HYDROGEN PRODUCTION BY AQUEOUS-PHASE REFORMING OF GLYCEROL FROM THE BIODIESEL MANUFACTURING

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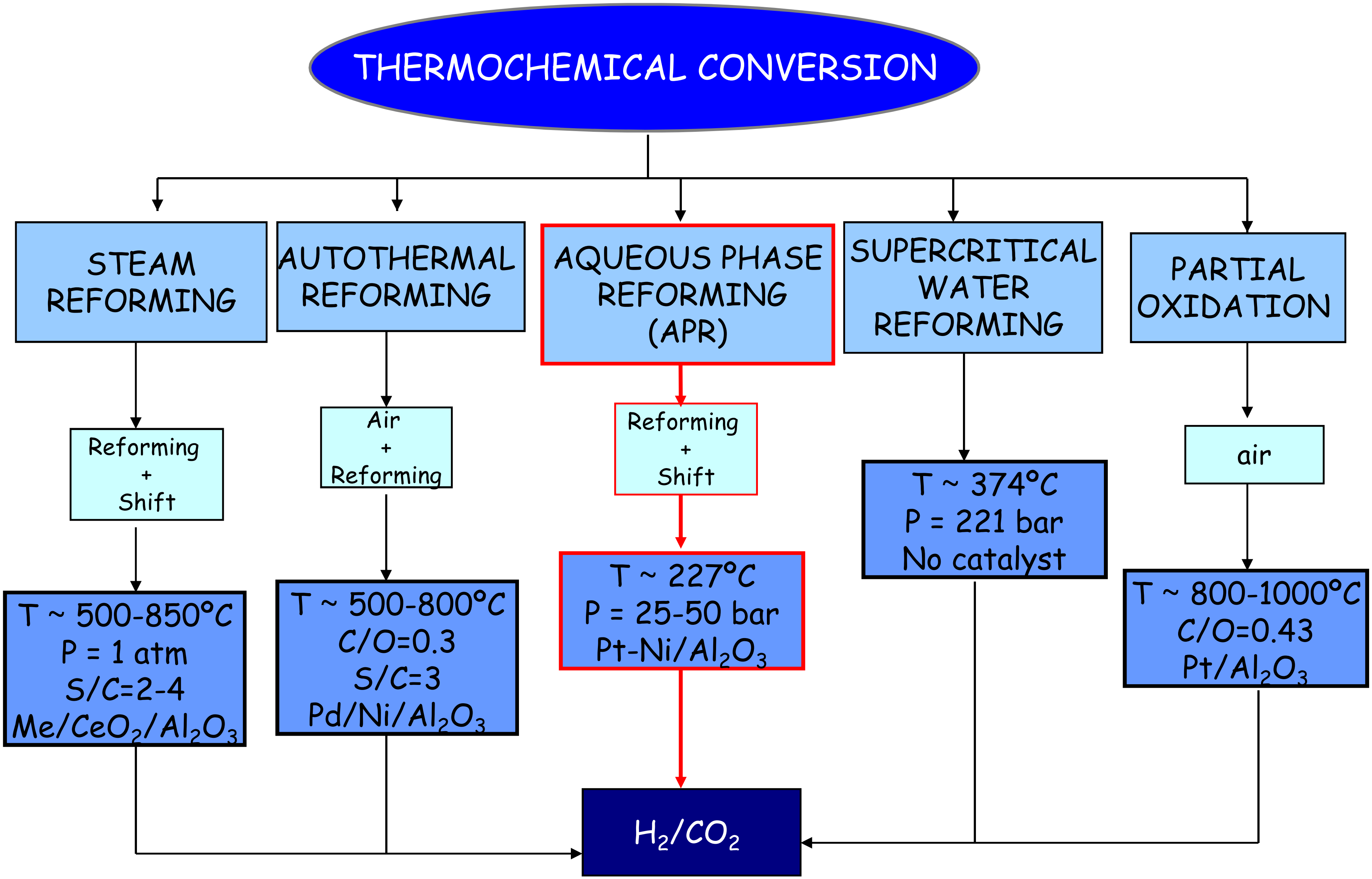
OUTLINE

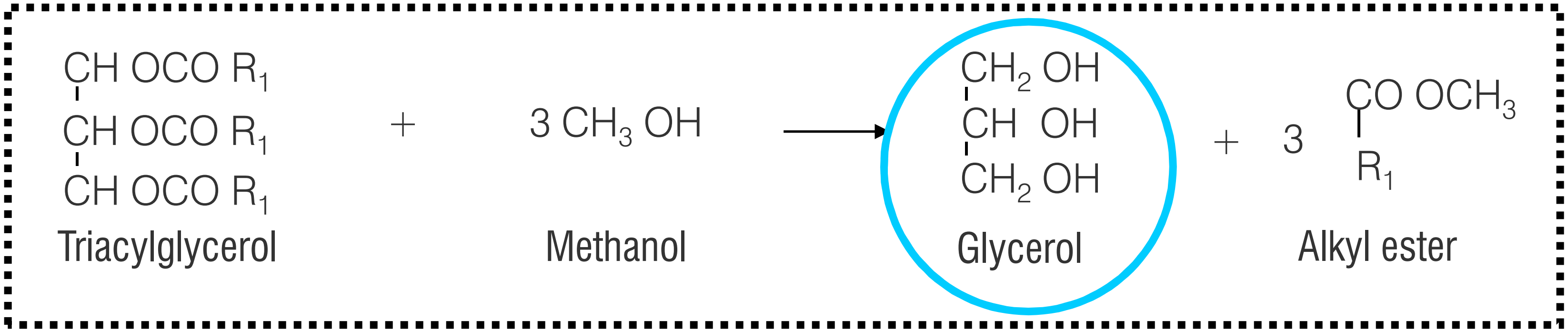
1. INTRODUCTION AND OBJECTIVES
2. EXPERIMENTAL METHOD
3. EXPERIMENTAL RESULTS
    - Effect of the feedstock and the glycerol content
    - Effect of the catalyst composition
4. CONCLUSIONS

OUTLINE

1. INTRODUCTION AND OBJECTIVES



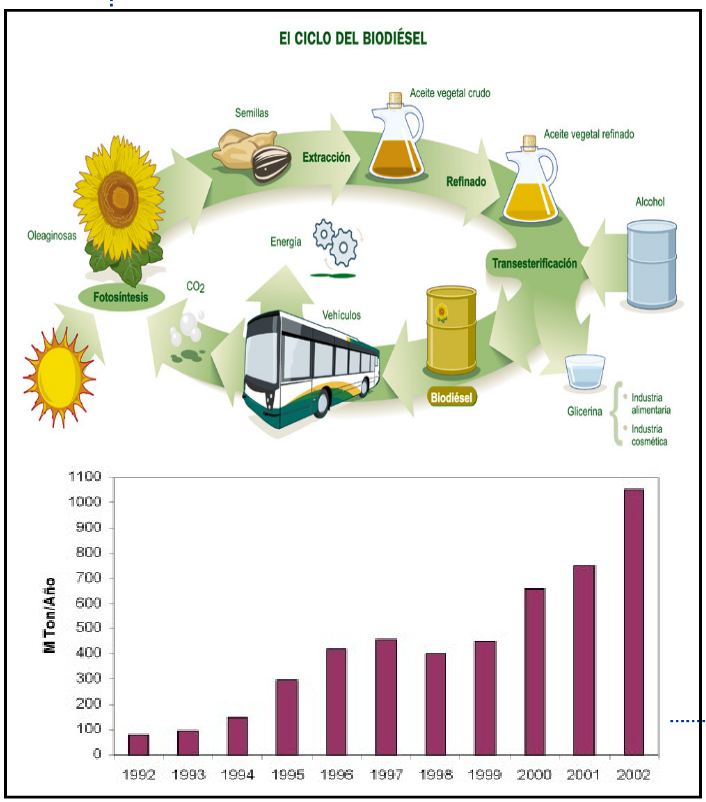
Adhikari et al. Ener. Conv. Management (2009) 2600-2604.



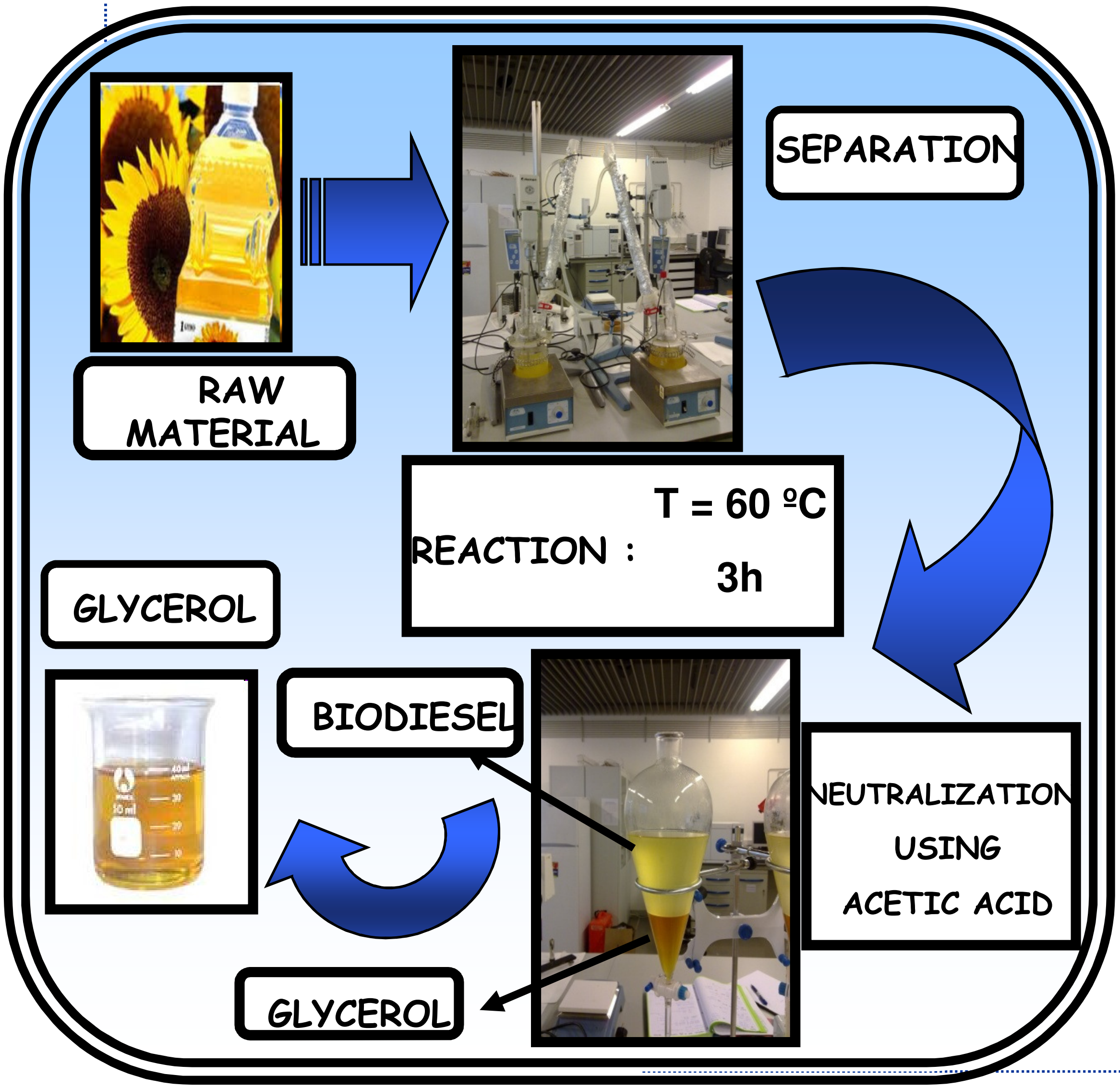
valuable products

H_2

USES:
- **$CO + H_2$**
- **fuel cells**



Synthesis of biodiesel in the laboratory:



Reagents:

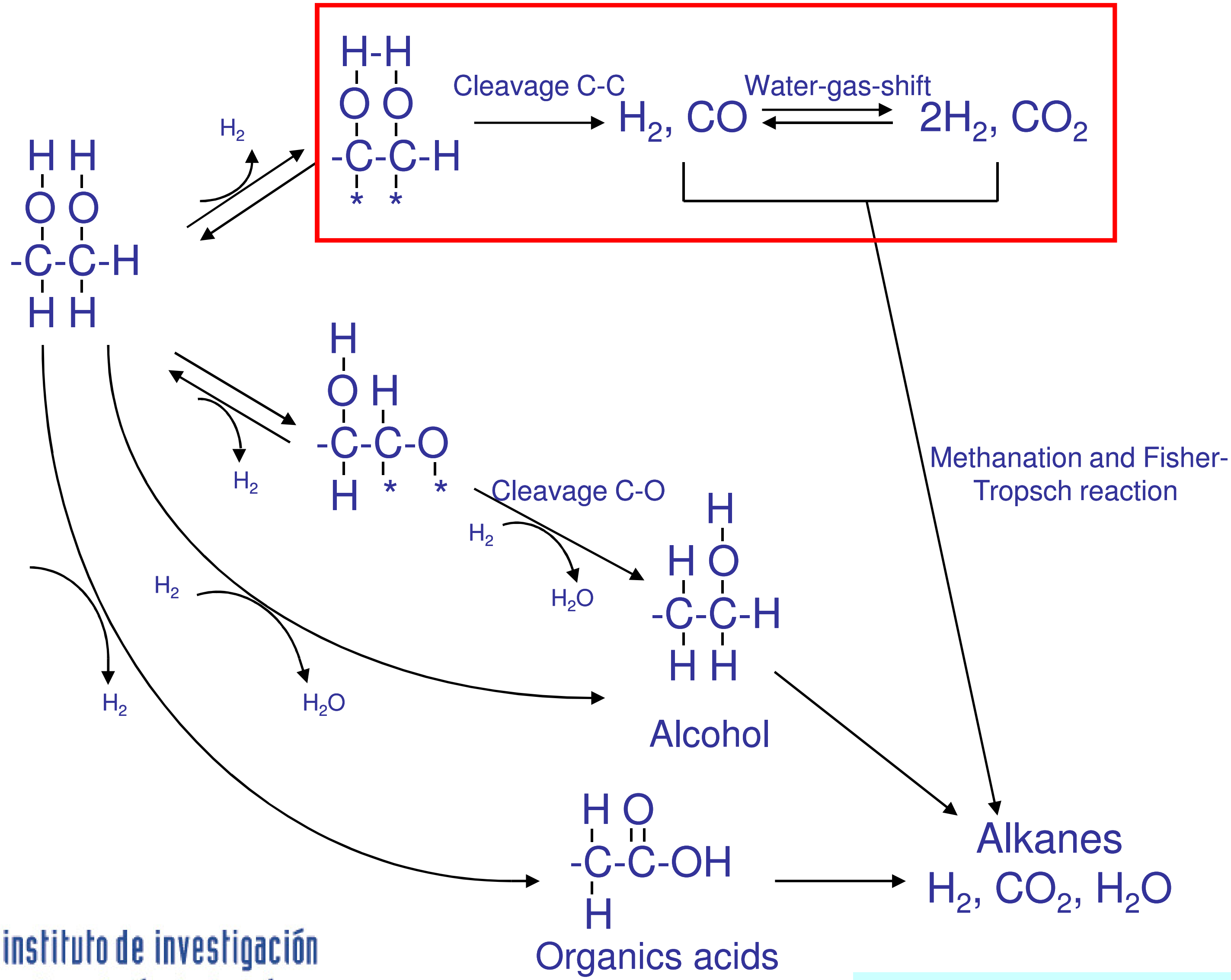
- **Pure glycerol (chem)**
- **Glycerol from biodiesel manufacturing (co-prod):**

<u>Average of organics:</u>

MeOH: 4%

Acetic Acid: 38%

Glycerol: 58%



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

OBJECTIVES

- Experimental work with glycerol as a waste of biodiesel process at micro-scale reactor.

- Development of suitable catalysts for the process:

    - Adequate catalytic activity and selectivity towards H_2.

    - Resistance to deactivation.

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2. EXPERIMENTAL METHOD

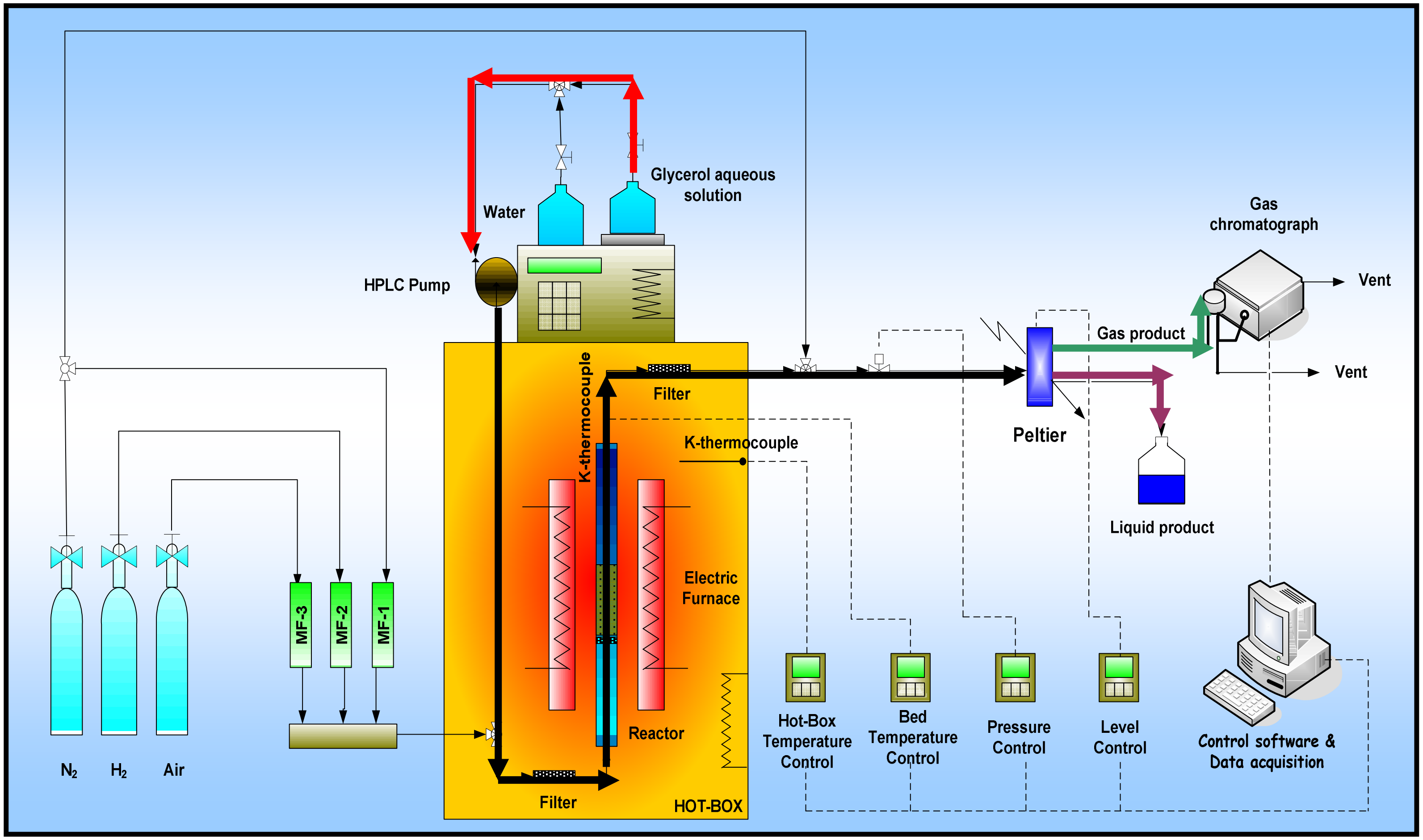
Experimental conditions:

- T = 500 K
- P = 33 bar
- Glycerol aqueous solution 2-10 wt%
- Liquid flow rate: 1 mL/min
- WHSV = 3 (g glycerol/ g catalyst h)
- Run time: 5 h

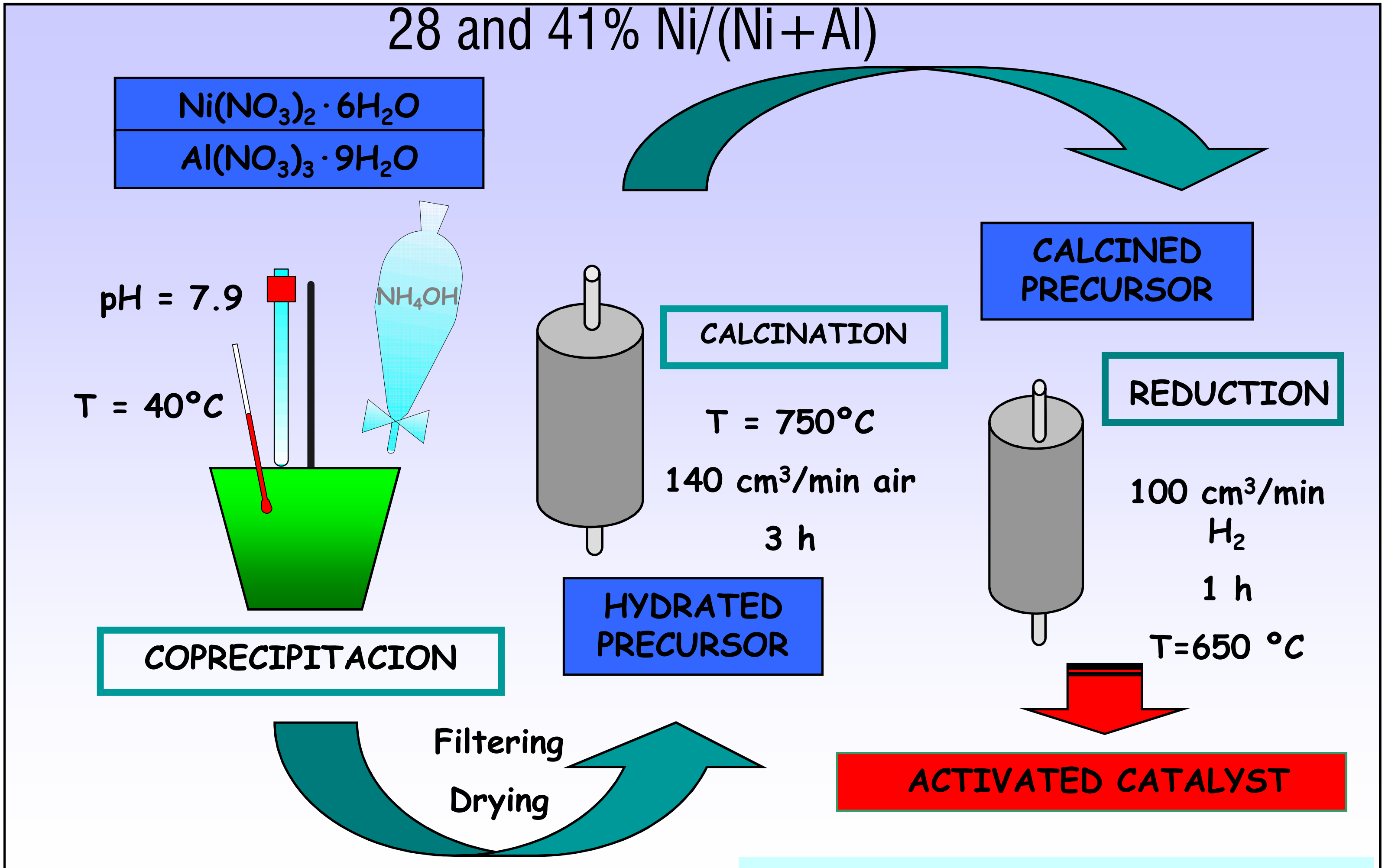
Characteristics:

- Micro-scale reactor test.
- Fixed bed (sand + catalyst particle sizes: 320-160 μm.
- Upward flow.
- Stainless steel reactor (9mm i.d).

Experimental system



Catalysts prepared by a coprecipitation method



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

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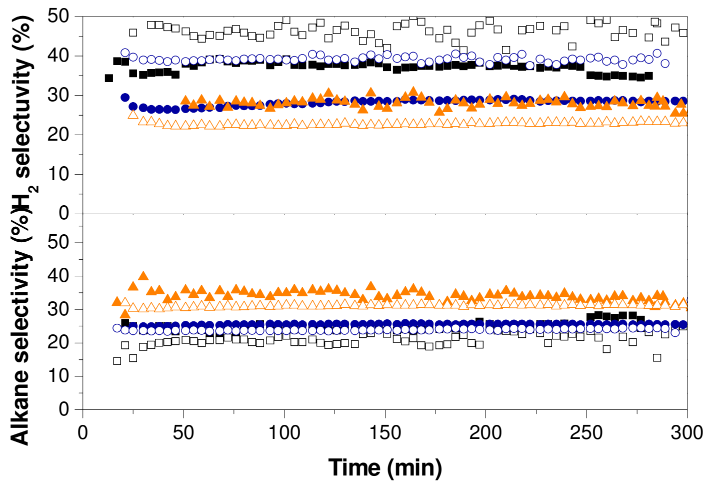
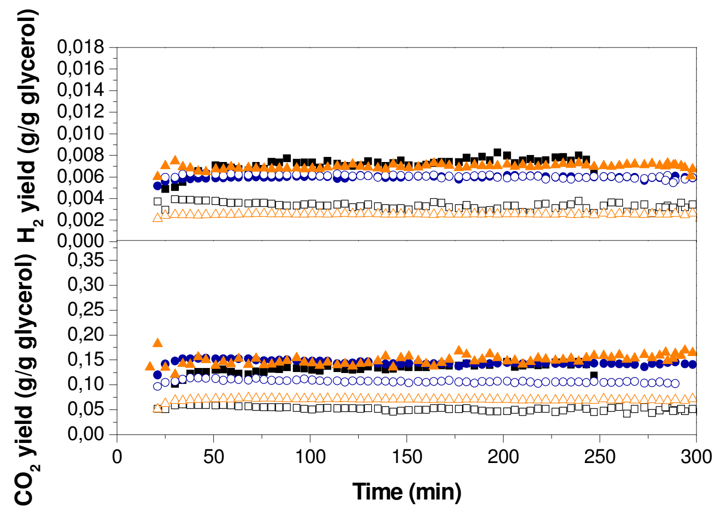
3. EXPERIMENTAL RESULTS

- **Effect of the feedstock and the glycerol content**

Effect of the feedstock and the glycerol content:



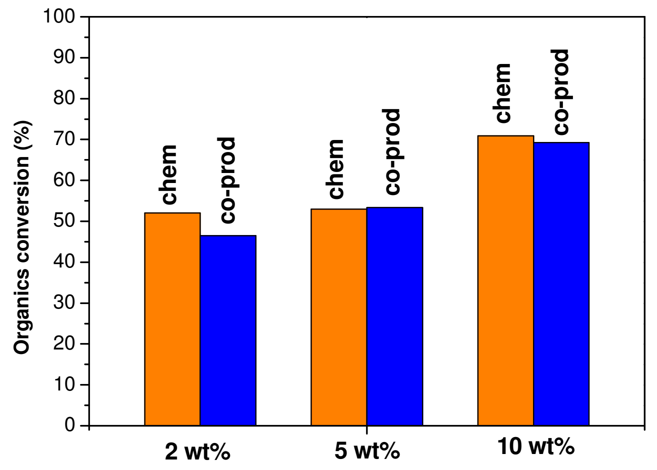


2% chem (■)	5% chem (●)	10% chem (▲)
2% co-prod (□)	5% co-prod (○)	10% co-prod (Δ)

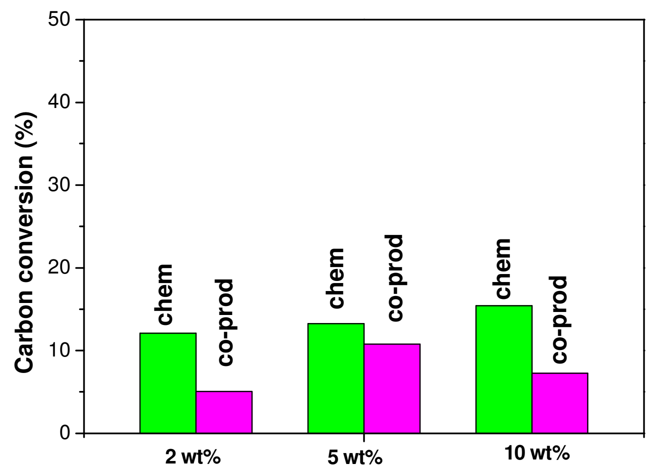
Catalyst: 28% Ni

- The co-prod glycerol showed higher hydrogen selectivity and smaller alkane selectivity.
- Constant gas yield values were obtained with time, no deactivation was observed.
- ↓ H_2 and CO_2 yields when the co-prod glycerol is fed.

3. Results



- Organic conversion is similar between both feedstock. However, an improvement was observed with the highest glycerol content.



- Higher carbon conversion to gas is obtained in glycerol from chemical reagent compared to co-product in biodiesel manufacturing.

Effect of the feedstock and the glycerol content:

Yield(g chemical/g organics)	2% chem	2% co-prod	5% chem	5% co-prod	10% chem	10% co-prod
MeOH	**0.0574**	**0.0617**	**0.0256**	**0.0382**	**0.0167**	**0.0180**
EtOH	0.0213	0.0280	0.0181	0.0244	0.0482	0.0042
Acetol	0.1305	0.1250	0.0800	0.0873	0.0502	0.0480
Acetic acid	0.1435	0.4110	0.0618	0.6092	0.0289	0.2869
Propylene glycol	0.0535	0.1529	0.0954	0.0711	0.1488	0.0118
Ethylene glycol	**0.0951**	**0.0592**	**0.0615**	**0.0460**	**0.0580**	**0.0155**

- Product yields ↓ when the glycerol content ↑

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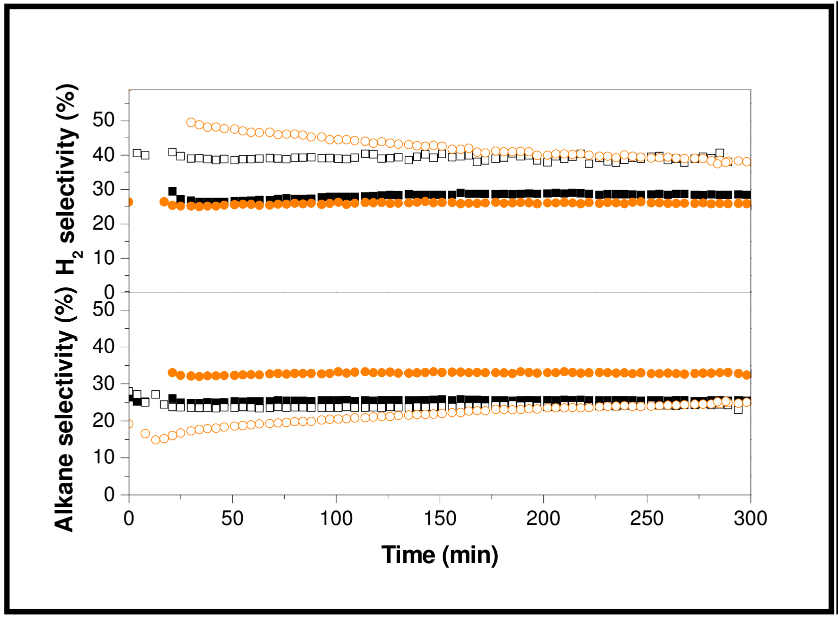
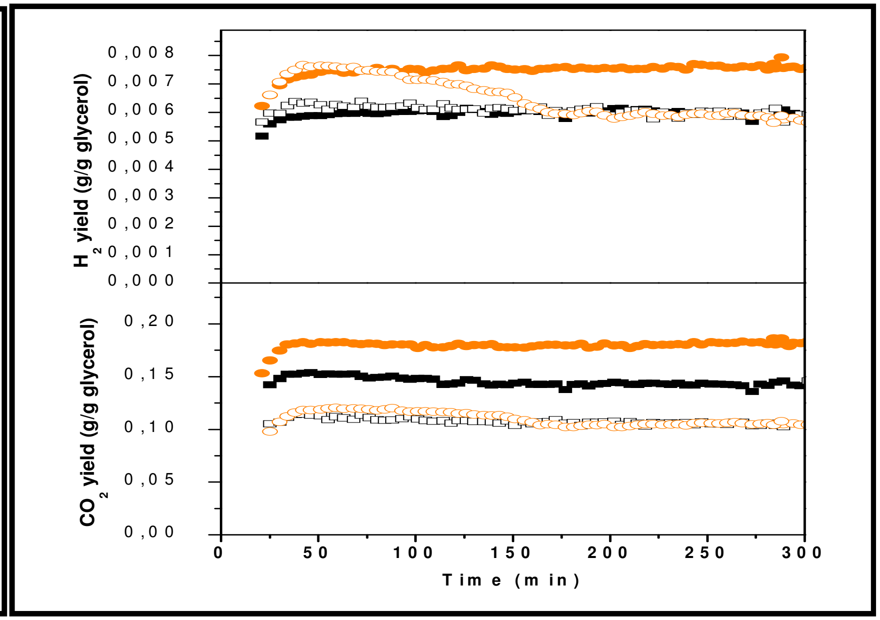
3. EXPERIMENTAL RESULTS

- **Effect of the catalyst composition**

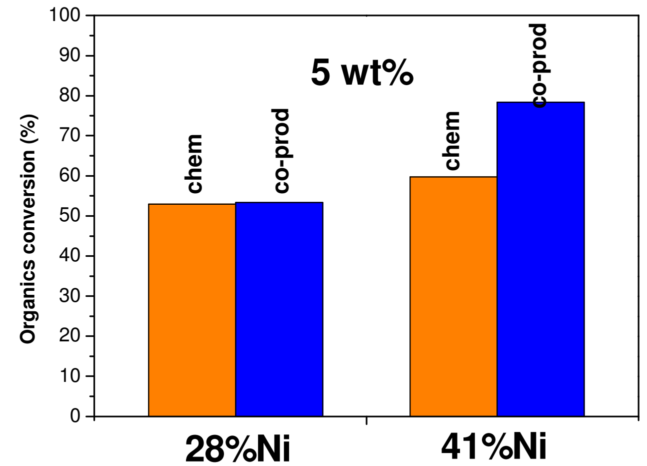
Effect of the catalysts composition:



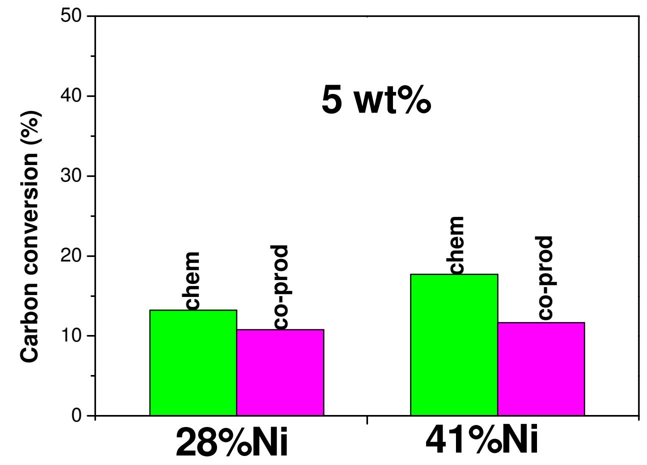


28% Ni chem (■)	41% Ni chem (●)
28% Ni co-prod (□)	41% Ni co-prod (○)

- 41 wt% Ni catalyst tested showed a slightly deactivation in co-prod glycerol.
- Co-prod glycerol: H_2 and CO_2 yields are similar for both catalysts, after deactivation period of 41 wt% Ni catalyst.
- Chemical glycerol: H_2 and CO_2 yields ↓ when %Ni ↓



- The organic conversion is similar for both feeds and catalysts except for the 41% Ni catalyst and co-product feeding, that is higher.



- Higher carbon conversion to gas is obtained in glycerol from chemical reagent.

Effect of the catalysts composition:

Yield (g chemical/g organics):	28% Ni 5% chem	28% Ni 5% co-prod	41% Ni 5% chem	41% Ni 5% co-prod
MeOH	**0.0256**	**0.0382**	**0.0280**	**0.0316**
EtOH	0.0181	0.0244	0.0140	0.0019
Acetol	0.0800	0.0873	0.0607	0.0672
Acetic acid	**0.0618**	**0.6092**	**0.0591**	**0.2924**
Propylene glycol	0.0954	0.0711	0.0878	0.0390
Ethylene glycol	0.0615	0.0460	0.0887	0.0408

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4. CONCLUSIONS

CONCLUSIONS

- The co-prod glycerol showed higher hydrogen selectivity and smaller alkane selectivity.
- Organic conversion is similar between both feedstock. However, an improvement was observed with the highest glycerol content.
- Higher carbon conversion to gas is obtained in glycerol from chemical reagent compared to co-product in biodiesel manufacturing.
- Co-prod glycerol showed a slightly deactivation in 41 wt % Ni catalyst tested.

FUTURE WORK

- Upgrade of waste biomass aqueous streams from several industrial processes; cheese whey and black liquor in a bench scale.

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