Synthesis gas by catalytic steam reforming of bio-oil.

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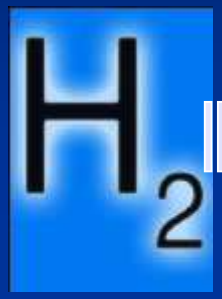
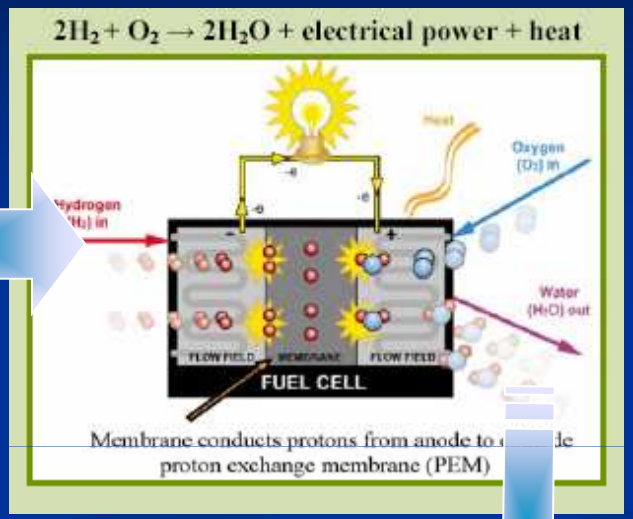
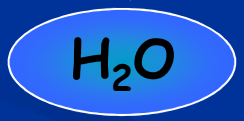
Grupo de Procesos Termoquímicos

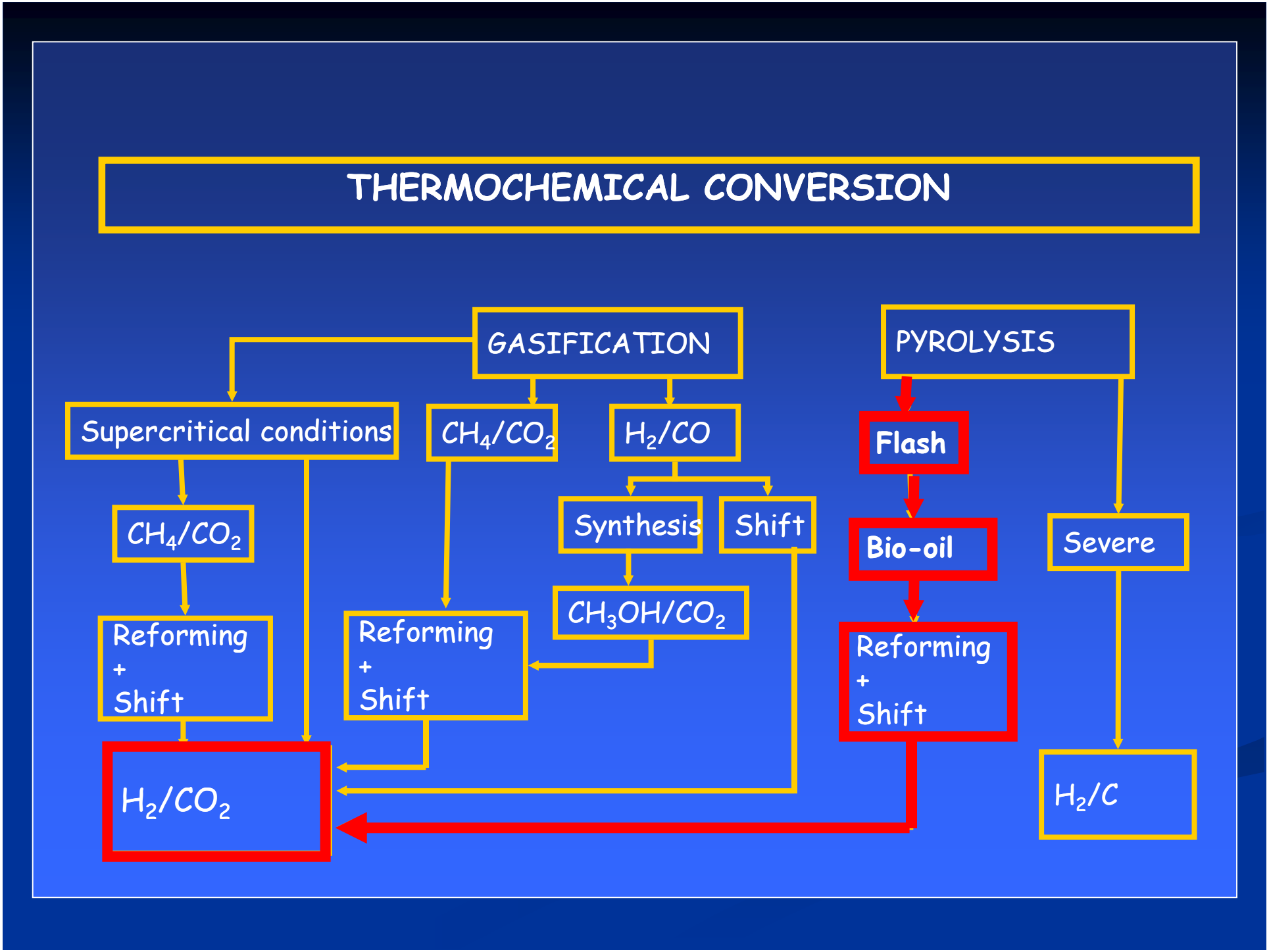
Hydrogen economy:







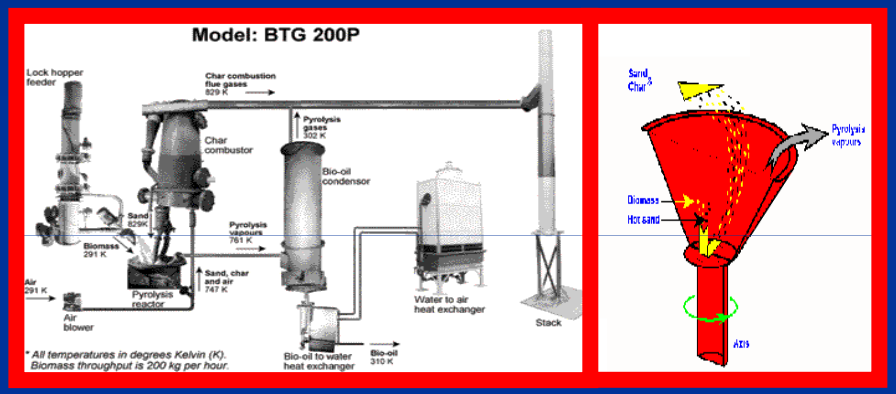
- Increasing interest in Hydrogen economy:
  - Several chemical uses.
  - Utilization as clean fuel in high energetic efficiency systems like fuel cells in stationary, mobile or portable applications that can be used in vehicles.

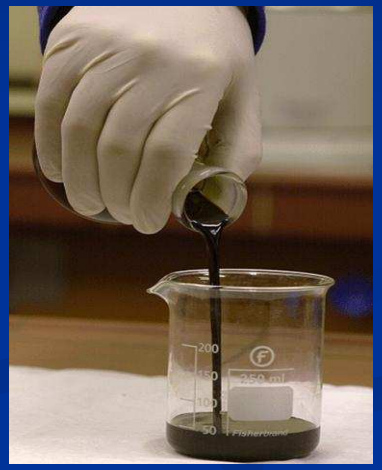

THERMOCHEMICAL CONVERSION
GASIFICATION
PYROLYSIS
Supercritical conditions
CH4/CO2
H2/CO
Flash
CH4/CO2
Synthesis
Shift
Bio-oil
Severe
Reforming + Shift
CH3OH/CO2
Reforming + Shift
Reforming + Shift
H2/CO2
H2/C

Steam reforming of pyrolysis liquids (Bio-oil):

Pyrolysis

Bio-oil



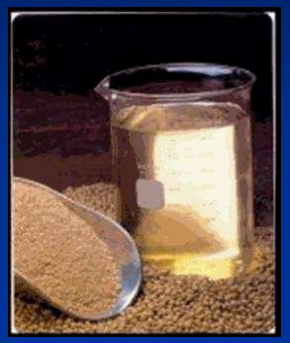


BTG process (fast pyrolysis)

- Complex mixture of organic compounds and water*.
- Are unstable and suffer from aging.

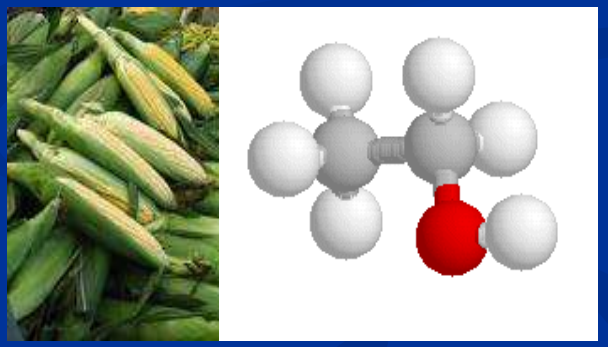
* Oasmaa, D. Meier, J. Anal. Appl. Pyr., 73 (2005) 323

Steam reforming:



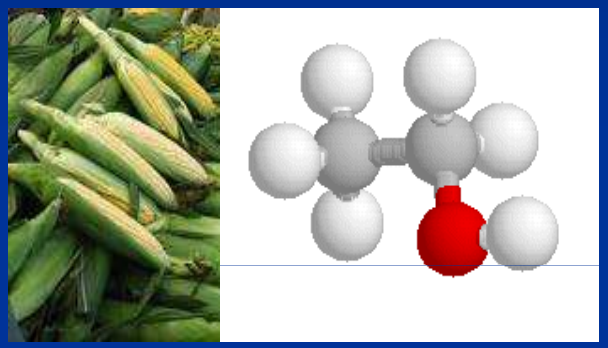
- Vegetable oils:
  - Sunflower
  - Soya
  - Rapeseed
  - Palm
  - …

- Trap grease

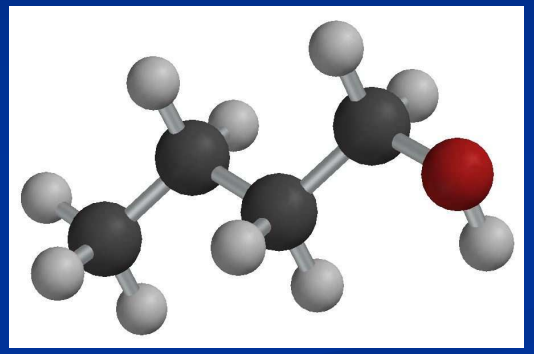


- Bioethanol

Steam reforming:



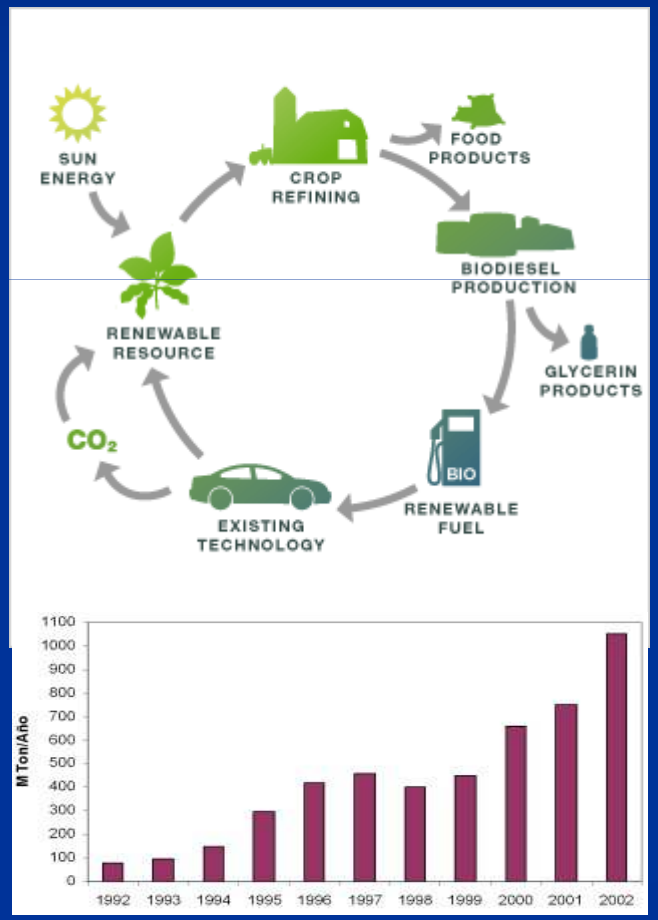
- Bioethanol



- Biobutanol

Steam reforming:

- 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

Steam reforming of pyrolysis liquids (Bio-oil):

Aqueous fraction

Higher stability

Ligninic fraction

High valuable coproducts from bio-oil*

* J. Shabtai, W. Zmierczak, E. Chornet, Evironment, Chemicals, Fibers and Materials (Ed. by R.P. Overend, E. Chornet) Vol2 (1997) 1507

OBJECTIVES:

- Experimental work with model compounds and with the aqueous fraction of bio-oil both at micro and bench scales.

- Development of suitable catalysts for the process:

  - Adequate catalytic activity and selectivity towards H_2.
  - Resistance to deactivation by coking deposition.
  - Resistance to attrition to work at fluidized bed.

- Development of the process at a bench-scale fluidized-bed facility and scale up to a demonstration plant.

CHARACTERISTICS OF BIO-OIL*

*(*Oasmaa and Meier, J. Anal. Appl. Pyrol. 73, (2005), 323)*

- Heterogeneous properties (feedstock)
- Colour: Dark red / brown
- Odour: smoke like
- Quite viscous at room temperature
- Thermally unstable (polymerization)
- High oxygen c
(ca. 40 % dry
- pH: 2.3 –

- Alcohols
- Carboxylic acids
- Sugars
- Aldehydes
- Ketones
- Complex carbohydrates
- Lignin derived materials

ORGANICS / WATER (85/15 w/w)

WATER ADDITION:

AQUEOUS FRACTION

WATER INSOLUBLE FRACTION (Pyrolytic lignin)

Catalytic Steam Reforming *(Czernik et al., 1997)*

Fine Chemicals *(Kelley et al., 1997; Shabtai et al., 1997)*

CHARACTERISTICS OF BIO-OIL*

*(*Oasmaa and Meier, J. Anal. Appl. Pyrol. 73, (2005), 323)*

Table 15
Determination of acids (wt.% based on wet liquid)

	No. 1			
	9[a]	12[a]	3[a]	5[a]
Formic acid	0.29	9.35		5.3
Acetic acid	2.7	7.84	3.31	5.0
Acrylic acid	0.05	0		
Propionic acid	0.17	0.63		
Iso-butyric acid	0.02	0.35		
Methacrylic acid	0.01			
N-Butyric acid	0.07	1.89		
Lactic acid	0.18			
Glycolic acid	0.34	0.62		
Crotonic acid	0.04	0		
Valeric acid	0.01	0.66		
Tiglic acid	0.01	0.06		
4-Methylpentanoic acid	0.01			
3-Hydroxypropanoic acid	Traces			
2-Oxobutanoic acid	0.17			
Levulic acid	0.11			
Benzoic acid	0.02			
Hexanoic acid				
Total	4.2			

[a] Laboratory No.

Table 17
Determination of aldehydes, ketones, and alcohols (wt.% based on wet li

	No. 1			
	9[a]	12[a]	3[a]	5[a]
Formaldehyde	0.84	8.92		3.3
Acetaldehyde	0.14	1.88		
Hydroxyacetaldehyde		3.32	6.42	7.7
Glyoxal		0.24		2.4
Acetol		2.07	7.82	7.1
1-Hydroxy-2-butanone			0.31	
2-Hydroxy-2- cyclopentene 1-one			0.46	
2-Hydroxy-3-methyl- 2-cyclopentene-3-one			0.5	
Propionaldehyde	0.05			
Acetone	0.08	0.21		
Furfural	0.49	0.2	0.81	
(5H)-Furan-2-one			0.6	
5-Hydroxymethylfurfural			0.52	
		1.03		
		0.09		
		0.37		
		2.85		
		0.37		
	1.6	21.6	17.4	20.

Table 18
Determination of sugars (wt.% based on wet liquid)

	No. 1		
	12[a]	3[a]	5[a]
Levoglucosan	3.98	4.83	7.5
Glucose			
Xylose	0.14		
Cellobiosan			2.3
Total	4.1	4.8	9.8

[a] Laboratory No.

- Alcohols
- Carboxylic acids
- Sugars
- Aldehydes
- Ketones
- Complex carbohydrates
- Lignin derived materials

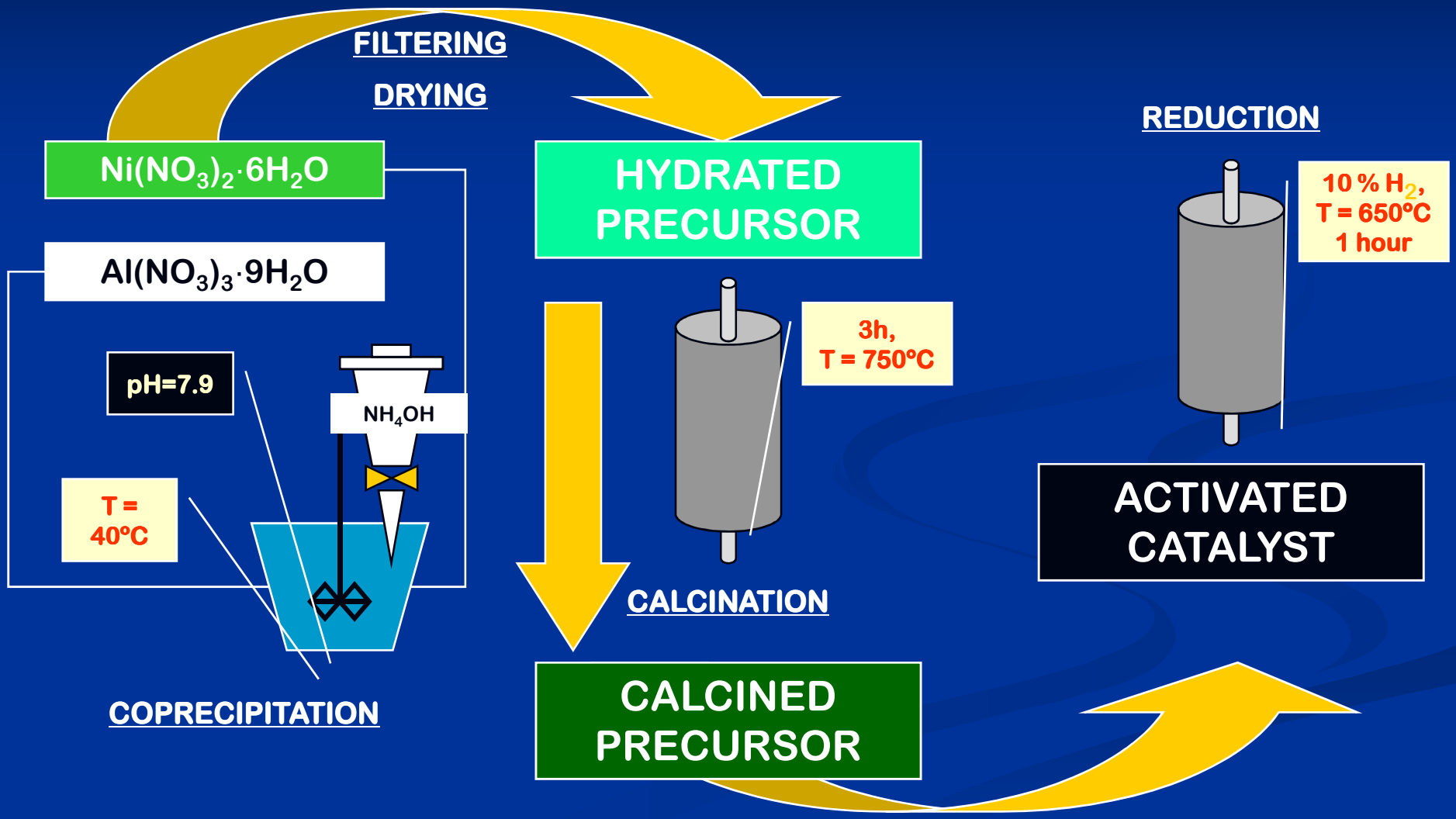
Great complexity!

↓

Experimental work with model compounds:

- Acetic acid
- Acetol
- 1-Butanol
- D-Fructose

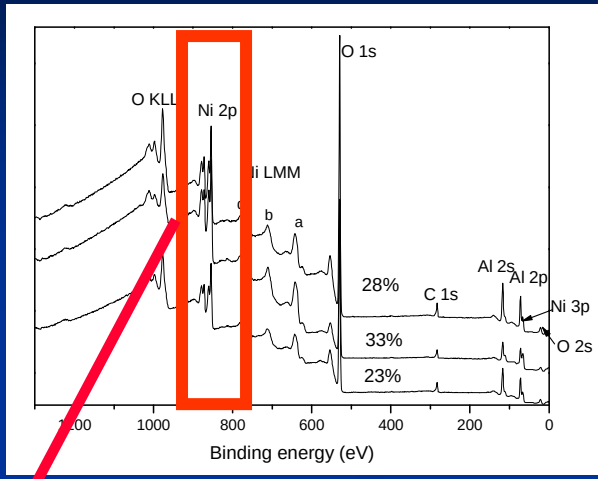
CATALYSTS PREPARED AT INCREASING pH



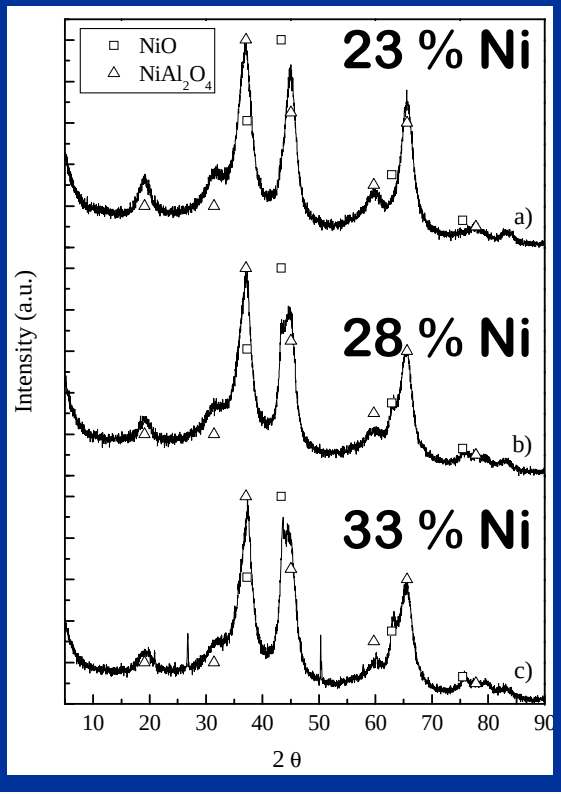
Characterization: Catalysts prepared at increasing pH

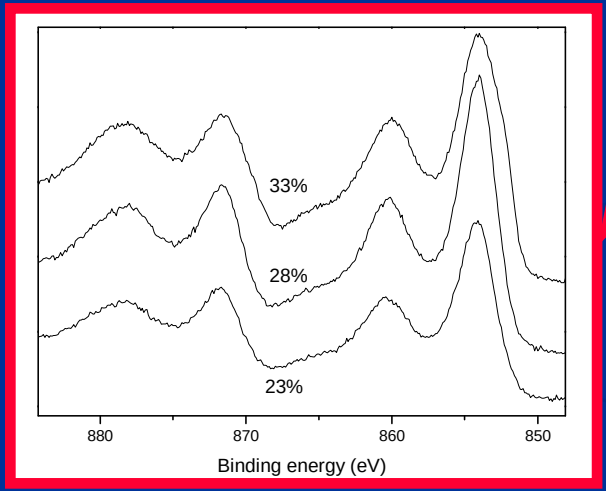
XPS

Sample	Ni $2p_{3/2}$	
23 %	856.6 (2.9)	–
28 %	856.0 (2.8)	–
33 %	856.0 (2.9)	854.3 (1.8)



XRD





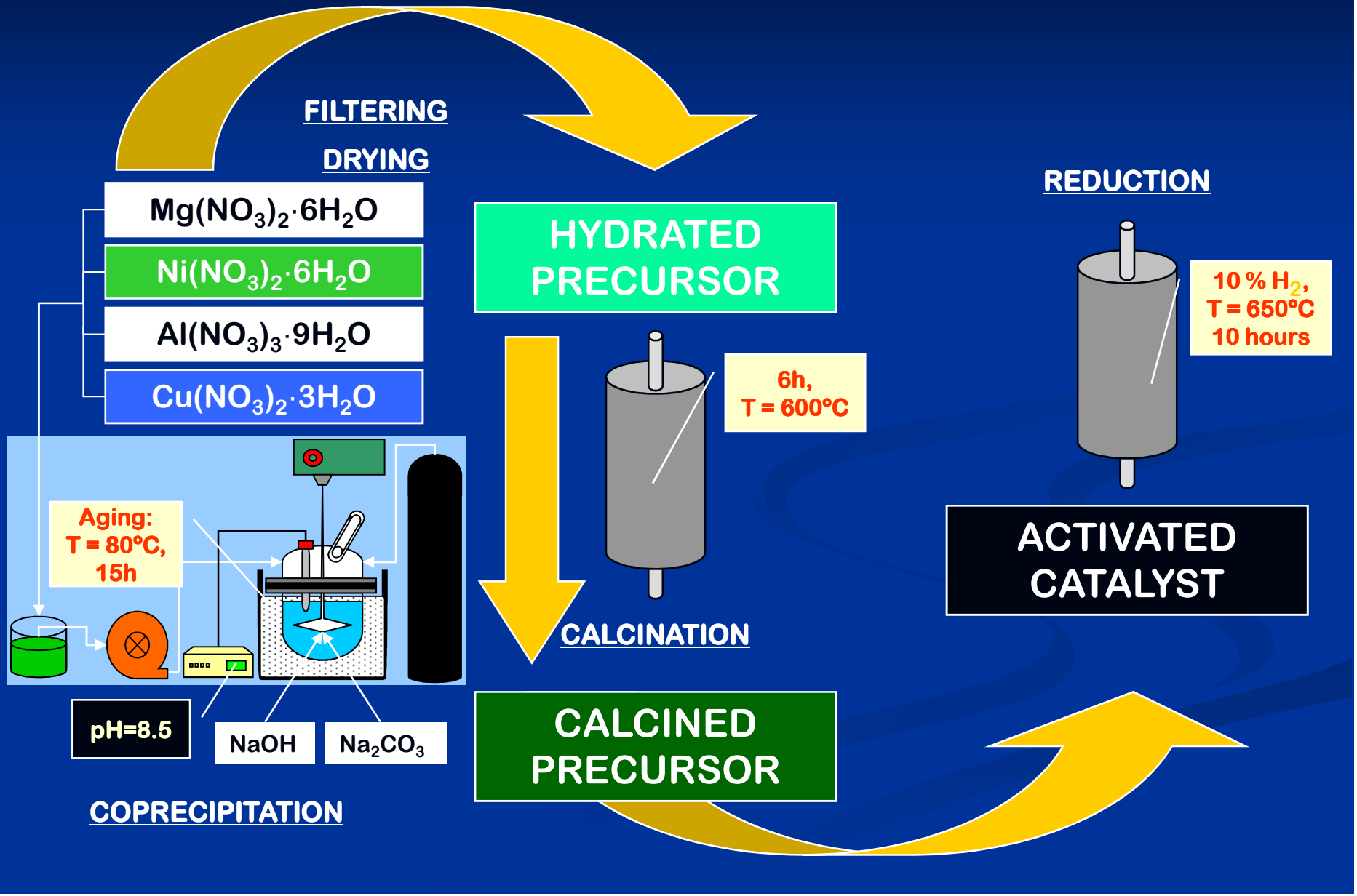
BET:

- 23 % Ni → S_g = 205 m^2/g
- 28 % Ni → S_g = 205 m^2/g
- 33 % Ni → S_g = 180 m^2/g

➔ ICP – OES:

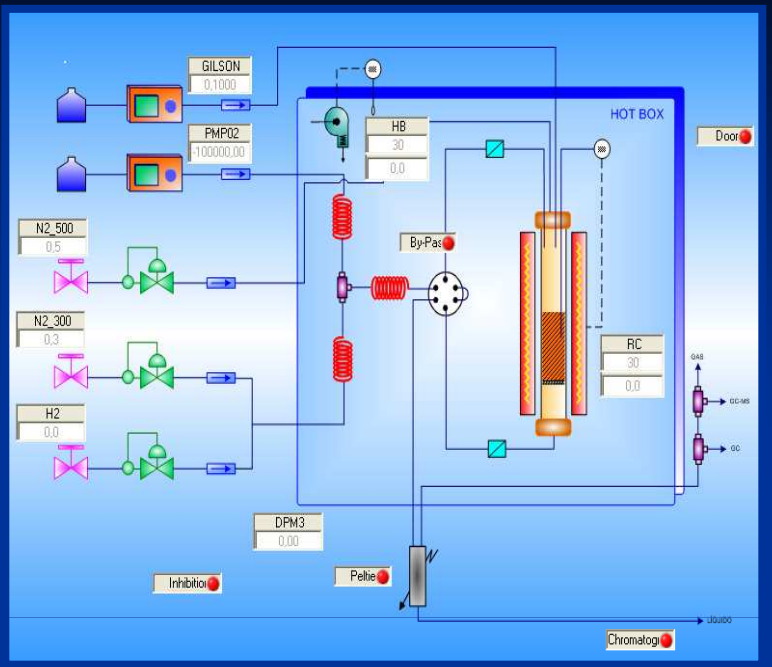
Theoretical	Real
23 %	22.0 %
28 %	26.9 %
33 %	32.1 %

CATALYSTS PREPARED AT CONSTANT pH



Study with Microactivity plant*:

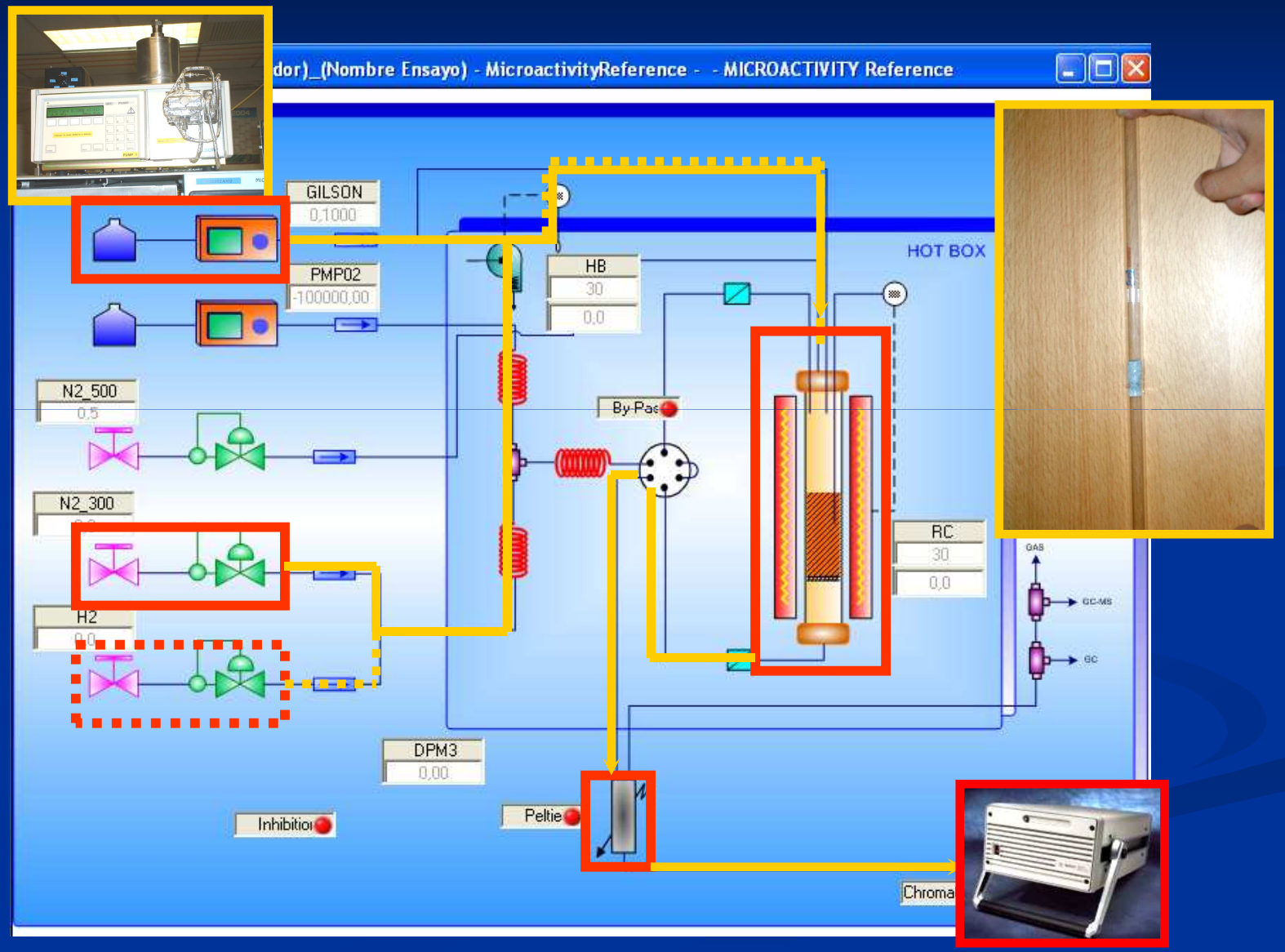
- Microactivity plant:
  - Micro-scale fixed bed
- Experiments with different model compounds:
  - Acetic acid
  - Acetol
  - 1-Butanol
  - D-Fructose
- Optimized experimental conditions:
  - 650ºC
  - 1 h previous reduction



* Nickel content of the catalyst: 23, 28 and 33 % (Ni/(Ni+Al) relative at. %)
  * Ni/Al modified with Cu and Mg: Collaboration with the Norwegian University of Science and Technology (NTNU, Trondheim (Norway)).

*Results reported by Bimbela, F. et al., J. Anal. Appl. Pyrol., 79 (2007) 112

Fixed bed microactivity setup

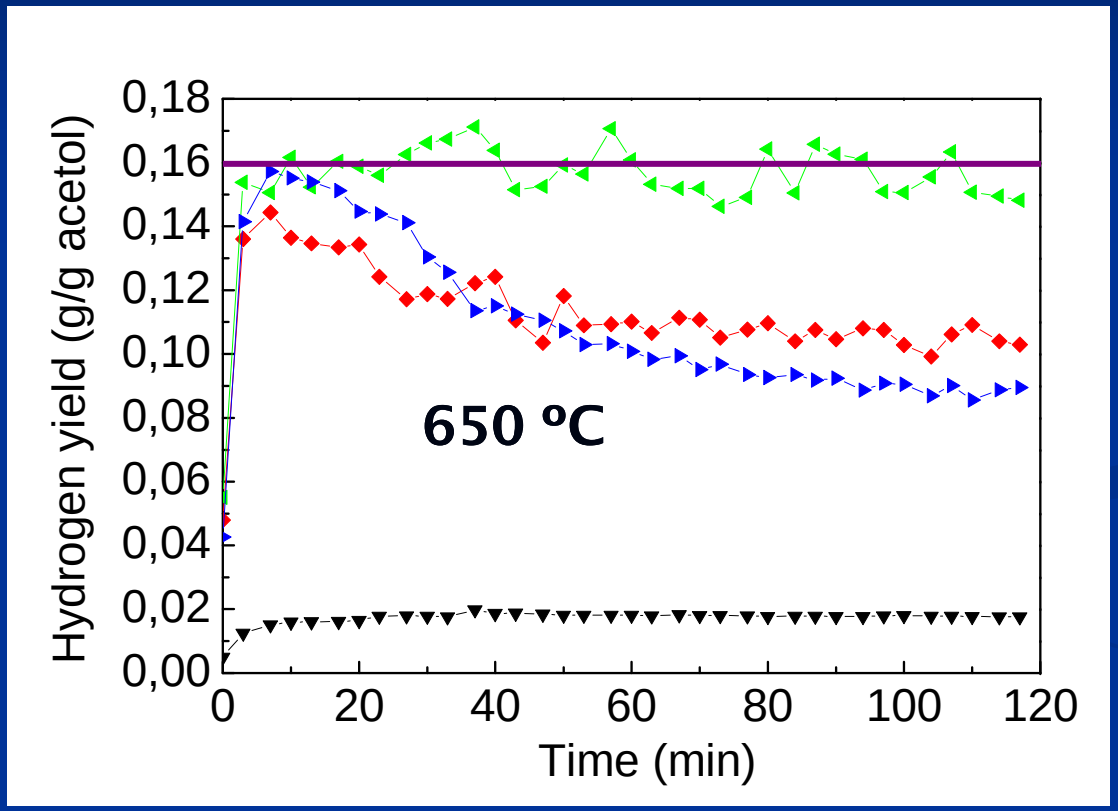


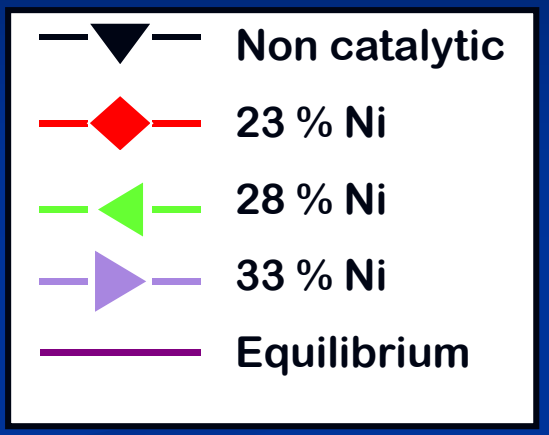
Experimental Conditions

- Atmospheric pressure, reaction temperature set at 650°C.
- Liquid feeding rate: 0.15 mL/min of acetic acid aqueous solution (23% w/w)
- 0.05 g of catalyst and ca. 1.5 g sand (particle size: 160-320 μm)
- W/m_{HAc} ~ 1.46 $g_{catalyst} \cdot min/g_{acetic\ acid}$, S/C molar ratio = 5.58
- $G_{c1}HSV \sim 28500\ h^{-1}$
- 1 h reduction time
- 2 h reaction time

Catalytic steam reforming of ACETOL: Influence of the nickel content and reaction temperature

($W/\underline{m}_{Ac}$ = 0,88 g cat·min/g Ac)

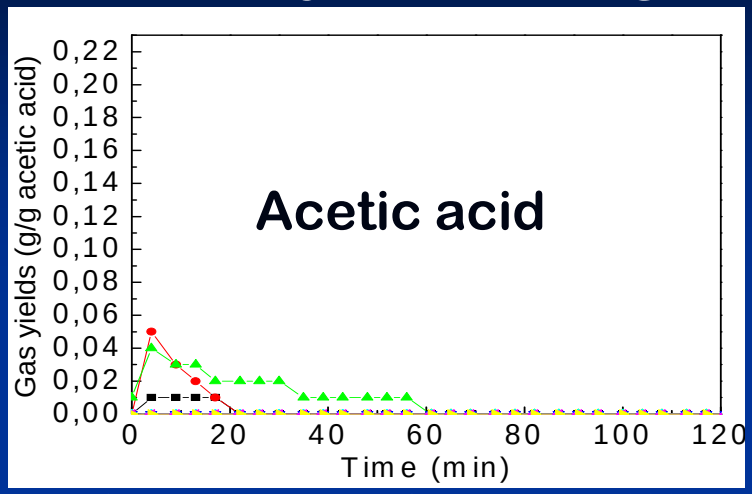


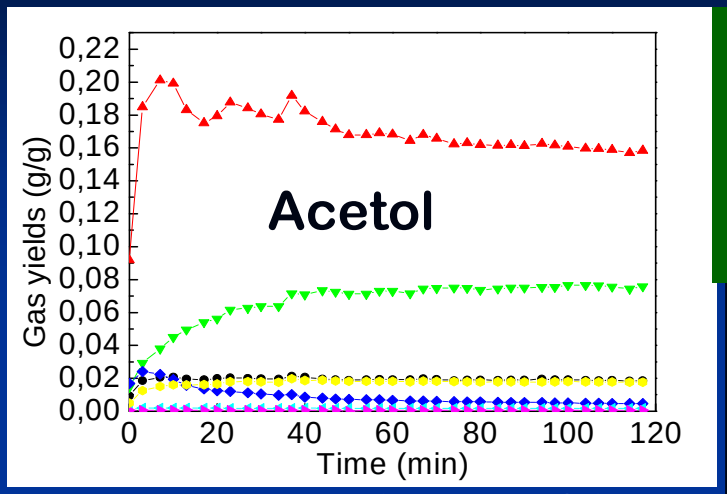


650 ºC: Better performance: 28 % Ni.
23 % y 33 % display similar performances.

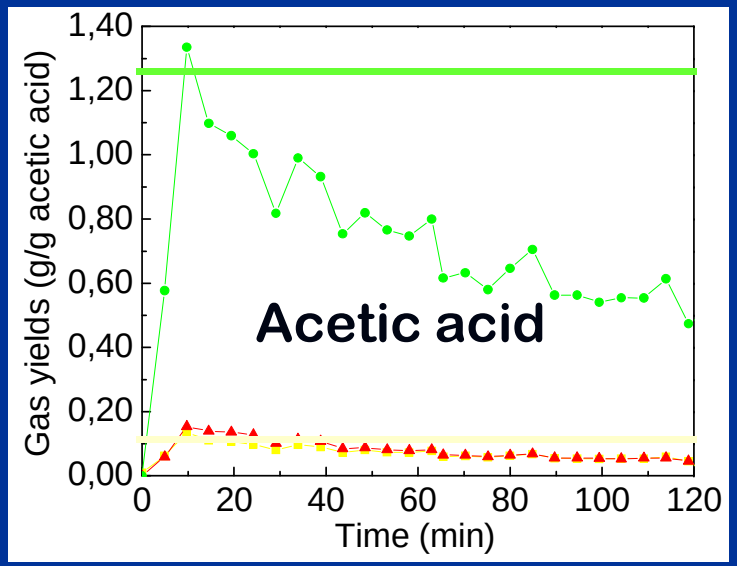
ACETIC ACID VS ACETOL

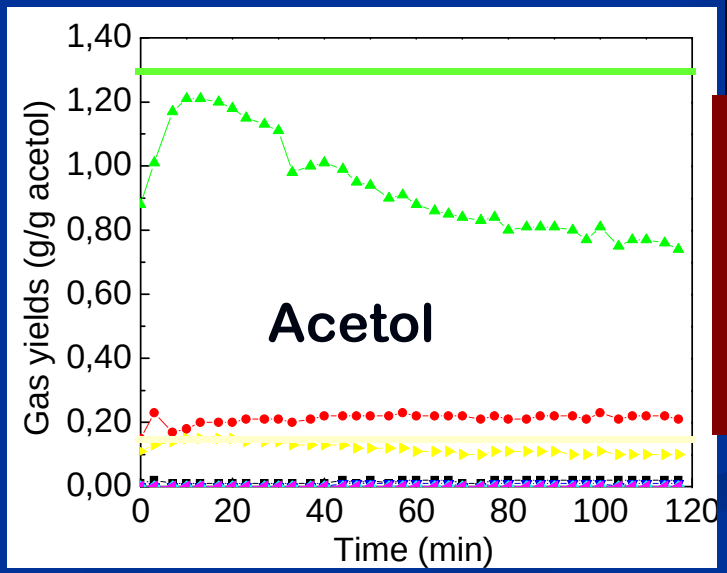
Non catalytic reforming, 650 ºC



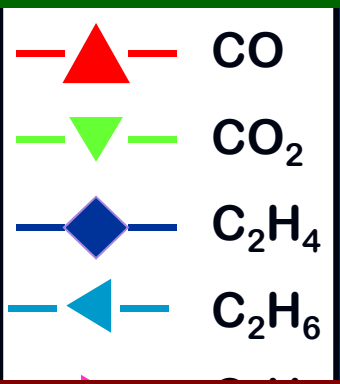


Catalytic Reforming. W/$\underline{m}_{org}$ = 1.46 g·min/g, 650 ºC





- Significant non catalytic reforming for acetol.



- Slower decrease of the catalytic activity for acetol.

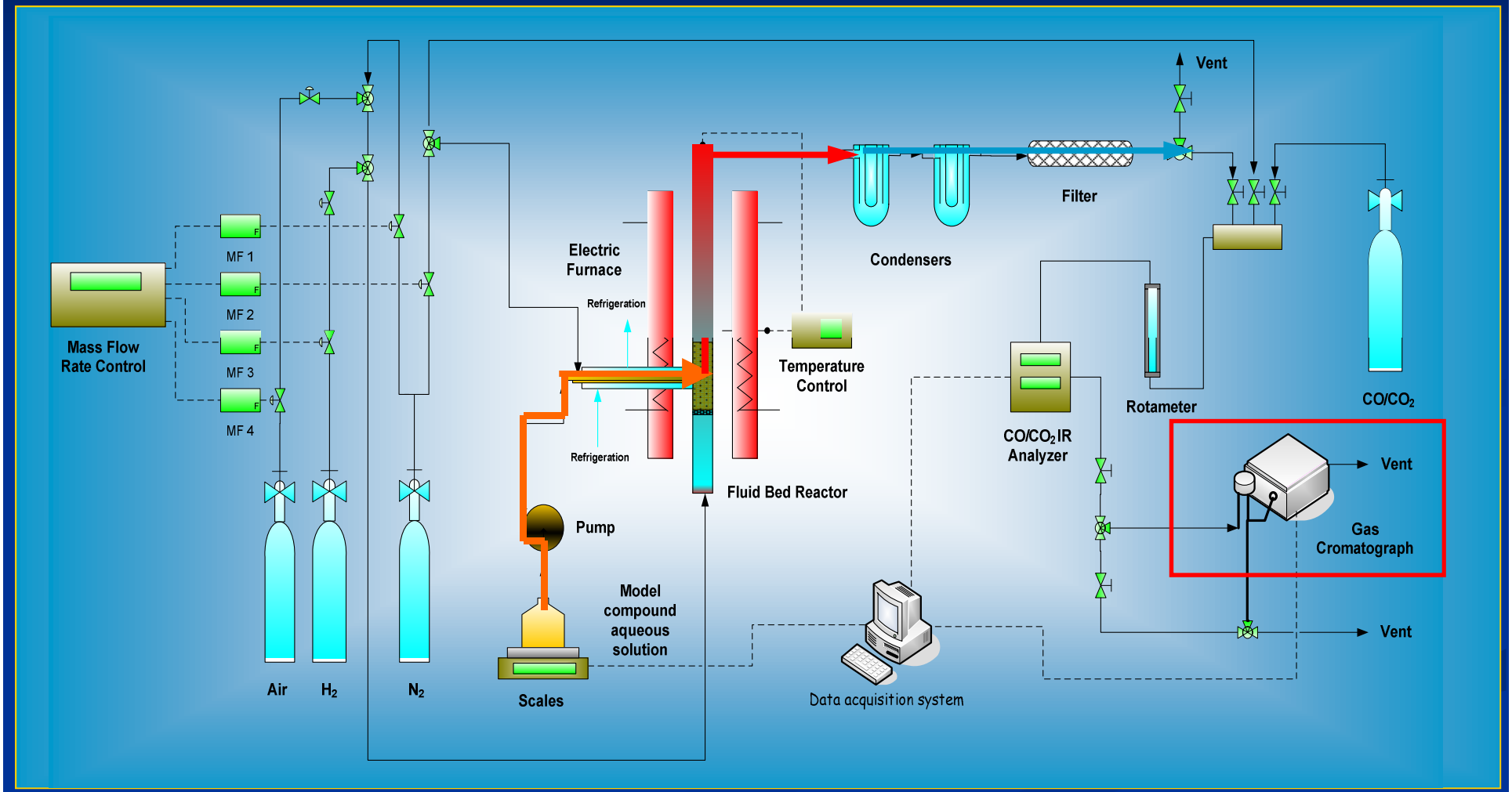
ACETIC ACID VS ACETOL

Chemical	Acetic acid	Acetol
Temperature (°C)	650	650
Catalyst Ni content (%)	33	33
Reaction time (h)	2	2
W/m_{org} (g cat min/g comp)	1.46	1.47
$G_{C1}HSV$ (h^{-1})	28537	34430
Carbon conversion (%)	49.10	73.30
Gas yields (g/g comp)		
H_2	0.073	0.119
CO	0.079	0.209
CO_2	0.721	0.926
CH_4		0.014
C_2H_4		0.004
Gas composition (% mol, N_2 and H_2O free)		
H_2	65.61	66.88
CO	5.03	8.38
CO_2	29.36	23.58
CH_4		1.02
C_2H_4		
C_2H_6		

ACETOL:

- ✓**Better catalytic reforming:**
  - **Much higher carbon conversion.**
  - **Greater gas yields.**
- ✓**CH_4, C_2H_4 and C_2H_6 detected.**
- ✓**Product gas compositions:**
  - **similar H_2**
  - **higher CO**
  - **lower CO_2**

Fluidized bed plant:



Experimental conditions

- Atmospheric pressure and 650°C temperature
- Liquid flow rate: 0.75-0.77 ml/min acetic acid aqueous solution
- 7 cm height bed: 1,1 g catalyst and ~ 38 g sand (particle size of 160-320 μm)
- W/m_{HAc} ~ 6 $g_{catalyst}$·min/$g_{acetic\ acid}$, S/C molar ratio = 5.58
- u/u_{mf} = 10 G_{c1}SHV ~ 6800 h^{-1}
- 2 h reaction time

Screening of catalysts. Attrition tests.

- Fluidization attrition requirements: % weight loss/h < 0.5 % weight/h*
- Maximum resistance to attrition for D catalyst

Catalyst	A*	A2*	B	B2	C	C2	D	D2	E†
Relative atomic % (Ni/(Ni+Al)	15	15	28	28	28	28	28	28	33
Calcination temperature (°C)	750&750	900&750	750	850	750	900	750	900	850
Ca/Ni molar ratio	0.32	0.32	0	0	1.29	1.29	0.31	0.31	5.00
Ca/Al molar ratio	0.06	0.06	0	0	0.50	0.50	0.12	0.12	2.50
Attrition (% weight loss/h)	0.62	0.46	1.16	0.99	1.47	0.69	0.22	0.16	3.25

*Prepared by impregnation. Support calcined at 900°C and impregnated precursor calcined at 750°C.

†Prepared by coprecipitation method at constant pH (precipitating agent: NaOH and $NaNO_3$ solution).

Catalysts:

Catalyst	Preparation method	wt% Ni	Mg/Al molar ratio	Ca/Al molar ratio	Attrition rate (wt%/h)*	Sustainable fluidizable catalyst
NiAl	Coprecipitation	28.5	0	0	1.16	No ✗
NiMgAl0.26	Coprecipitation	29.3	0.26	0	0.27	Yes ✓
NiCaAl0.12	Coprecipitation	26.3	0	0.12	0.22	Yes ✓
NiCaAl0.03 imp	Impregnation	7.5	0	0.03	0.46	Yes ✓

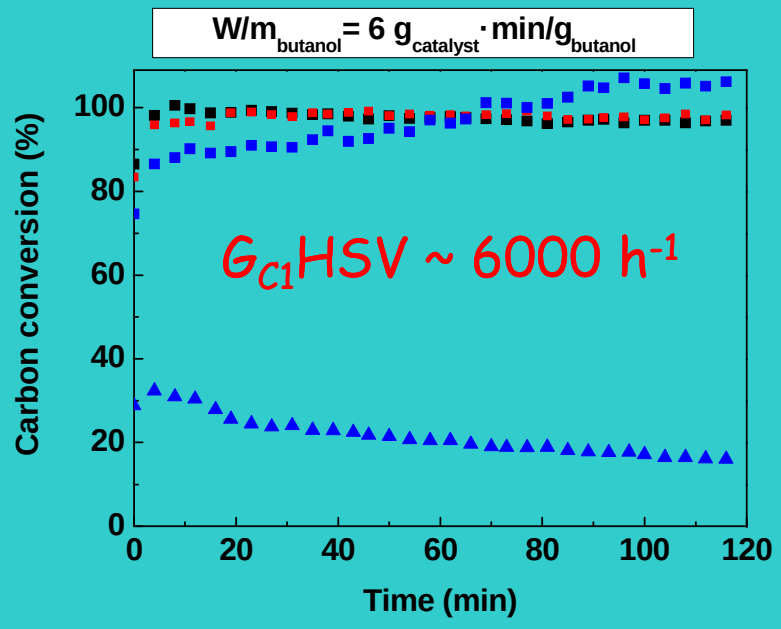
* wt%/h: weight of catalyst lost per hour.
Sustainable fluidizable catalyst when attrition rate < 0.5 wt%/h.

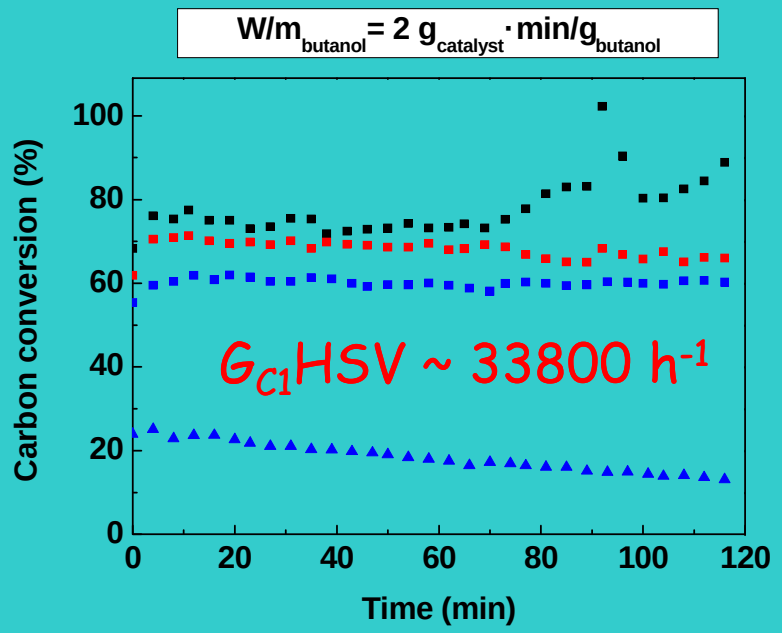
* K.A. Magrini-Bair, S. Czernik, R. French, Y.O. Parent, E. Chornet, D.C. Dayton, C. Feik, R. Bain, Appl. Catal. A, 318 (2007) 199.

Butanol steam reforming:

- NiAl
- NiMgAl 0.26
- NiCaAl 0.12
- NiCaAl 0.03 imp

➢Complete carbon conversion at $G_{C1}HSV$ of araund 6000 h^{-1}





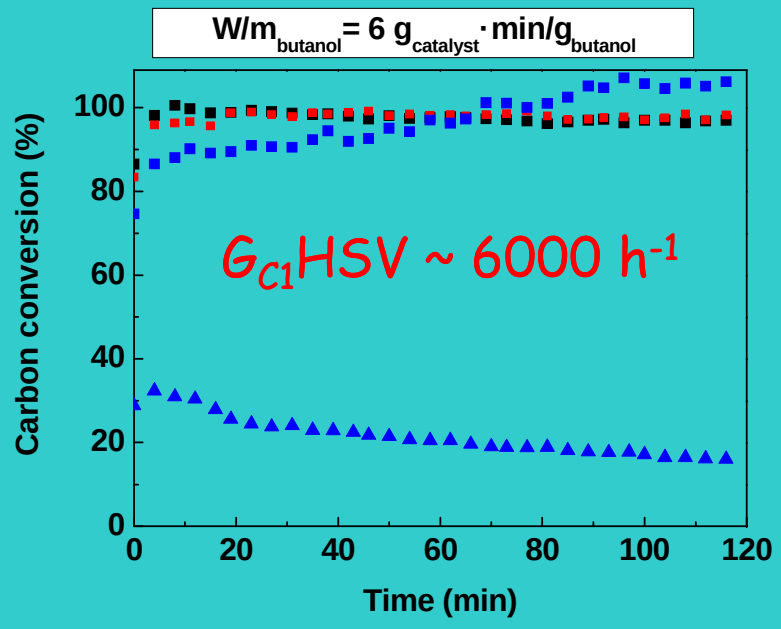
650ºC, 1 atm, S/C = 14.7, u/u_{mf} = 10

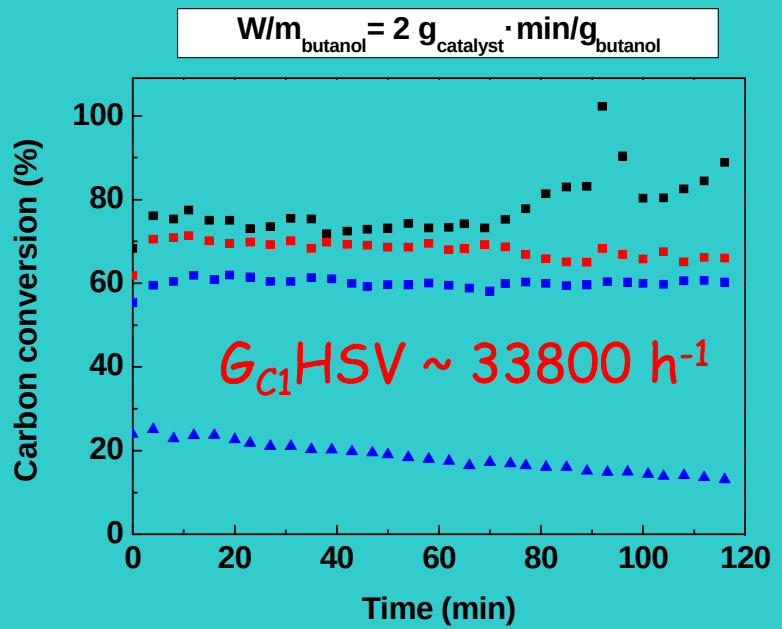
Butanol steam reforming:

- NiAl
- NiMgAl 0.26
- NiCaAl 0.12
- NiCaAl 0.03 imp

➢Except with the impregnated catalyst CaAl 0.03 imp → low activity. ☹👎

Its catalytic activity is lower in butanol steam reforming than in acetic acid or acetol steam reforming where 99% and 88% carbon conversion were obtained respectively. ☺👍



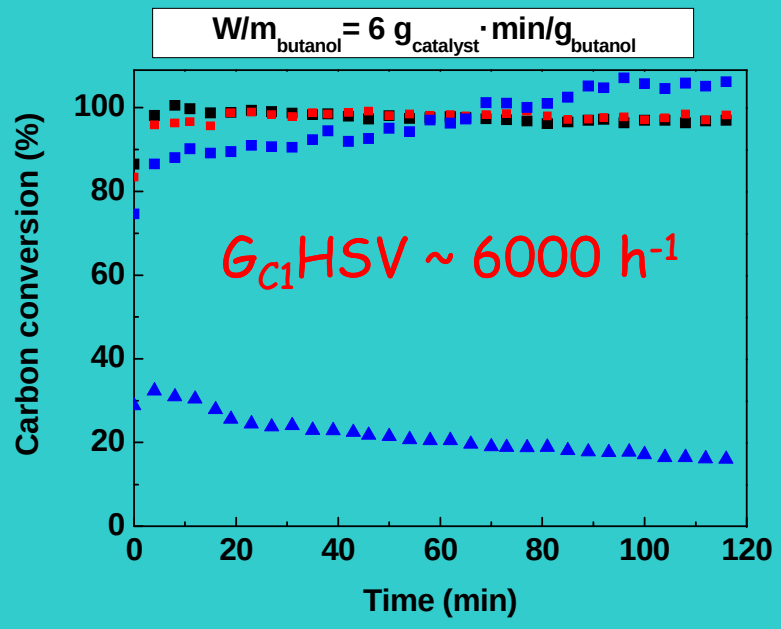


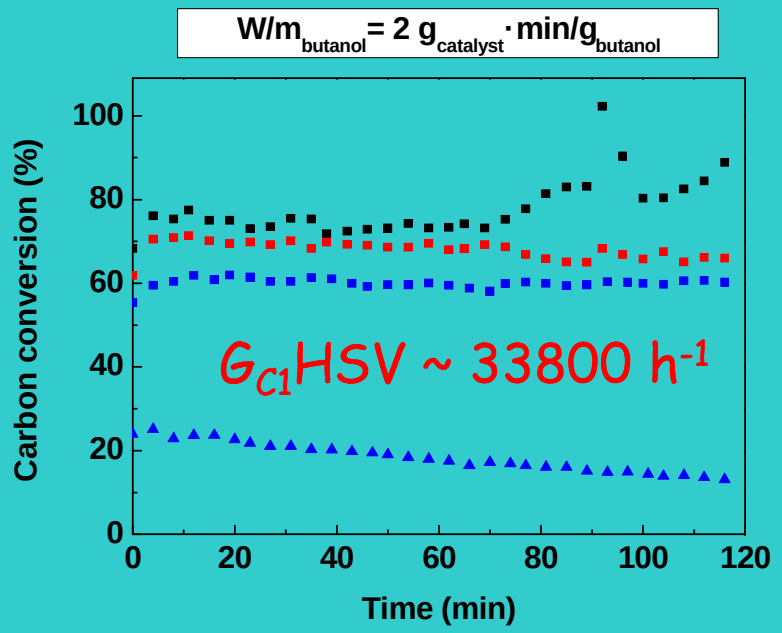
650ºC, 1 atm, S/C = 14.7, u/u_{mf} = 10

Butanol steam reforming:

- NiAl
- NiMgAl 0.26
- NiCaAl 0.12
- NiCaAl 0.03 imp

➢Mg and Ca modified coprecipitated catalysts can perform with a good activity and with a higher resistance to attrition than the non modified Ni/Al catalyst.

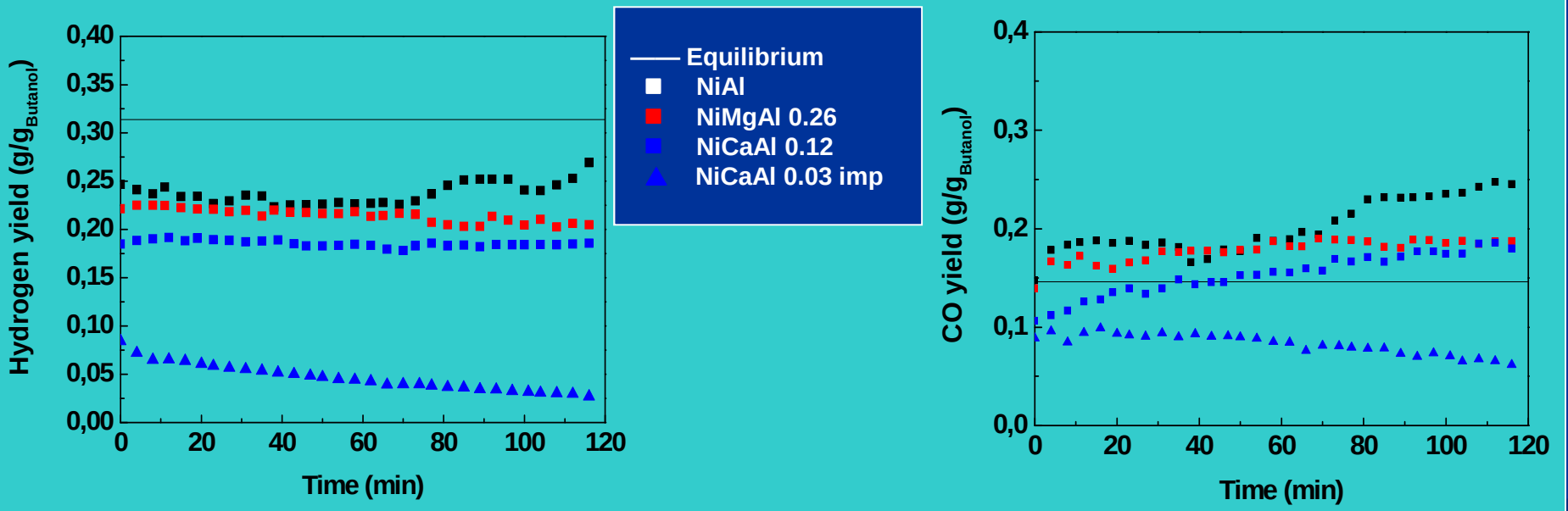




650ºC, 1 atm, S/C = 14.7, u/u_{mf} = 10

Butanol steam reforming:

650ºC, 1 atm, S/C = 14.7, u/u_{mf} = 10, $W/m_{butanol}$ = 2 $g_{catalyst}$·min/$g_{butanol}$

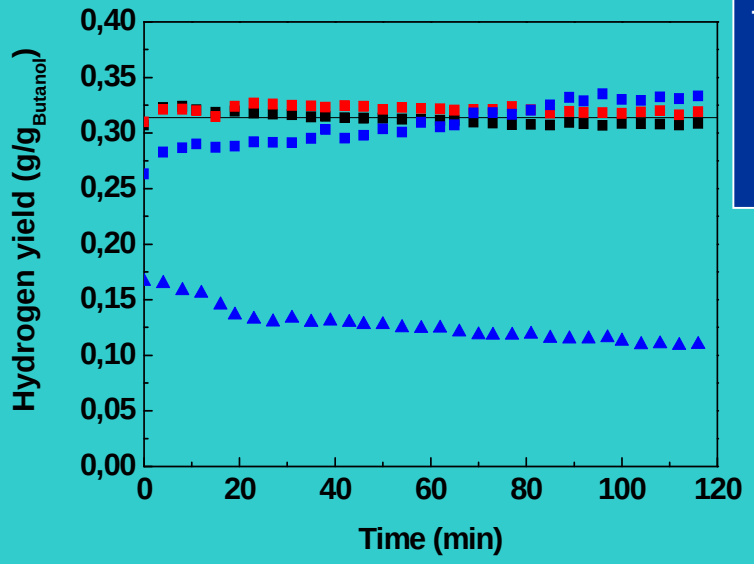


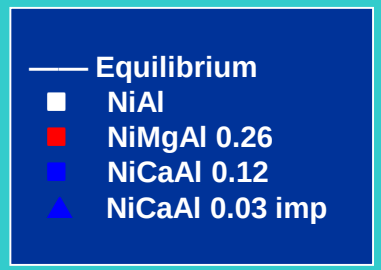
➢Mg and Ca modified catalysts showed close hydrogen yields to the non modified catalysts..

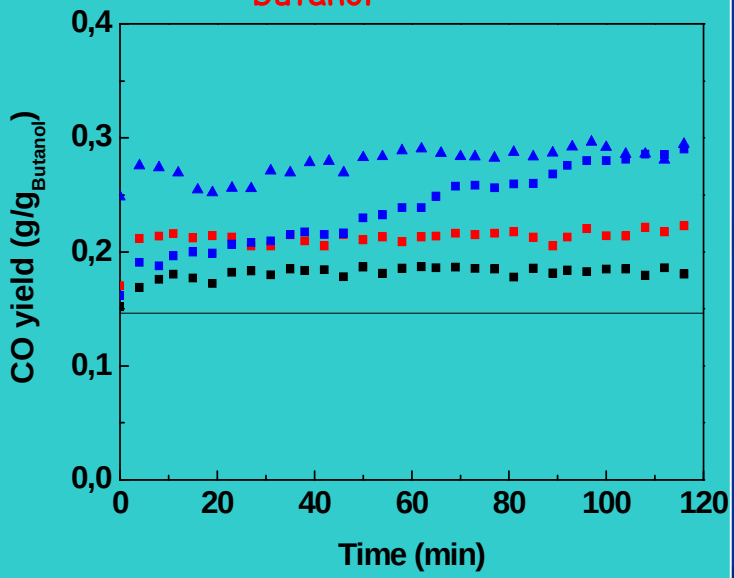
Butanol steam reforming:

650°C, 1 atm, S/C = 14.7, u/u_{mf} = 10, $W/m_{butanol}$ = 6 $g_{catalyst} \cdot min/g_{butanol}$

$W/m_{butanol}$ from 2 to 6







➢Equilibrium hydrogen yields are reached with all the catalysts.

Aqueous fraction of bio-oil

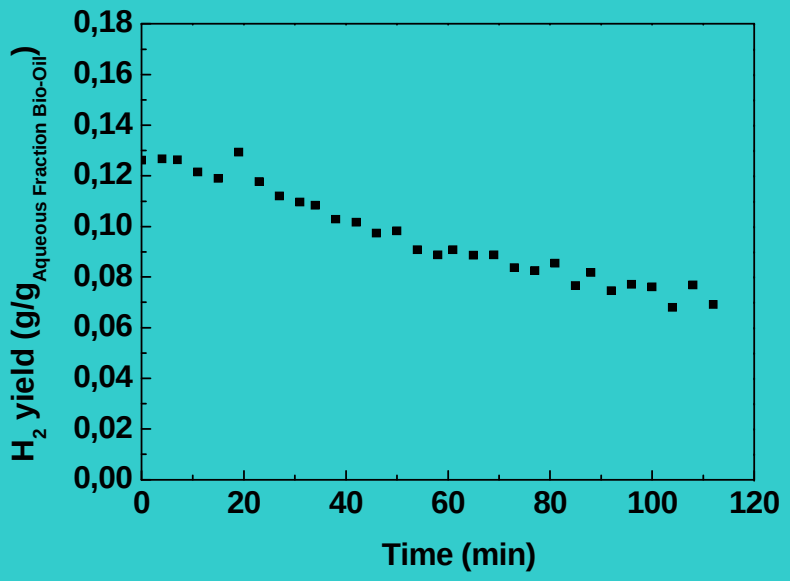
- Bio-oil supplied by BTG (technology based on rotating cone reactor)
- Aqueous fraction prepared by dropwise water addition with continuous stirring
- Elemental analysis: $C_{1.4}\ H_{3.4}\ O_1$.
- S/C = 7.64
- pH = 2.52
- Water/organic mass ratio: 85/15

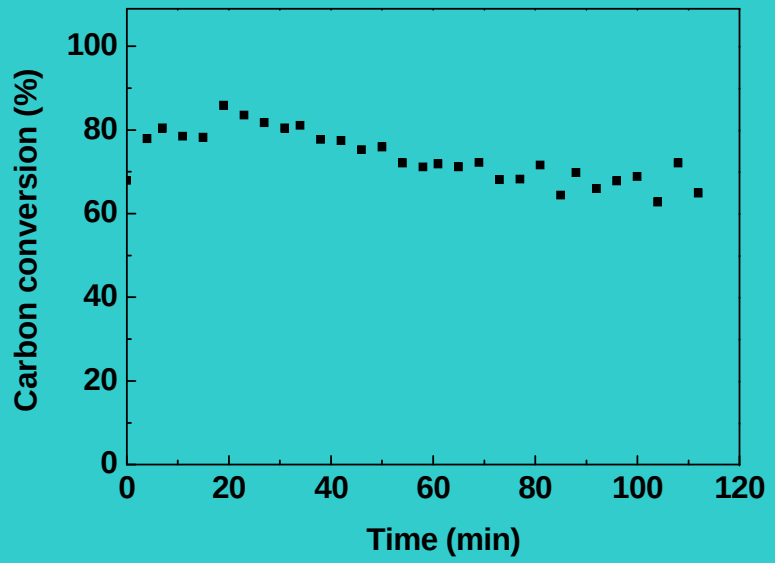
Steam reforming of the aqueous-phase of bio-oil:

NiAl catalyst
28.5 wt% Ni

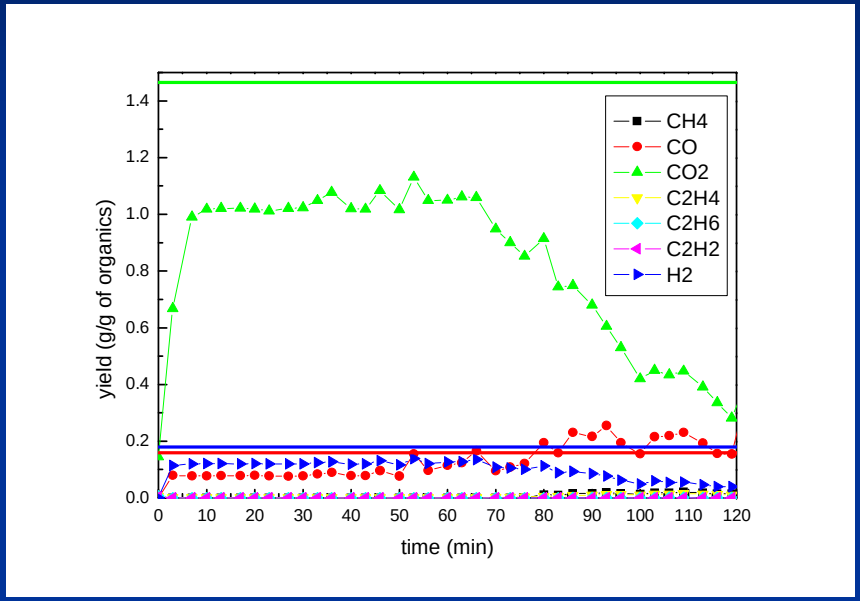
- 73.5% carbon conversion
- 63.3% H2 (%mol, N_2 and H_2O Free)

650ºC, 1 atm, S/C = 7.64, u/u_{mf} = 10
$W/m_{Aqueous\ Fraction\ of\ Bio\text{-}Oil}$ ~ 4, $G_{C1}SHV$ ~ 11800 h^{-1}





Catalytic steam reforming of the aqueous fraction



- Average gas composition (vol. %):
  - H_2 = 67.4
  - CO = 6.3
  - CO_2 = 25.5
  - CH_4 = 0.5

- Experimental conditions: 2 h reaction at 650 °C, G_{C1}HSV = 19000 h^{-1}
- No operational problems detected
- Recovery (liquid+gas) = 97.5 %
- Carbon conversion averages 70 % during the first hour of reaction
- 28 % Ni catalyst reduced in diluted H_2 (H_2:N_2 1:10 vol.) at 650 °C for 1 h
- Other catalysts tested: 23 % and 33 % Ni (increasing pH method) and 0, 1, 3, 5 and 10 % Cu (constant pH method)

Synthesis gas by catalytic steam reforming of bio-oil.

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