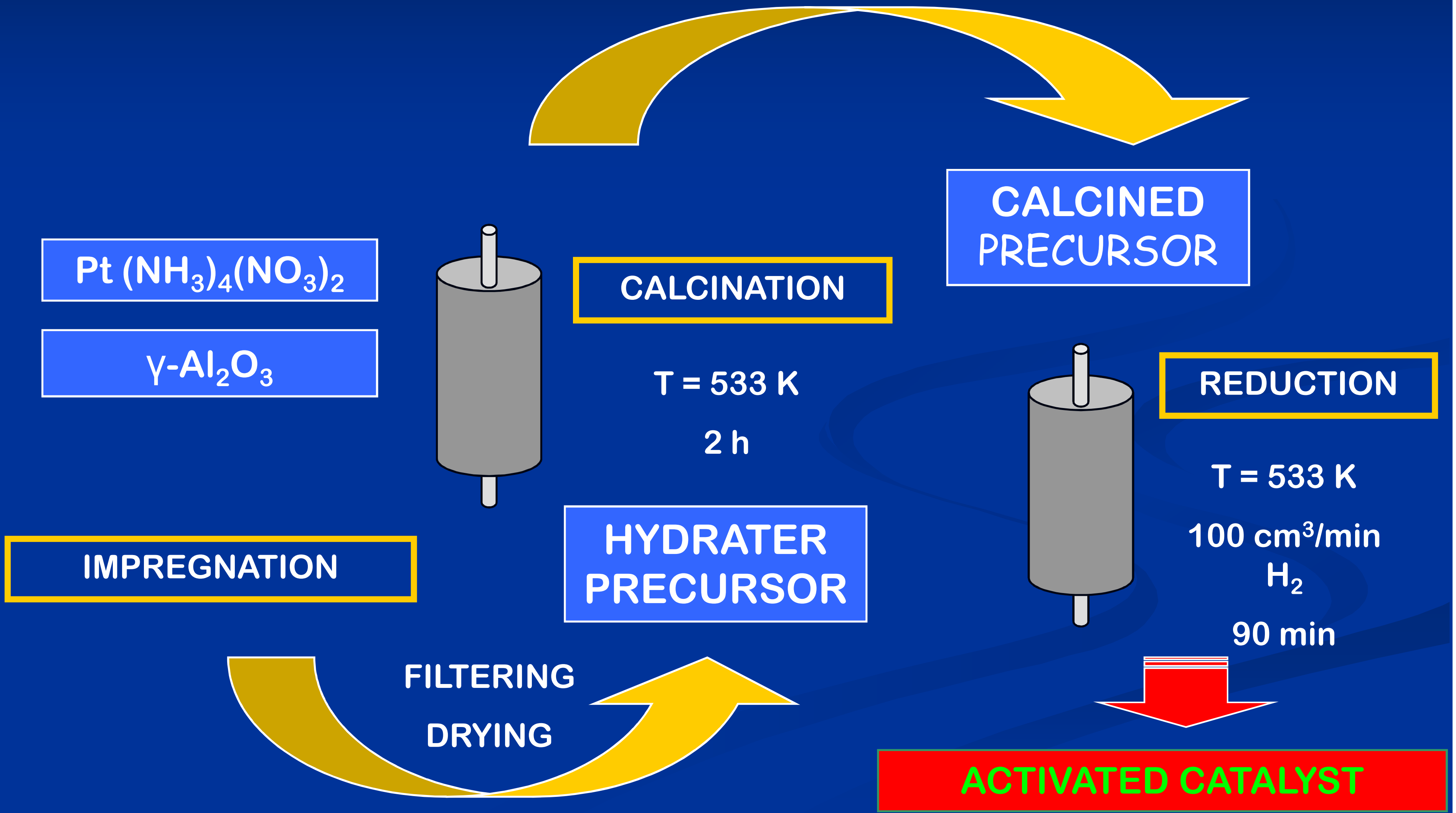
w_{bed} = 5 g $w_{catalyst}$ = 0.25 - 1 g   (particle size = 160 – 320 μm)

W/m $_{ethylene\ glycol}$ ~ 5 - 30 g catalyst · min / g ethylene glycol

t = 5 h

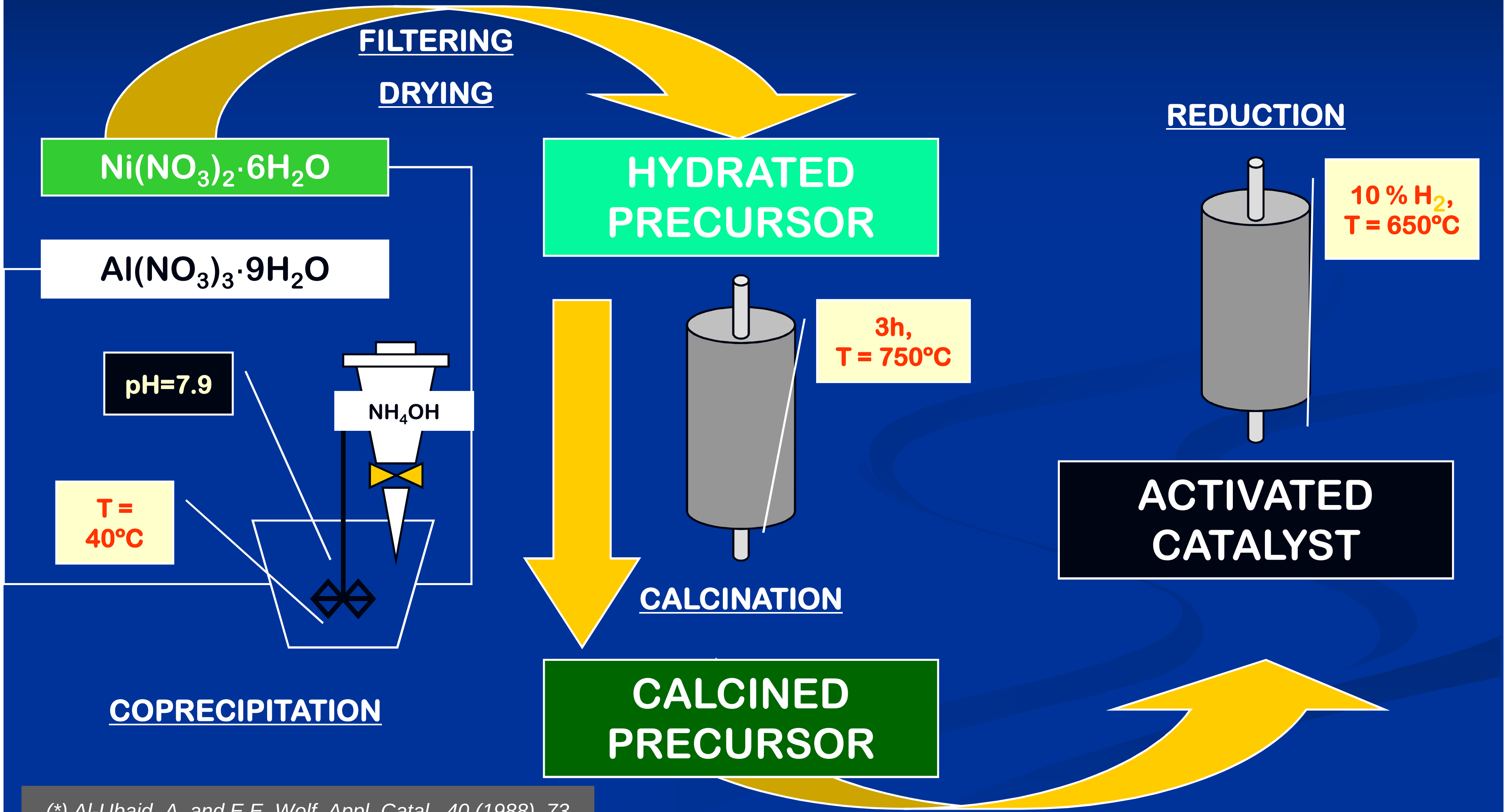
CATALYST

Type: research, Platinum incipient wetness impregnation, prepared following



CATALYSTS

Type: research, Nickel co-precipitated, hydrotalcite-like, prepared following (*)



(*) *Al-Ubaid, A. and E.E. Wolf, Appl. Catal., 40 (1988), 73*

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INFLUENCE OF THE SYSTEM PRESSURE

Run #	1	2	3	4
Pressure (bar)	27	30	33	36
Recovery	95.30	96.99	98.69	95.05
Carbon conversion (%)	9.89	11.12	11.42	14.71
Gas yields (g/g ethylene glycol):				
H_2	0.0146	0.0166	0.0171	0.0227
CO_2	0.1322	0.1459	0.1548	0.2033
CO	0.0005	0.0005	0.0005	0.0006
CH_4	0.0001	0.0001	0.0003	0.0006
C_2H_6	0.0004	0.0005	0.0004	0.0004
Gas composition (mol %N_2 and H_2O free):				
H_2	70.67	71.24	71.76	70.68
CO_2	28.99	28.4	27.87	28.85
CO	0.16	0.15	0.13	0.14
CH_4	0.06	0.07	0.13	0.24
C_2H_6	0.12	0.13	0.11	0.09
Selectivity (%):				
H_2	95.85	98.12	97.08	96.27
Alkane	1.01	1.19	1.25	1.39

T = 500 K

$w_{catalyst}$ = 0.5 g

3 wt% Pt/Al_2O_3

Run #	3
Temperature (K)	500
Weight catalyst (g)	0.5
Catalyst	3%Pt
Pressure (bar)	33
Recovery	98.69
Carbon conversion (%)	11.42
Gas yields (g/g ethylene glycol):	
H_2	0.0171
CO_2	0.1548
CO	0.0005
CH_4	0.0003
C_2H_6	0.0004
Gas composition (mol %N_2 and H_2O free):	
H_2	71.76
CO_2	27.87
CO	0.13
CH_4	0.13
C_2H_6	0.11
Selectivity (%):	
H_2	97.08
Alkane	1.25

INFLUENCE OF THE SYSTEM PRESSURE

- ✓No deactivation for H_2.
- ✓Lower CO content.

$$C_2H_6O_2 + 2H_2O \rightarrow 2CO_2 + 5H_2$$

$$H_2\ selectivity = \frac{molecules\ H_2\ produced}{C\ atoms\ in\ gas\ phase} x \frac{1}{R} x100$$

R is defined as the H_2/CO_2 reforming ratio which value is 5/2

$$Alkane\ selectivity = \frac{C\ atoms\ in\ gaseous\ alkanes}{total\ C\ atoms\ in\ gas\ phase\ product} x100$$

INFLUENCE OF W/m

Run #	5	3	6	7
Catalyst weight (g)	0.25	0.5	1	1.5
$W/m_{ethylene\ glycol}$ (g catalyst min/g ethylene glycol)	5	10	20	30
Catalyst	3% Pt	3% Pt	3% Pt	3% Pt
Recovery	97.59	98.69	95.63	104.29
Carbon conversion (%)	6.48	11.42	32.13	50.99
Gas yields (g/g ethylene glycol):				
H_2	0.0101	0.0171	0.0444	0.0701
CO_2	0.0894	0.1548	0.3971	0.6343
CO	0.0003	0.0005	0.0011	0.0053
CH_4	0.0002	0.0003	0.0011	0.0034
C_2H_6	0.0002	0.0004	0.0009	0.0009
Gas composition (mol %, N_2 and H_2O free):				
H_2	70.94	71.76	70.81	70.27
CO_2	28.65	27.87	28.75	28.92
CO	0.15	0.13	0.13	0.37
CH_4	0.14	0.13	0.22	0.38
C_2H_6	0.11	0.11	0.09	0.07
Selectivity (%):				
H_2	97.32	97.08	96.63	94.17
Alkane	1.26	1.25	1.38	1.85

T = 500 K

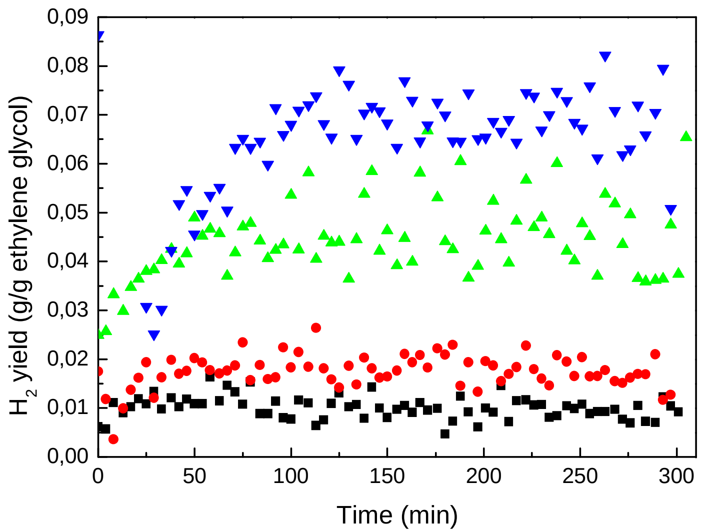
P = 33 bar

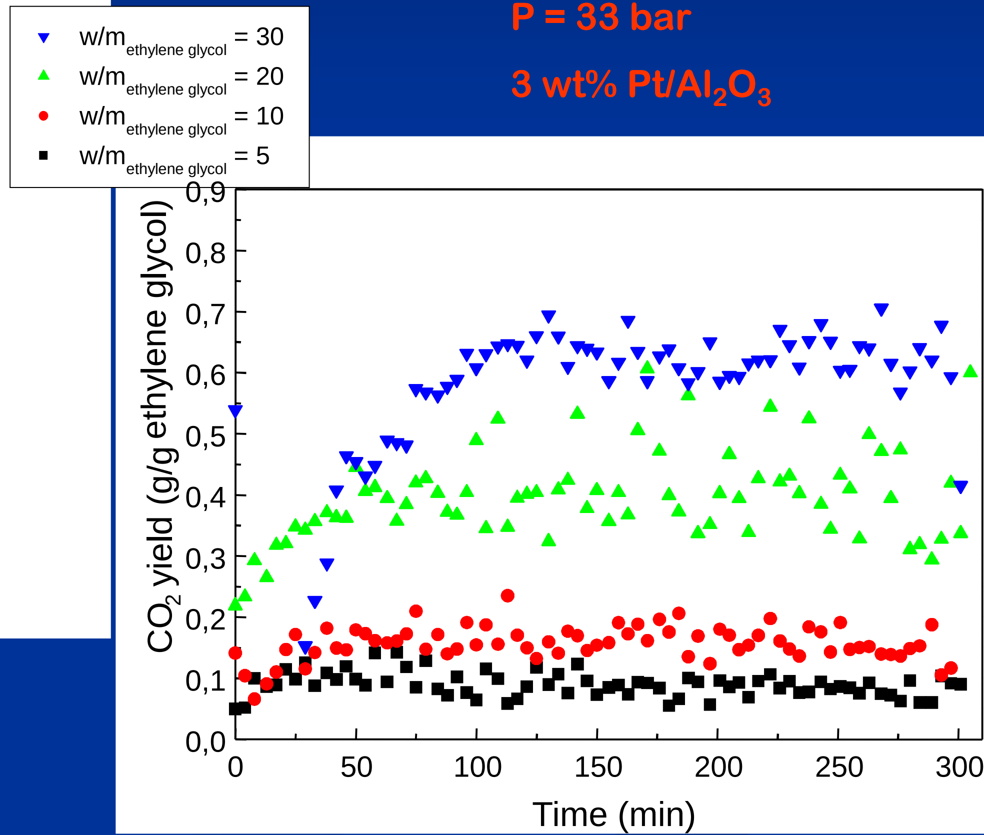
INFLUENCE OF W/m

T = 500 K

P = 33 bar

3 wt% Pt/Al_2O_3

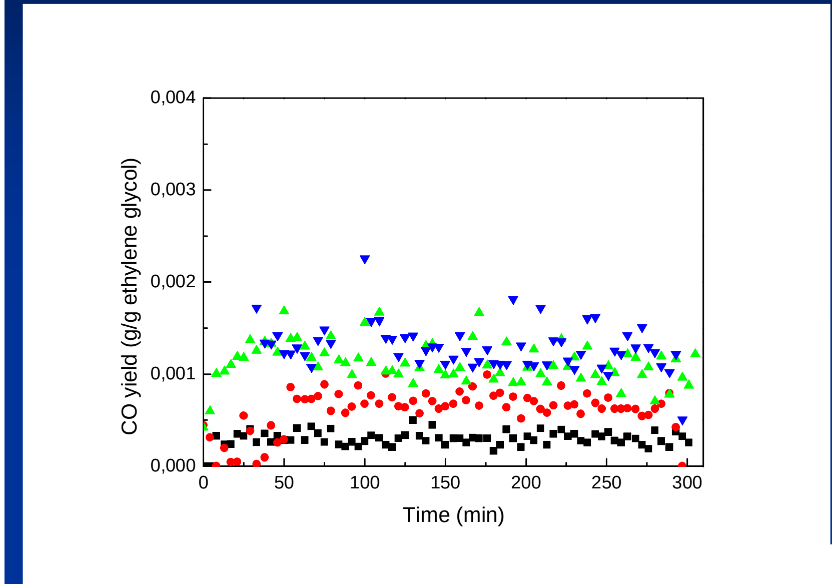


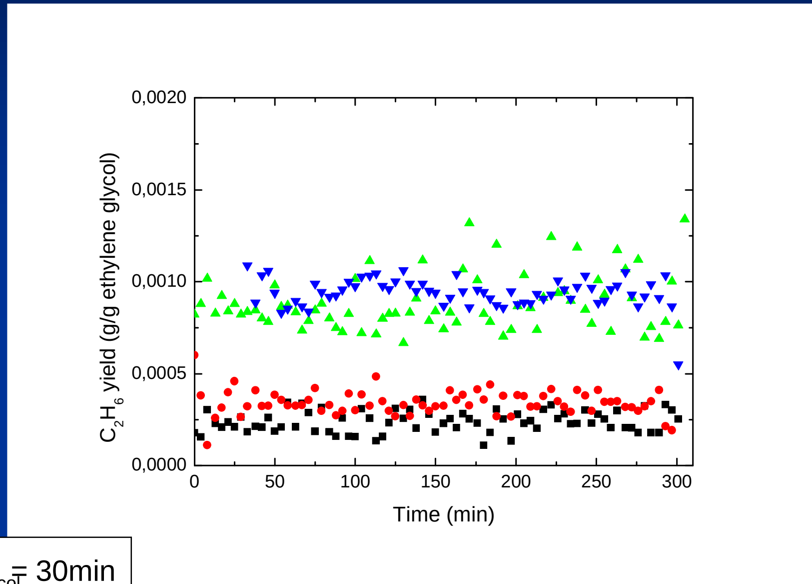


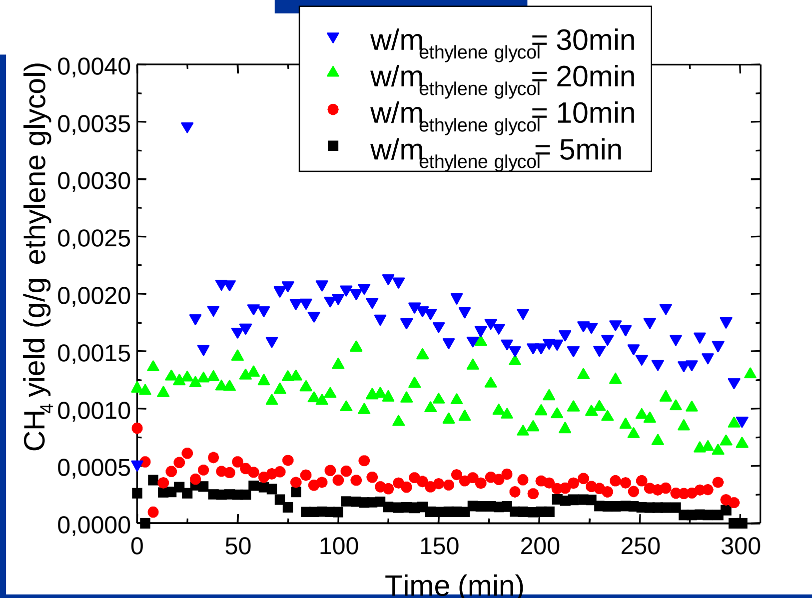
W/m ↑ carbon conversion ↑

W/m ↑ gas yield ↑

INFLUENCE OF W/m







T = 500 K

P = 33 bar

3 wt% Pt/Al_2O_3

INFLUENCE OF CATALYST

Run #	6	8	9
Catalyst weight (g)	1	1	1
$W/m_{ethylene\ glycol}$ ($g_{catalyst}$ min/$g_{ethylene\ glycol}$)	20	20	20
Catalyst	3% Pt	1% Pt	28 % Ni
Recovery	95.63	96.95	98.83
Carbon conversion (%)	32.13	18.50	22.98
Gas yields (g/$g_{ethylene\ glycol}$):			
H_2	0.0444	0.0259	0.0246
CO_2	0.3971	0.2359	0.2283
CO	0.0011	0.0013	0.0252
CH_4	0.0011	0.0004	0.0156
C_2H_6	0.0009	0.0003	0.0020
Gas composition (mol %, N_2 and H_2O free):			
H_2	70.81	70.49	63.27
CO_2	28.75	29.06	26.72
CO	0.13	0.24	4.63
CH_4	0.22	0.15	5.03
C_2H_6	0.09	0.06	0.35
Selectivity (%):			
H_2	96.63	95.28	68.26
Alkane	1.38	0.91	15.43

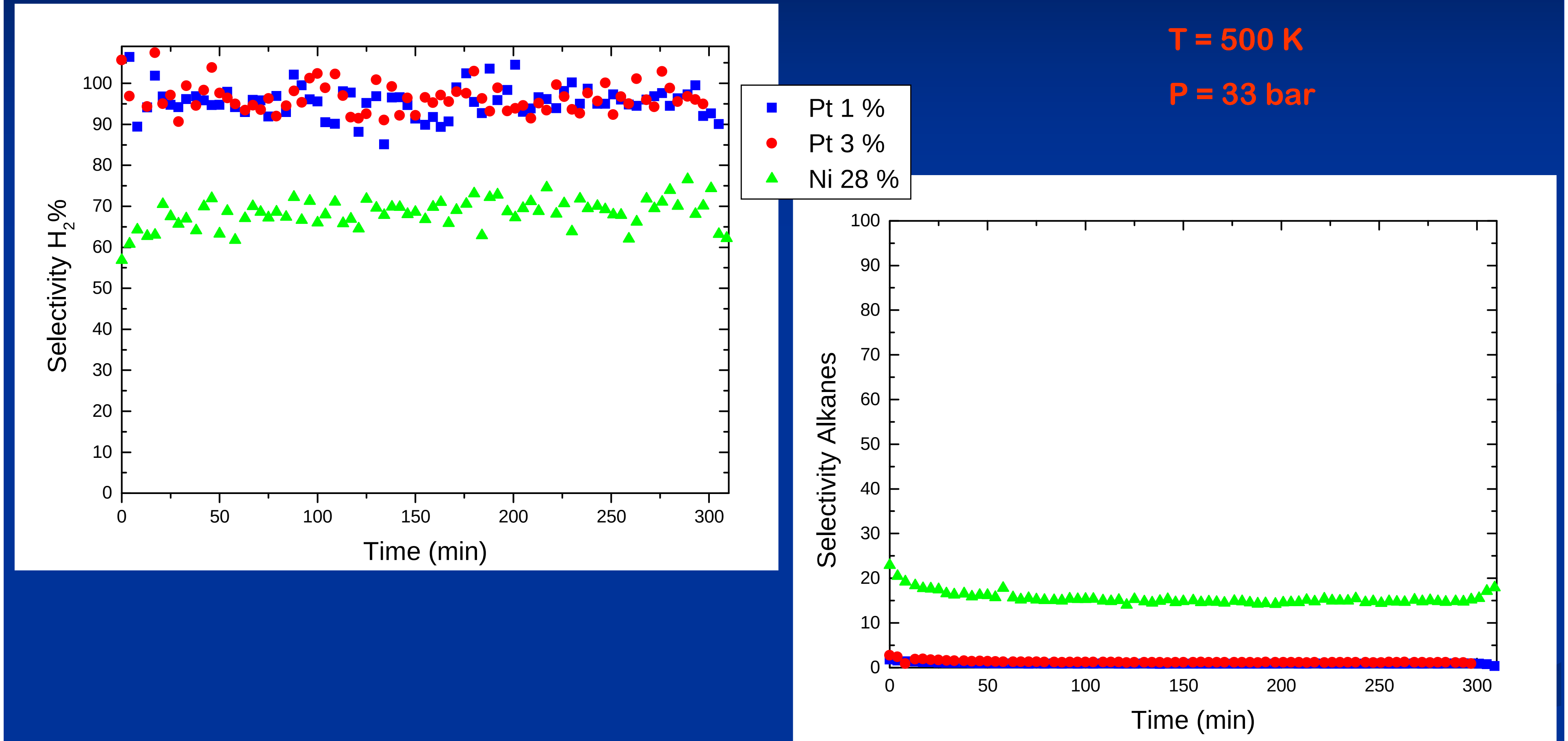
T = 500 K

P = 33 bar

INFLUENCE OF CATALYST

T = 500 K

P = 33 bar



Hydrogen selectivity: 3 wt% Pt = 1 wt% Pt > 28 wt% Ni

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CONCLUSIONS:

1. <u>Influence of the system pressure:</u>

- ✓ Higher carbon conversion to gas with pressure.
- ✓ No deactivation from hydrogen is observed.

2. <u>Influence of W/m ethylene glycol:</u>

- ✓ Higher carbon conversion with W/m ratio (50.99% for 30 g catalyst min/g ethylene glycol).
- ✓ Hydrogen selectivity was almost unchanged.
- ✓ Gas yields increases with W/m ratio.

3. <u>Influence of catalyst:</u>

- ✓ Hydrogen selectivity: 3 wt% Pt = 1 wt% Pt > 28 wt% Ni

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