



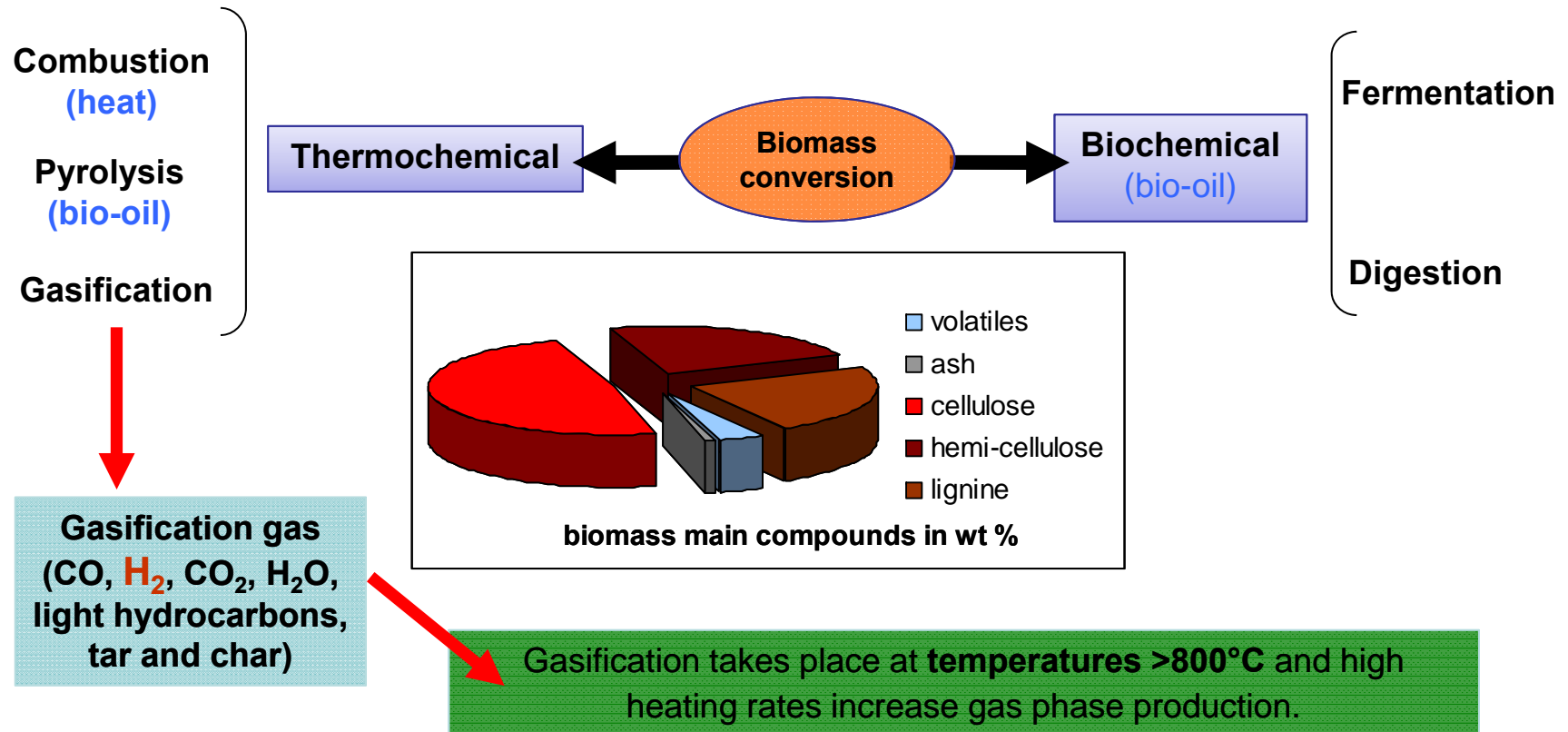
DEVELOPMENT OF CATALYTIC SYSTEMS FOR TAR REMOVAL IN GASIFICATION PROCESSES

P. Ammendola



Biomass conversion technologies

Because of the low energy density of the biomass many practical applications require that it should be first transformed into gaseous, liquid or solid derived-fuels



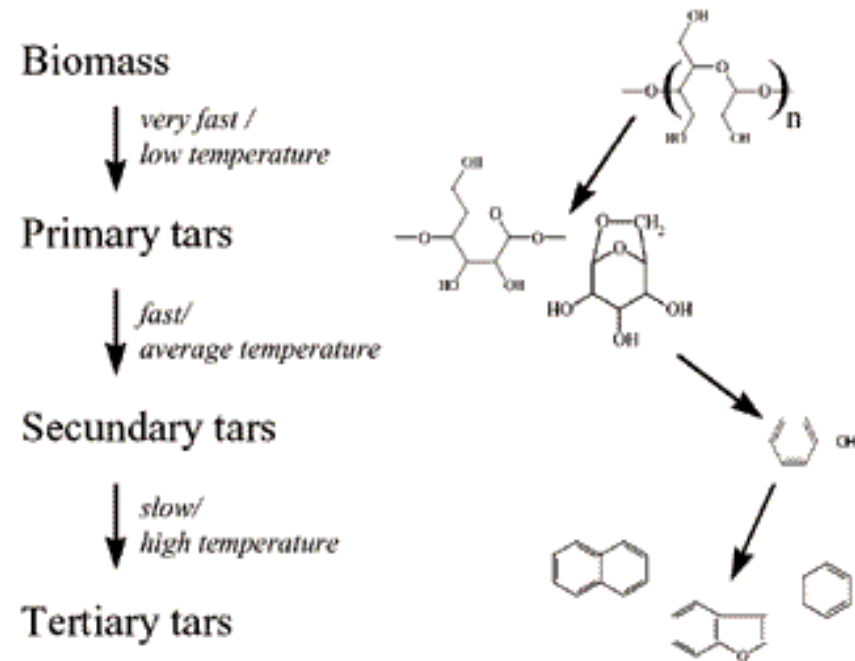


Biomass gasification - Tar production

The gasification of the biomass particle occurs through a fast pyrolytic step which leads to particle devolatilisation producing permanent species and larger condensable molecules called **primary tars**.

Secondary reactions involving primary tars initiates at 700-850°C producing **secondary tars**.

At higher temperatures, tertiary conversion starts (**tertiary tars**) and the soot formation is observed simultaneously.



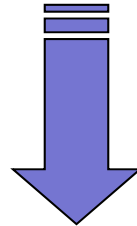
All reactions (cracking, partial oxidation, (re)polymerisation, and condensation reactions) take place in the gas phase between permanent gases and tar vaporized species.



Biomass gasification -Tar issues

Nevertheless, in a gasification process tars represent a severe drawback, since they:

- can condense and plug pipes and block filters
- have, in general, a negative effect on the downstream processes on the produced gas
- and, more important, result in a loss of energetic efficiency of gasification due to incomplete carbon conversion



conversion of these products into permanent gases is required to transform biomass into a suitable fuel for internal combustion engines, gas turbines, fuel cells or a feedstock for chemical synthesis



Catalytic tar conversion

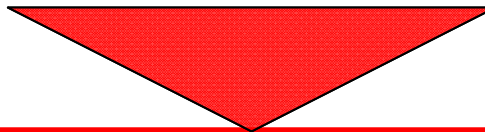
Both mechanical methods and thermal cracking have been proposed for tar removal:

- mechanical methods (such as filtration or wet scrubbing) do not allow energy recovering from tars which are just removed from product gases and, generally, require multiple expensive downstream operation units
- thermal cracking requires temperatures higher than 1100°C to convert them.

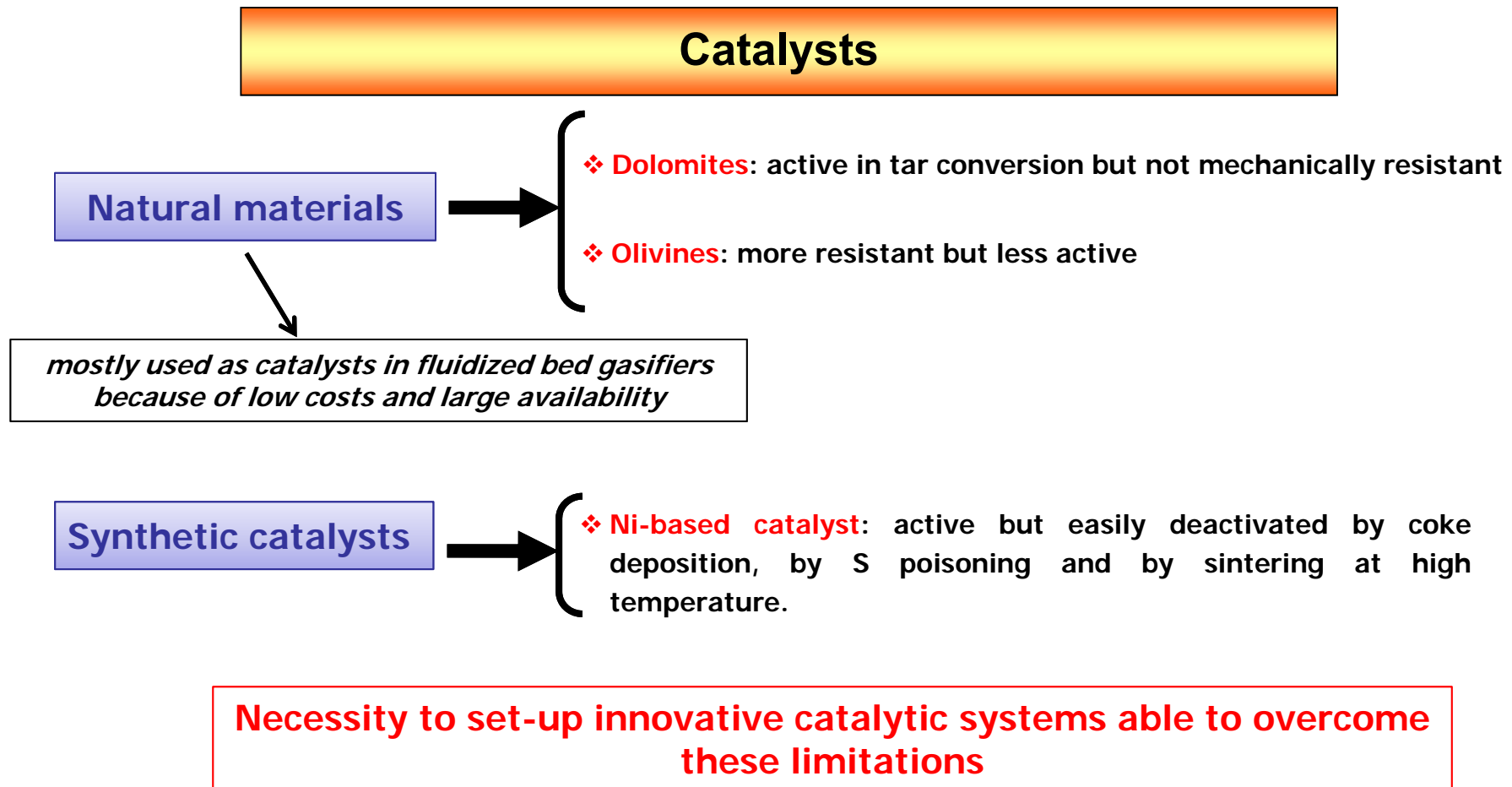
The catalytic tar conversion has been proposed to overcome these drawbacks: it can be operated at significantly lower temperatures (650-850°C) and can remove tar and, at the same time, increase the total gas yield

The use of a catalyst during biomass gasification process has different goals:

1. increasing gas formation
2. Modifying the gas composition promoting reforming reactions of hydrocarbons contained in the gas phase (*reforming properties*).



The gas phase fraction and the hydrogen content can be enhanced provided that tar conversion is catalytically promoted since tars represent a non-negligible unconverted part of the products



Literature studies on catalytic screening of new synthetic catalysts have been generally carried out adopting a single fixed bed catalytic reactor operated with one or more tar model compounds (such as toluene, benzene, naphtalene)

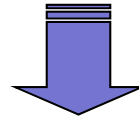


IRC-CNR research activities

Development of a new highly performing synthetic catalyst to improve tar conversion into a hydrogen-rich gas

Requirements:

- mechanical and thermal stress resistance for **longer life-time**
- deactivation due to **coke deposition** on its surface has also to be **limited**
- easy to **regenerate**
- rather **cheap**



Development of a reactor configuration to evaluate catalytic activity under more realistic conditions than using a tar model compound

Requirements:

- **small scale** plant to allow **catalytic screening** with **small amounts** of catalysts
- also useful for **biogenic material characterization**
- operation under different conditions (**pyrolysis, oxy-pyrolysis, gasification**)



Biomass

Maple wood chips (800-900 μm) with low ash content (0.6 wt %) were used as biomass fuel

Proximate analysis (as received)	
Moisture, %wt.	8.9
Volatiles, %wt.	74.6
Fixed carbon, %wt.	15.9
Ash, %wt.	0.6

LHV, MJ/kg	
16.6	

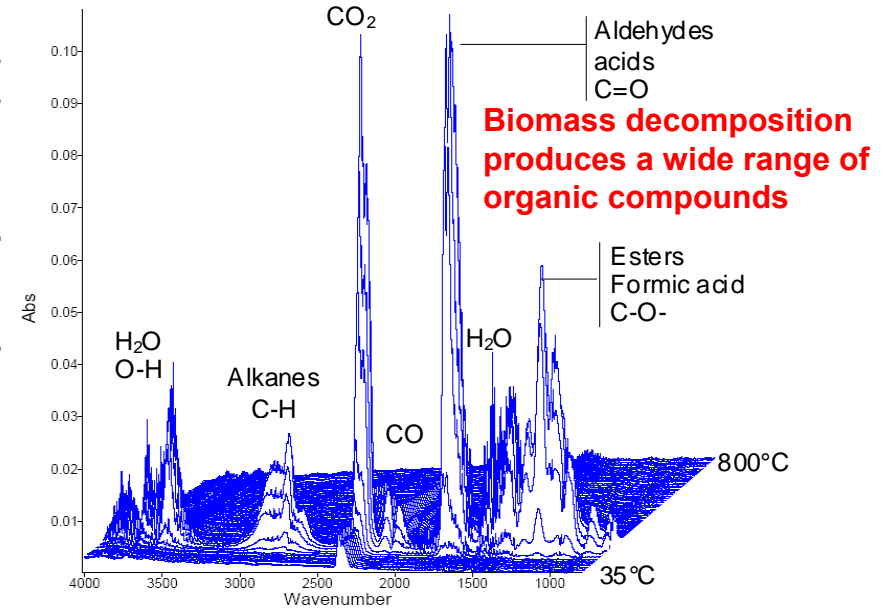
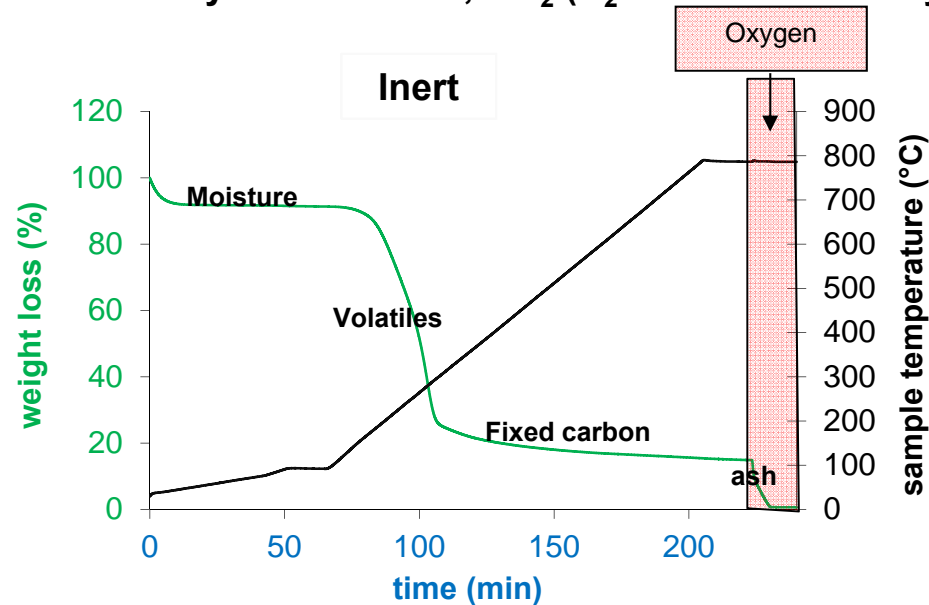


Ultimate analysis (dry basis)	
Carbon, %wt.	46.3
Hydrogen, %wt.	5.6
Nitrogen, %wt.	0
Oxygen, %wt.	47.5
Ash, %wt.	0.6



Biomass TG/FTIR analysis

The maple wood chips **pyrolytically** decomposes in the temperature range 150°C-350°C, producing mainly water followed by volatiles: CO, CO₂ (H₂ is not detected by IR), hydrocarbons and oxygenates



Biomass decomposition produces a wide range of organic compounds

This technique allows the possible **comparison** between different biomass fuels, **BUT.....**

....It can not be useful for a catalytic screening (by placing the catalyst over the solid fuel), since the catalyst must be in its **temperature range of activity (500-900°C)**, whereas biomass decomposes at much lower temperatures



Necessity to use a different set-up for a rapid catalytic screening using small amounts of catalyst and biomass and allowing the contact between catalyst (kept at a fixed temperature in its range of activity) and volatiles emitted from biomass upon its devolatilization (primary tars)

DEVELOPMENT OF CATALYTIC SYSTEMS FOR TAR REMOVAL IN GASIFICATION PROCESSES

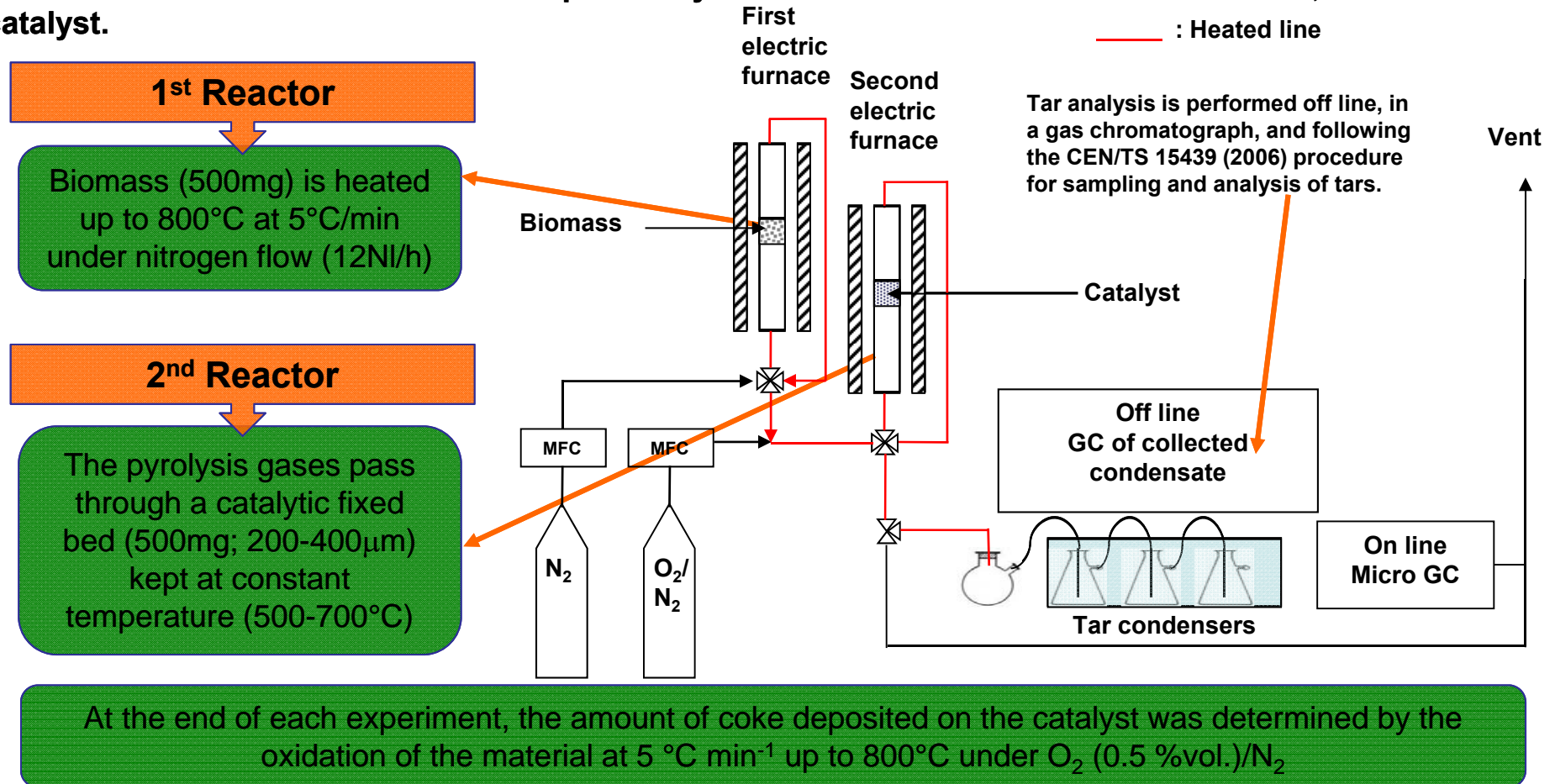
1) H. Yang / Energy & Fuels 18 (2004) 1814-1821. P. Ammendola

IEA Bioenergy - Task 33 Meeting and Workshop, May 13-15, 2014, Ischia Island (Italy)



Lab-scale fixed bed reactor for catalytic screening

Two fixed bed reactors in series independently heated: the first contains the biomass, the second the catalyst.



Catalytic activity is thus measured as difference between the yields and type of gas, liquid and solid (char and coke) products



Preliminary tests - I

Two blank runs were carried out before catalytic tests under pyrolysis conditions:

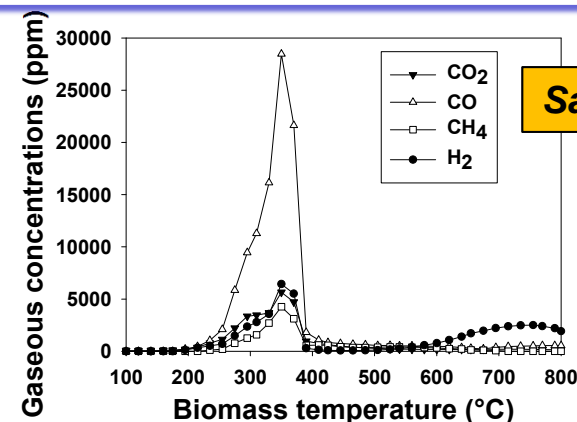
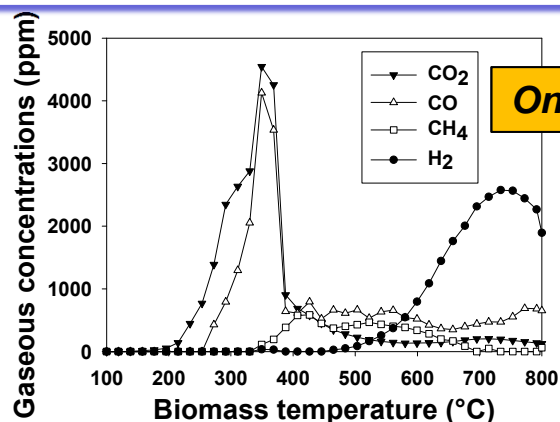
1. The second reactor was excluded → quantitative and qualitative analysis of biomass pyrolysis products
2. The second reactor was loaded with inert sand → evaluation of possible occurrence of thermal cracking reactions at 700°C

Solid, liquid and gas yields on dry basis

Sample	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
-	16.6	-	74.6	7.8
Sand	17.6	-	48.3	32.3

Both char yield and total yield of liquid and gas (corresponding to volatile species) in the first blank run are in agreement with the results of proximate analysis of biomass

Main gas products produced by the biomass as a function of decomposition temperature



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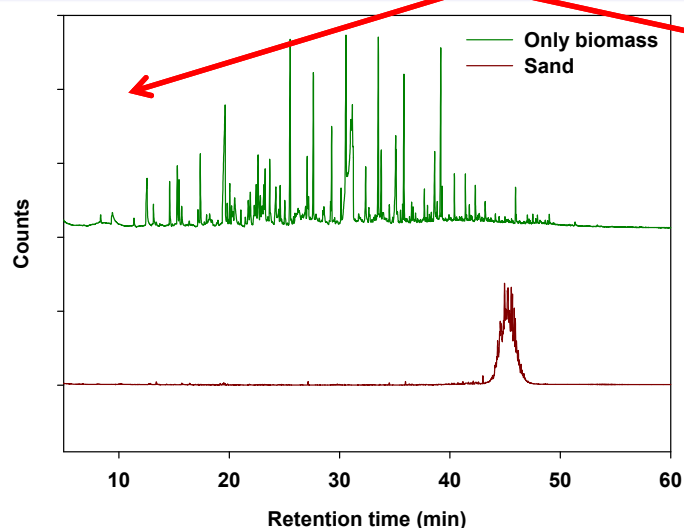


Preliminary tests - II

Light hydrocarbon yields

Sample	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈	nC ₄	nC ₅	1-pentene	1-hexene
-	1.3	0.7	0.6	0	1.1	0.2	1.3	1.6
Sand	50.0	307.0	42.0	56.0	38.0	2.7	6.7	1.3

Results of off-line GC-analysis on liquid products



Compound	Biomass	Sand
Creosol	8.19	-
Guaiacol	10.09	-
Indene	-	0.07
Phenol	2.51	1.84
3-Methylphenol	2.52	0.03
Naftalene	-	0.02
Fluorene	0.02	-
Phenanthrene	0.11	<0.01
Antracene	-	-
Fluoranthene	<0.01	<0.01
Pyrene	<0.01	<0.01
Benz(a)Anthracene	<0.01	0
Chrysene	<0.01	<0.01
Benzo(k)Fluoranthene	<0.01	-
Benzo(b)Fluoranthene	<0.01	-
2-MetylPhenol	0.98	0.02
4.MethylPhenol (p-cresol)	2.34	0.57
2,4-DimethylPhenol (2,4-Xylenol)	0.03	0.13
2,4,5-Trichlorophenol	<0.01	-
2,3,5,6-Terachlorophenol	<0.01	-
TOTAL (µmol)	8.54	2.61



Catalytic formulation

Selection of a catalyst formulation with the following properties

Active phase: catalyst must be active in hydrocarbons (volatiles and permanent gases) **reforming** to improve the syngas production and has **oxidation properties** (preventing coke-induced deactivation of the catalyst)

Support: high surface area, good dispersion capacity and high mechanical and thermal resistance for longer life-time of the catalyst

Proposed catalyst: **small amounts of Rh promoted LaCoO₃ perovskite supported on high mechanical resistance γ -alumina**

CATALYTIC FORMULATION

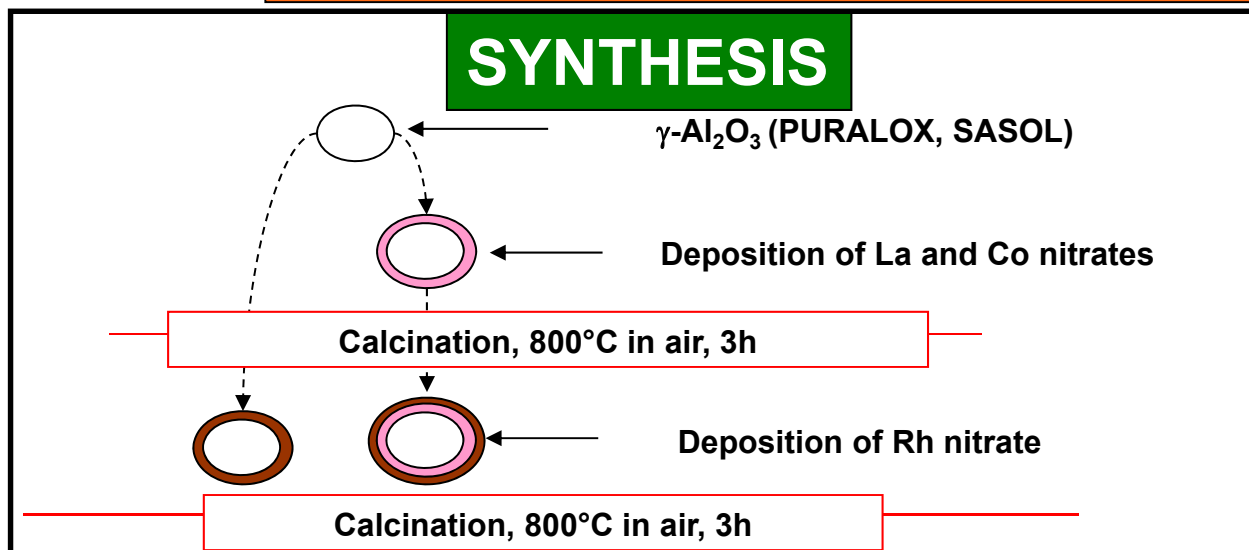


- Improvement of **hydrocarbons reforming activity** due to the presence of Rh
- Limitation of **coke formation** thanks to LaCoO₃ **oxidative properties**
- Improvement of **stability** through the introduction of a Rh into the perovskite matrix, **avoiding sintering**, and **lowering the amount of the expensive noble metal**.



Catalyst preparation

SYNTHESIS



The Rh/LaCoO₃/Al₂O₃ catalyst was prepared by wet impregnation

Samples containing 20 wt% LaCoO₃ or 1 wt% Rh only were also prepared for comparison with the bi-functional sample

CATALYSTS

Sample	Rh content (%wt)	Co content (%wt)	Surface area (BET) (m ² ·g ⁻¹)
LaCoO ₃ /Al ₂ O ₃	-	4.7	101
Rh/Al ₂ O ₃	0.84	-	134
Rh/LaCoO ₃ /Al ₂ O ₃	0.80	4.7	104

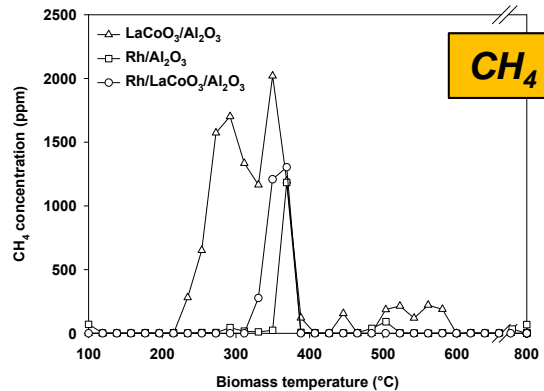
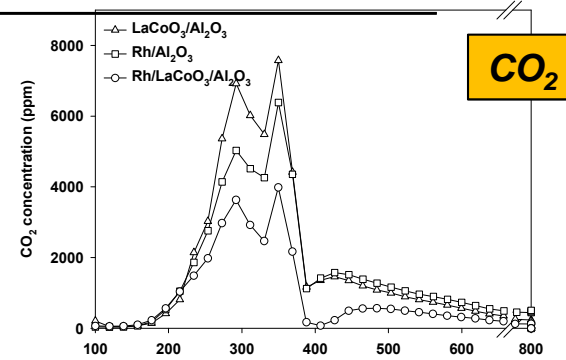
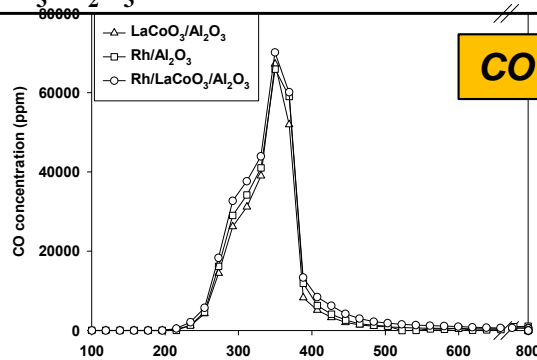
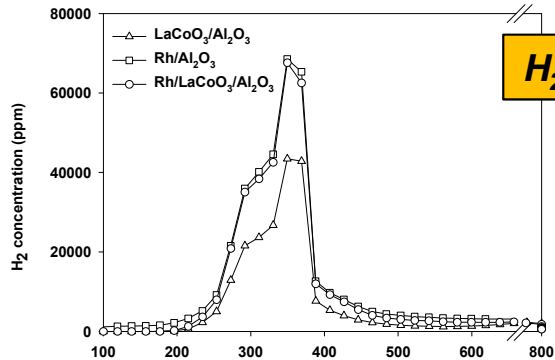
Samples calcined at 900°C were also prepared to test the stability of the catalytic system at higher temperatures



Results of catalytic screening at 700°C (pyrolysis conditions)

Solid, liquid and gas yields on dry basis

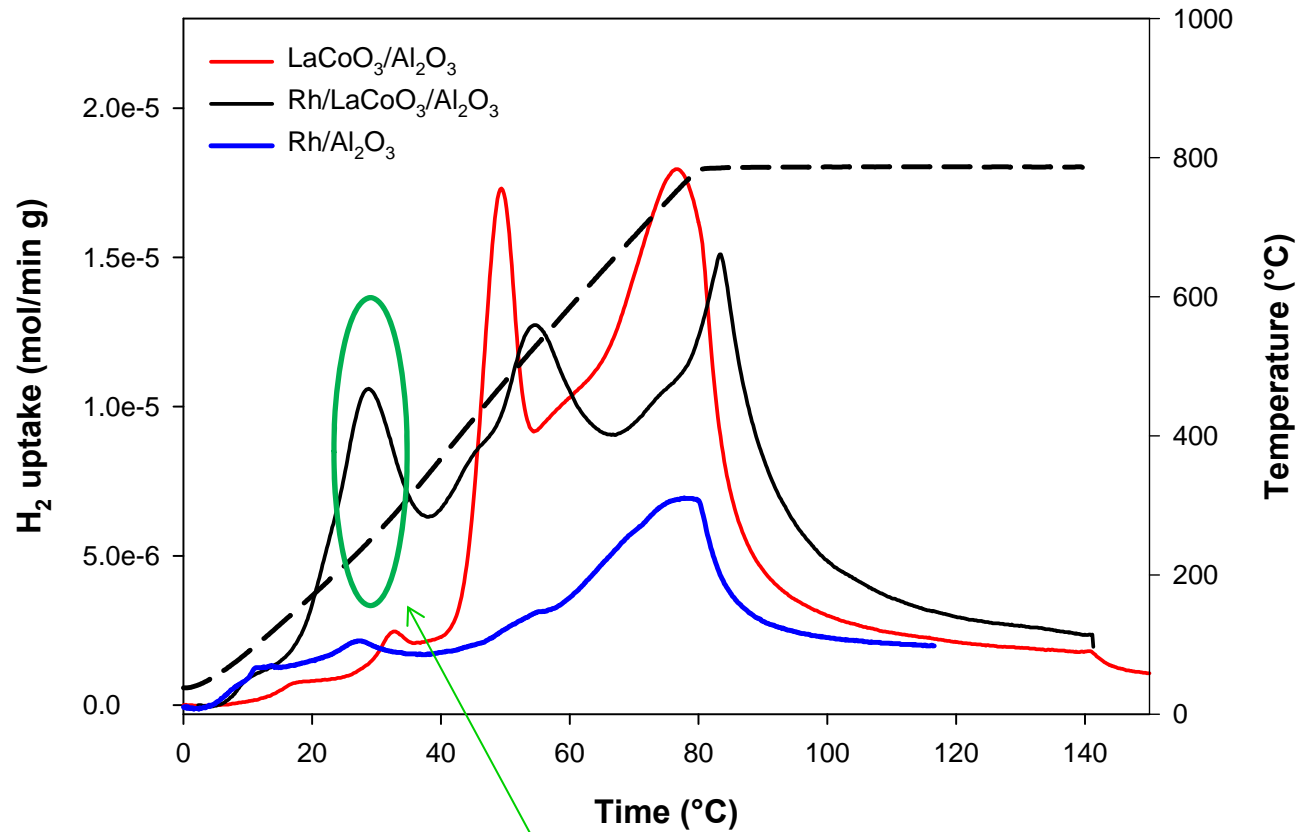
Catalyst	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
Rh/Al ₂ O ₃	16.5	2	-	76.5
LaCoO ₃ /Al ₂ O ₃	18.3	3.5	-	75.9
Rh/LaCoO ₃ /Al ₂ O ₃	18.0	1.1	-	77.6



- Traces of C₂H₆ and C₂H₄ have been detected only on the LaCoO₃/Al₂O₃ sample
- Similar results have been obtained for samples calcined at 900°C



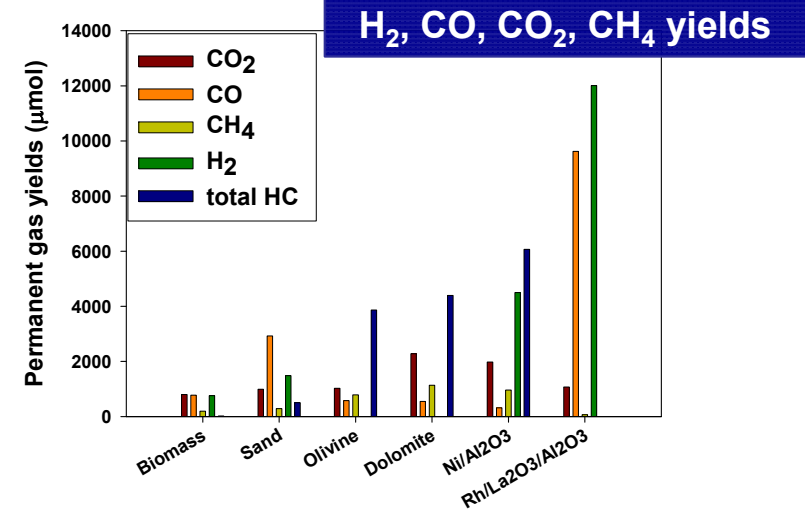
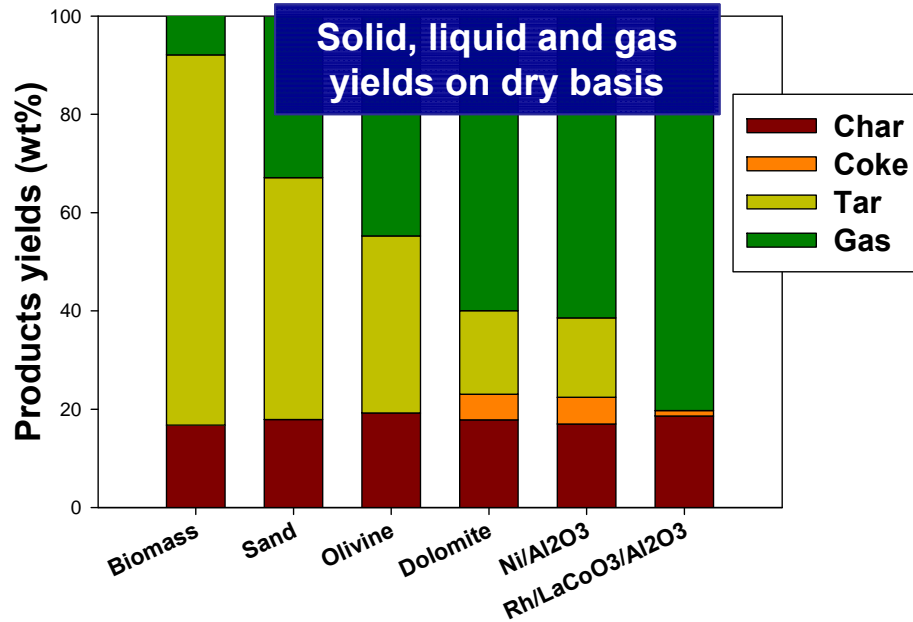
Catalyst characterization – H₂ TPR results



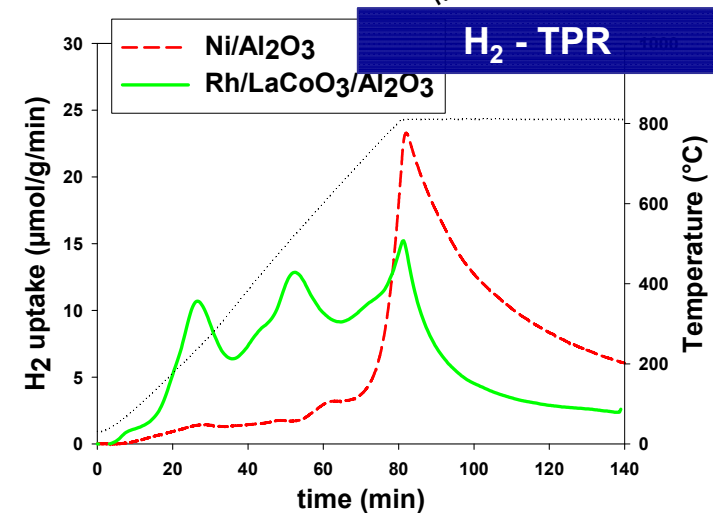
easily reducible rhodium oxide thanks to the barrier effect provided by the cobalt-lanthanum oxide



Comparison with conventional catalysts at 700°C (pyrolysis conditions)



- The Rh/LaCoO₃/Al₂O₃ completely converts tars and light hydrocarbons into a H₂-rich syngas, being by far more active than the Ni-catalyst, which is the most effective among the conventional materials
- Coke sensitivity has been also largely lowered
- The very good performances of the proposed catalyst is correlated to its easy reducibility under reaction conditions.





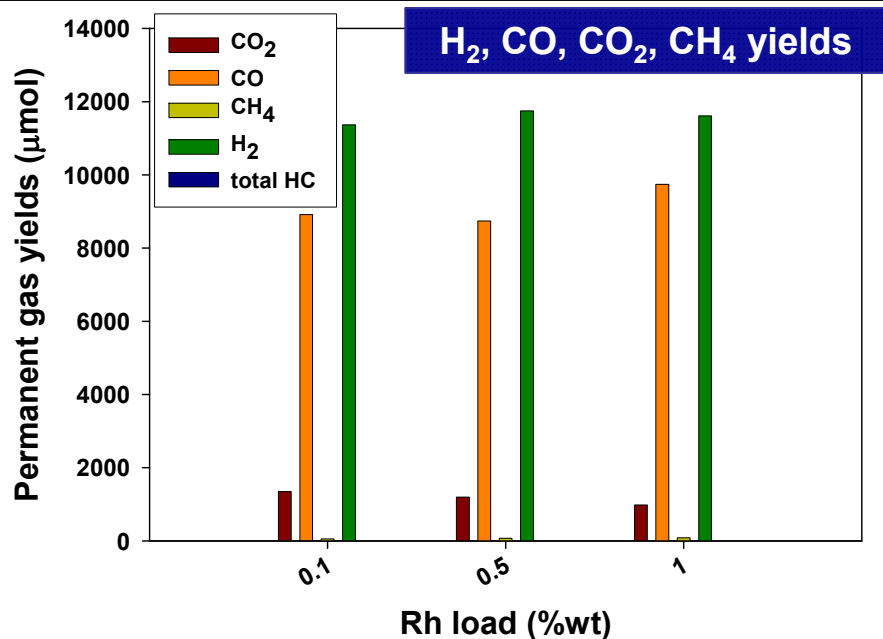
Effect of Rh load at 700°C (pyrolysis conditions)

Catalysts

Catalyst	Active elements (wt %)		BET (m ² ·g ⁻¹)
	Co	Rh	
1Rh/LaCoO ₃ /Al ₂ O ₃	4.72	0.80	104
0.5Rh/LaCoO ₃ /Al ₂ O ₃	4.50	0.45	99
0.1Rh/LaCoO ₃ /Al ₂ O ₃	4.40	0.08	101

Solid, liquid and gas yields on dry basis

Catalyst	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
1Rh/LaCoO ₃ /Al ₂ O ₃	18.0	1.1	-	77.6
0.5Rh/LaCoO ₃ /Al ₂ O ₃	16.7	1.7	-	70.7
0.1Rh/LaCoO ₃ /Al ₂ O ₃	16.8	3.6	-	73.0



•At 700°C a complete tar conversion can be obtained decreasing the Rh load down to 0.1 wt%

•The rhodium load reduction promotes the formation of a large fraction of highly dispersed rhodium active in reforming reaction whereas for a greater load less active metal aggregates are preferentially formed (DRIFT analysis)



Effect of operating temperature (pyrolysis conditions)

Solid, liquid and gas yields on dry basis

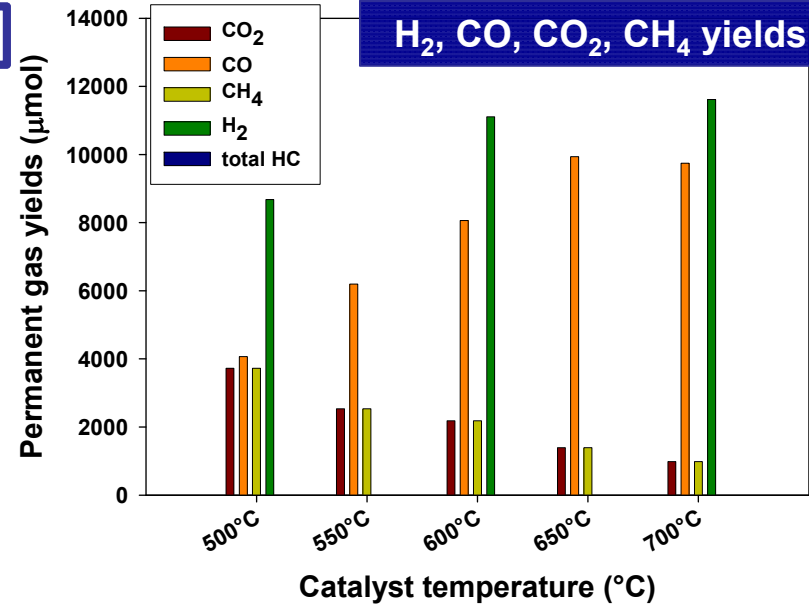
Rh/LaCoO₃/Al₂O₃

Catalyst temperature (°C)	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
700	18.0	1.1	-	77.6
650	17.5	2.4	-	75.5
600	17.0	4.9	-	77.4
550	17.8	5.7	4.6	65.4
500	17.3	7.9	9.5	68.0

Light hydrocarbon yields

Catalyst temperature (°C)	C ₂ H ₂	C ₂ H ₄	nC ₄	nC ₅	1-pentene	1-hexene
500	2.16	1.80	0.30	2.43	3.73	2.86
550	2.90	0.71	0.30	1.01	1.78	1.58
600	-	0.15	-	-	-	-

H₂, CO, CO₂, CH₄ yields



•The catalyst provides good performances in tar and light hydrocarbons conversion even when the temperature is lowered down to 600°C

•The TPR results suggest that at T≥600 °C the oxygen from supported rhodium oxide and perovskite is sufficiently labile to be involved in the hydrocarbons reforming and coke oxidation as well



Catalyst thermo-chemical stability (pyrolysis conditions) - I

During its use in tar conversion the catalyst undergoes several redox and thermal cycles and, consequently, permanent or reversible deactivation can occur affecting catalyst life-time

- *The **thermal and chemical stability** of Rh/LaCoO₃/Al₂O₃ catalysts has been investigated by performing cycles of tar conversion under pyrolysis conditions at 700° C followed by their regeneration (coke oxidation at 800° C)*
- ***Structural and chemical modifications** upon conversion/regeneration cycles have been studied by TPR/TPO analysis*

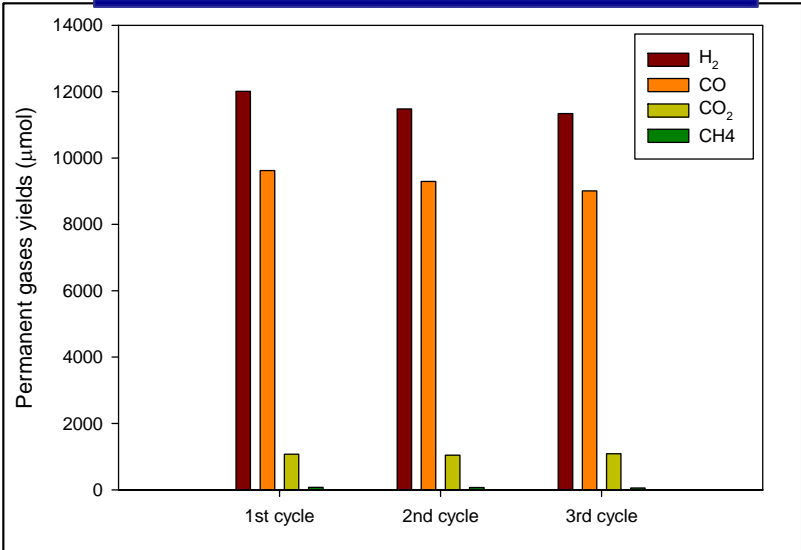


Catalyst thermo-chemical stability (pyrolysis conditions) - II

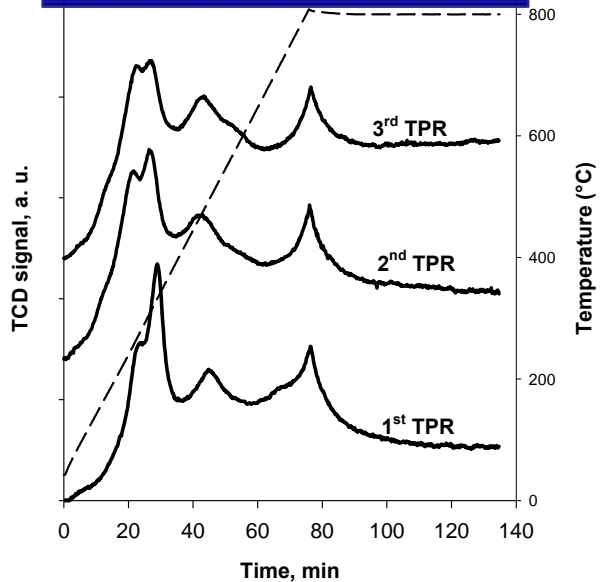
Solid, liquid and gas yields on dry basis

Catalyst	Cycle	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
		char	coke		
Rh/LaCoO ₃ /Al ₂ O ₃	1 st	17.0	1.3	-	75.0
	2 nd	17.0	1.7	-	72.4
	3 rd	17.2	2.1	-	71.0

H₂, CO, CO₂, CH₄ yields



H₂ TPR analysis



The 2nd and 3rd TPR highlight only a slight modification of the low temperature signal, associated to a promotion of the aggregation of Rh surface species, thanks to the barrier effect of perovskite



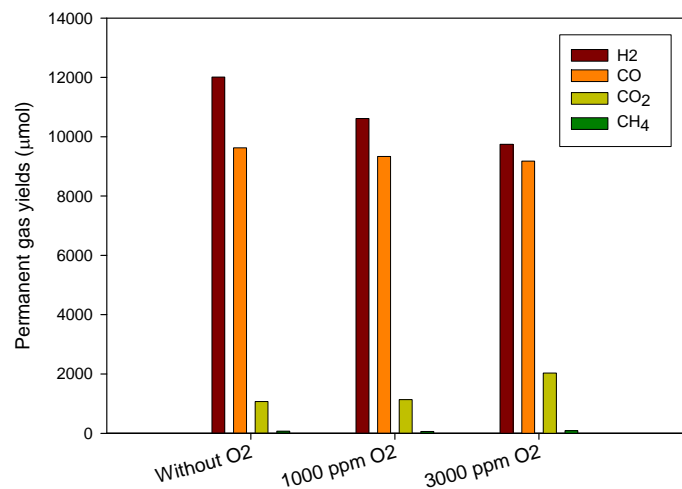
Effect of oxygen addition at 700°C

The performance of the Rh/LaCoO₃/Al₂O₃ catalyst has been also investigated in the conversion of tar produced during biomass devolatilization into syngas under partial oxidation conditions

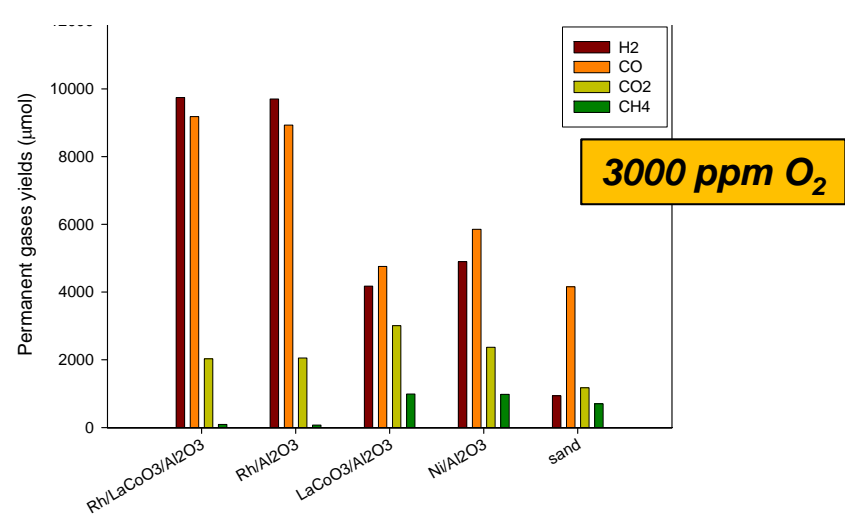
Solid, liquid and gas yields on dry basis

Oxygen content (ppm)	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
-	17.0	1.3	-	77.0
1000	17.5	0.9	2.3	75.2
3000	17.5	-	3.8	80.7

H₂, CO, CO₂, CH₄ yields

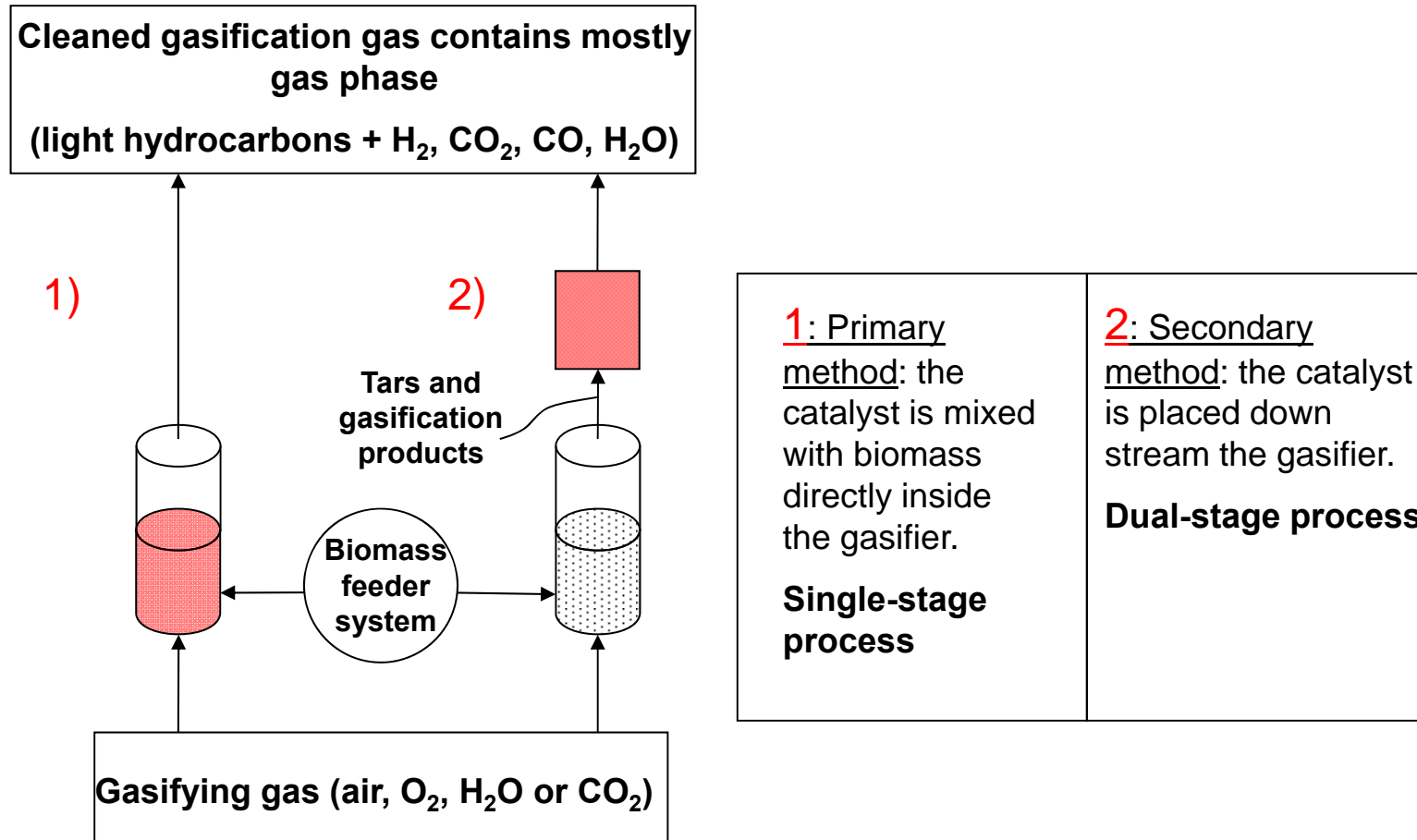


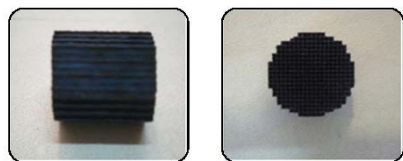
H₂, CO, CO₂, CH₄ yields





Catalytic tar removal





Monolithic systems (700°C)

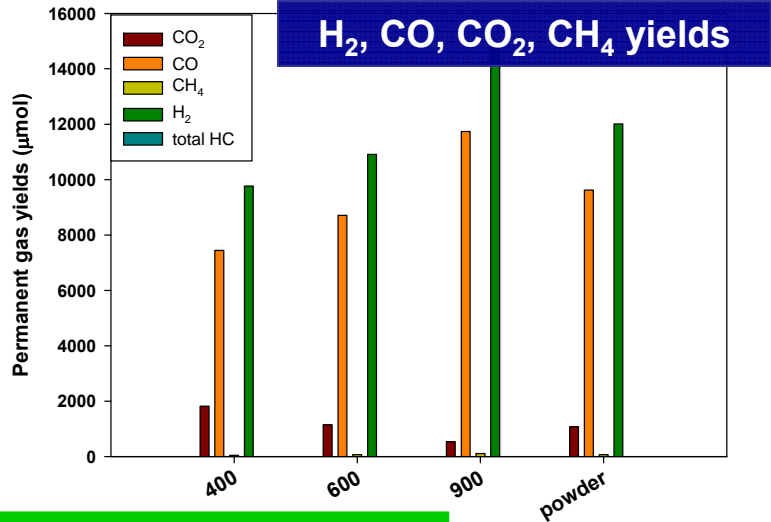
Structured catalysts as secondary catalysts represent a promising technology

- Advantages:**
- Reduced blocking due to solid particulate
 - Reduced pressure drops across the reactor

- Drawbacks:**
- Complex preparation phase, thus not allowing to obtain a full reproducibility of powder systems

Solid, liquid and gas yields on dry basis

sample	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
	char	coke		
400 cpsi	17.7	1.6	6.6	69.5
600 cpsi	18.1	0.8	4.7	72.9
900 cpsi	19.0	0.2	-	81.2
powder	17.0	1.3	-	77.0



The improvement of structured catalysts performance with increasing cell density is due to an enhancement of the external mass transfer



Conclusions

The IRC-CNR research activities on the catalytic tar conversion have been focused on:

Development of a reactor configuration to evaluate catalytic activity

- small scale plant to allow catalytic screening with small amounts of catalysts
- the catalyst is in contact with all volatile species emitted from biomass
- also useful for biogenic material characterization
- operation under different conditions (pyrolysis, oxy-pyrolysis, gasification)

Development of a Rh/LaCoO₃ synthetic catalyst to improve tar conversion into a hydrogen-rich gas

- both reforming and oxidation properties
- limited coke formation
- more active than conventional catalysts
- thermo-chemical stability
- active for temperatures higher than 600°C
- Rh load as low as 0.1wt%
- active both under pyrolysis and partial oxidation conditions
- possibility to be used in secondary reactors in the form of honeycombs



***Thank you for your
attention***



Effect of sulphur at 700°C (pyrolysis conditions) - I

Biomass as straw, cereals, grasses and fruit residues contains not negligible amounts of S, N and Cl which can hinder the catalyst activity, especially affecting the noble metal properties, since they chemically adsorb on active sites

During combustion of biomass 40-45% sulphur is integrated into ash; however, residual sulphur remains in the flue gases as SO₂

Under pyrolysis or gasification conditions sulphur can be present as H₂S

Solid, liquid and gas yields on dry basis

Rh/LaCoO₃/Al₂O₃

H ₂ S concentration in the feed (ppm)	Solid yield (%wt)		Tar yield (%wt)	Gas yield (%wt)
	char	coke		
0	18.0	1.1	-	77.6
20	16.8	2.4	-	75.0
200	18.1	3.0	-	69.5

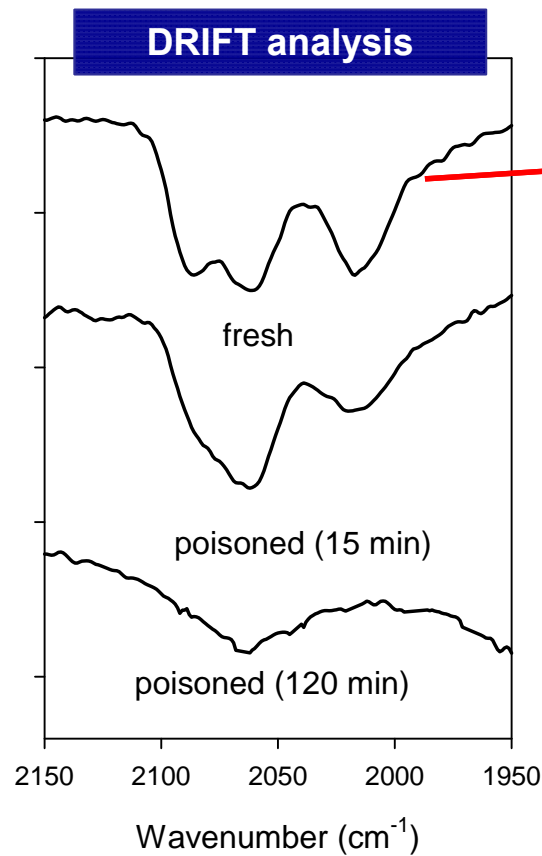
A reduction of gas yield balanced by an increase of coke deposition were observed upon sulphur addition. A reduction of gas yield is also related to the detection of unconverted light hydrocarbons (at 200 ppm of H₂S traces of C₂-C₃ hydrocarbons have been detected)

Fare il diagramma a barre dei gas



Effect of sulphur at 700°C (pyrolysis conditions) - II

The Rh/LaCoO₃/Al₂O₃ catalyst was treated in-situ with H₂S (20 ppm) under reducing conditions and CO was used as probe molecule to analyse amount and type of poisoned Rh sites



The doublet bands at 2090 and 2016 cm⁻¹ correspond to **isolated Rh sites**

The band at 2060cm⁻¹ is assigned to **Rh crystallites or clusters**

- Isolated Rh sites are selectively poisoned by sulphur under reducing conditions (20ppm, 1h)
- Since Rhodium is more dispersed in catalyst with a lower noble metal content, the catalyst with a lower Rh load are more easily deactivated
- The perovskite layer protects to some extent the Rh sites slowing the deactivation process