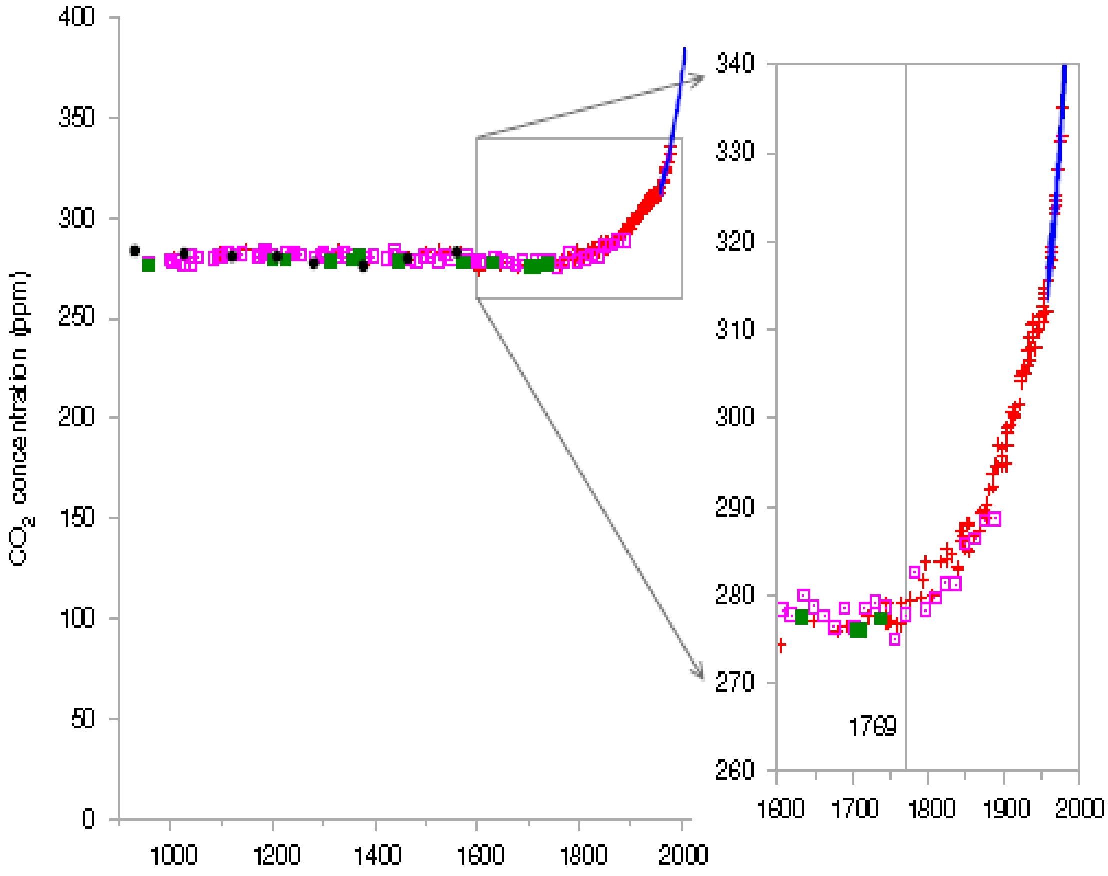
Energy Optimization via the Catalytic Upgrading of Side Products – The Case of Glycerol Hydrodeoxygenation

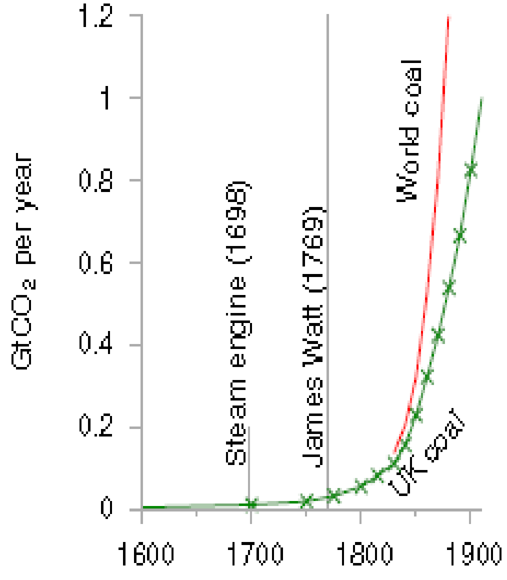
Gustavo A. Fuentes
Chemical Engineering
UAM-Iztapalapa
Mexico
gfuentes@xanum.uam.mx

Interconnectiveness 101
The Ford Pinto

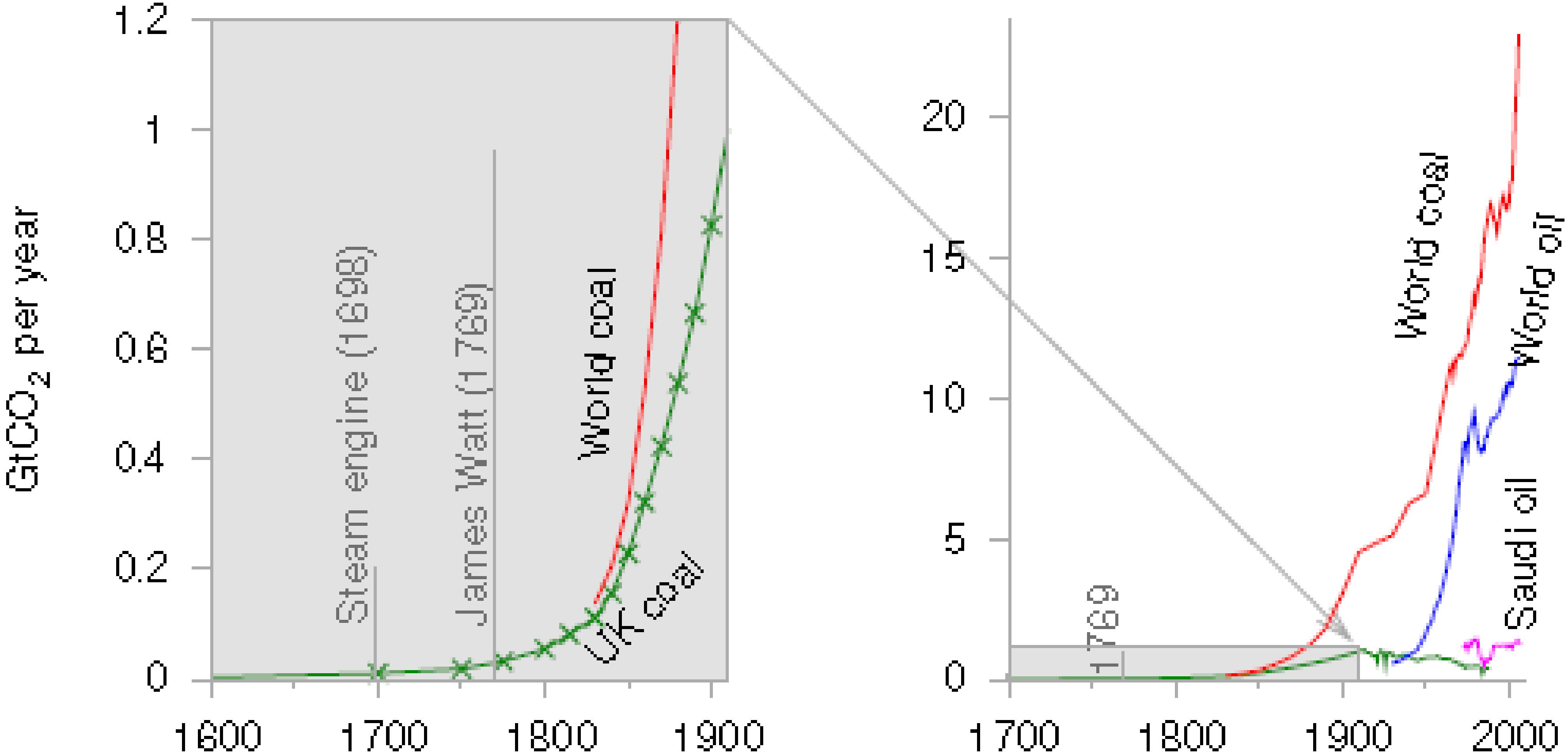
Fuentes – Klip
Varma

A more complex case: CO_2 in the atmosphere

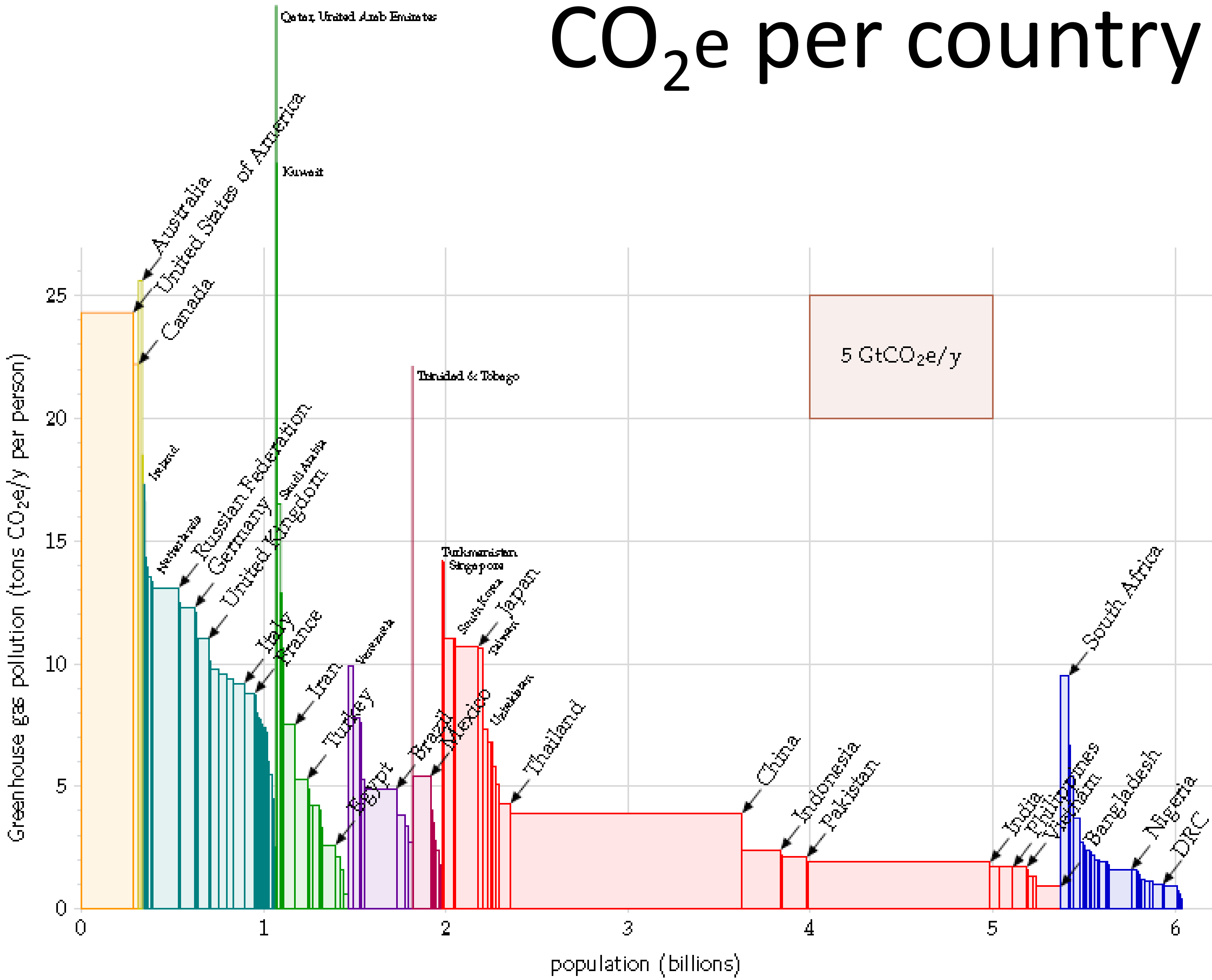




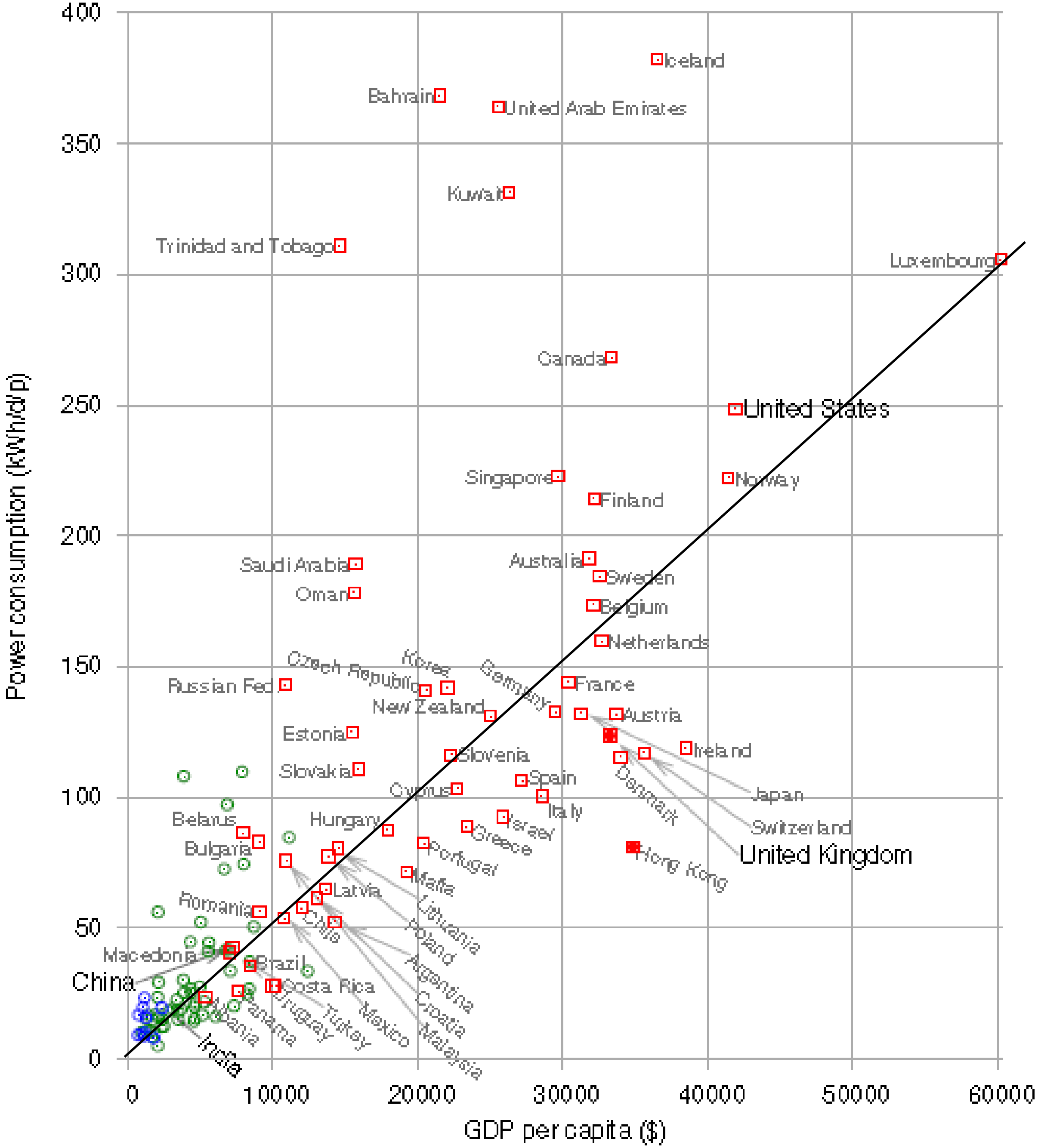
Coal is still very important!



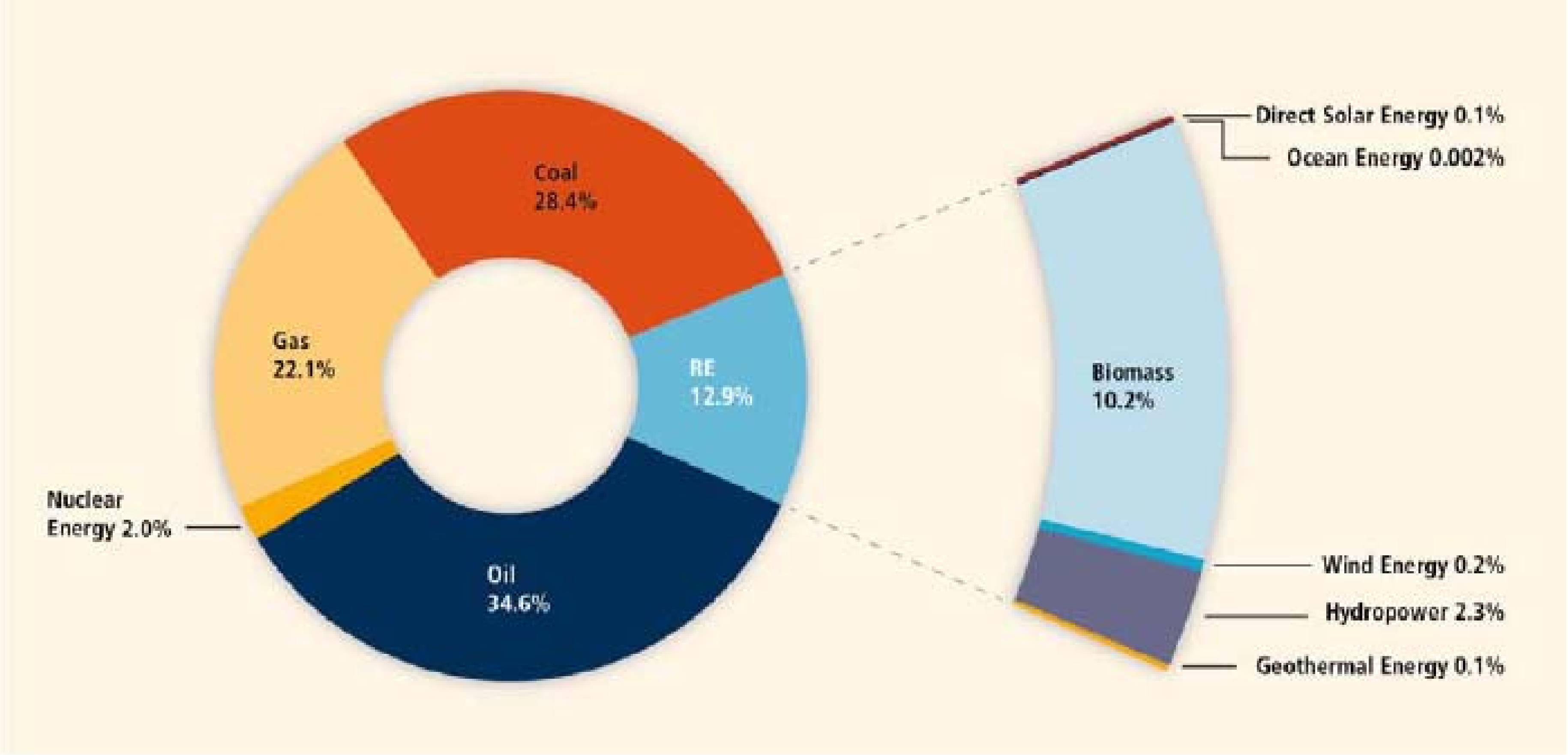
CO_2e per country



Consumption of energy vs. GDP per capita



Biomass use will be hard to change



Use of renewables

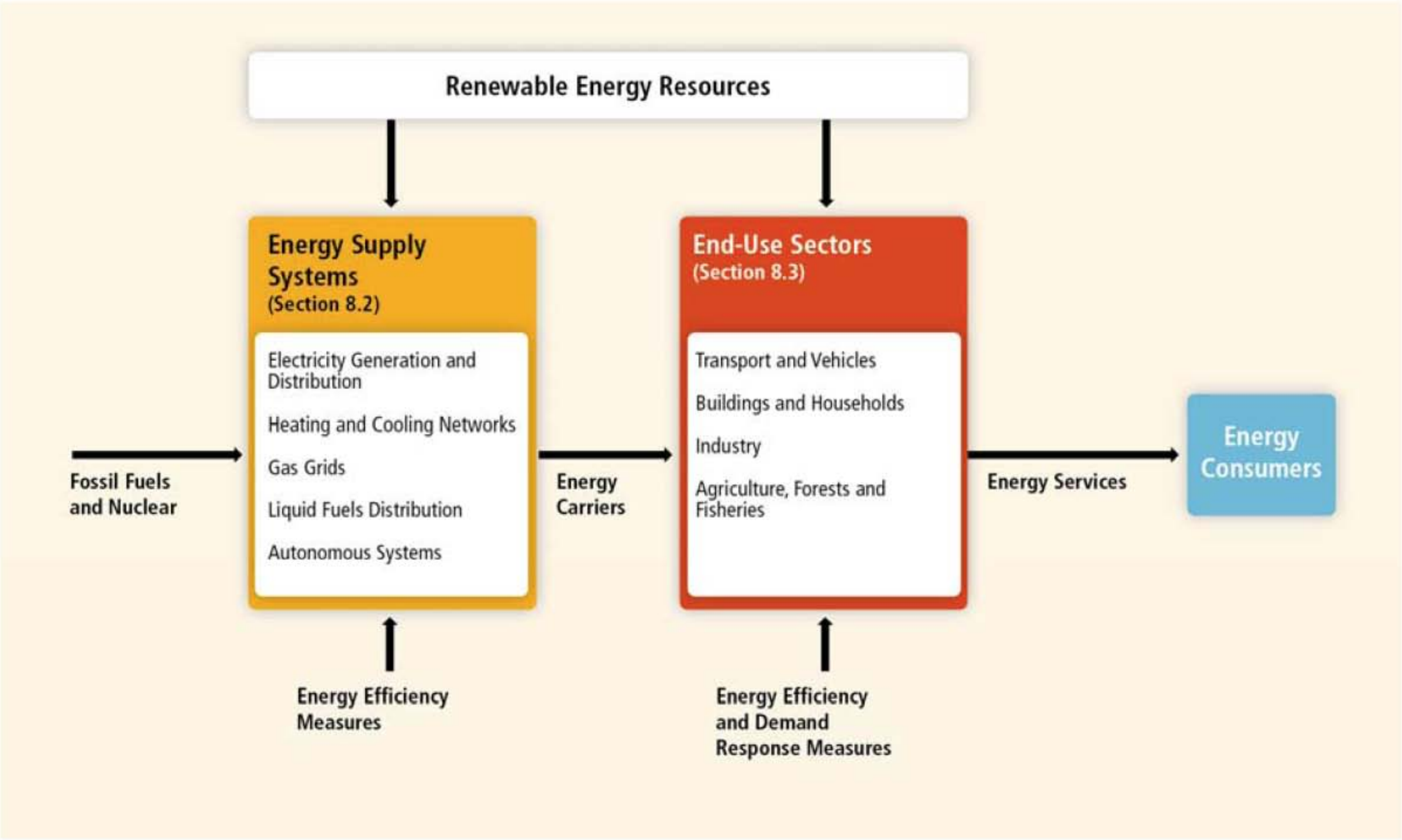
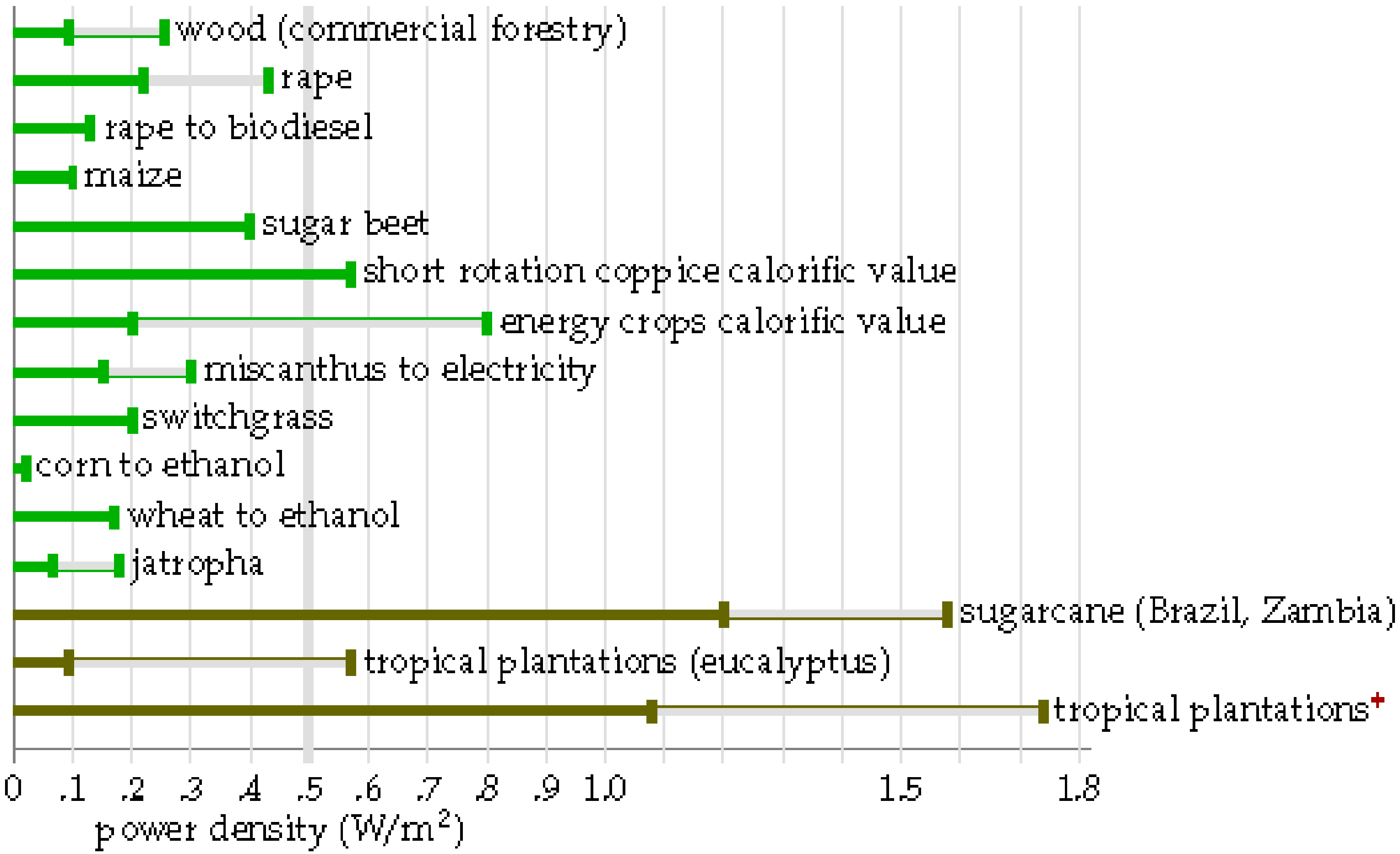


Figure SPM.7 | Pathways for RE integration to provide energy services, either into energy supply systems or on-site for use by the end-use sectors. [Figure 8.1, 8.1]

Gasoline and Diesel in Mexico

- Gasoline consumption is of the order of $1.272 * 10^8$ l/day
- Diesel consumption is about $5.15 * 10^7$ l/day
- Biofuels are only marginal.

Power density of crops



Bioethanol in Mexico

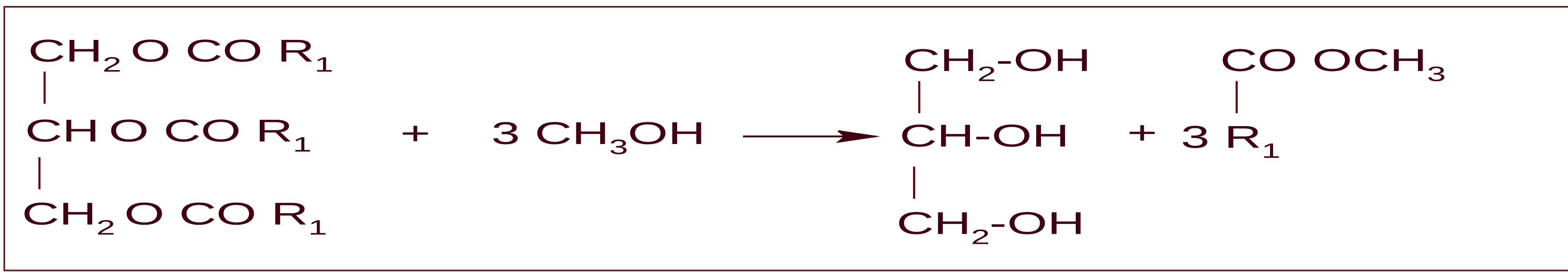
- Bioethanol from Sugarcane
  - 80 ton/ha-year give about 17600 l ethanol.
  - At 6kWh/l → 1.2 W/m^2
- Bioethanol from Corn
  - 1.05 l/m^2 at $23.4*10^6$ J/l give 0.02 W/m^2

Assuming no losses from processing

- Energy Crops
  - 0.5 W/m^2 →0.2 W/m^2
  - If we used 13% of the total surface of the country (roughly the tillable surface) we would get 11.3 kWh/person-day
- Compare with the world-average oil consumption of roughly 23kWh/person–day.

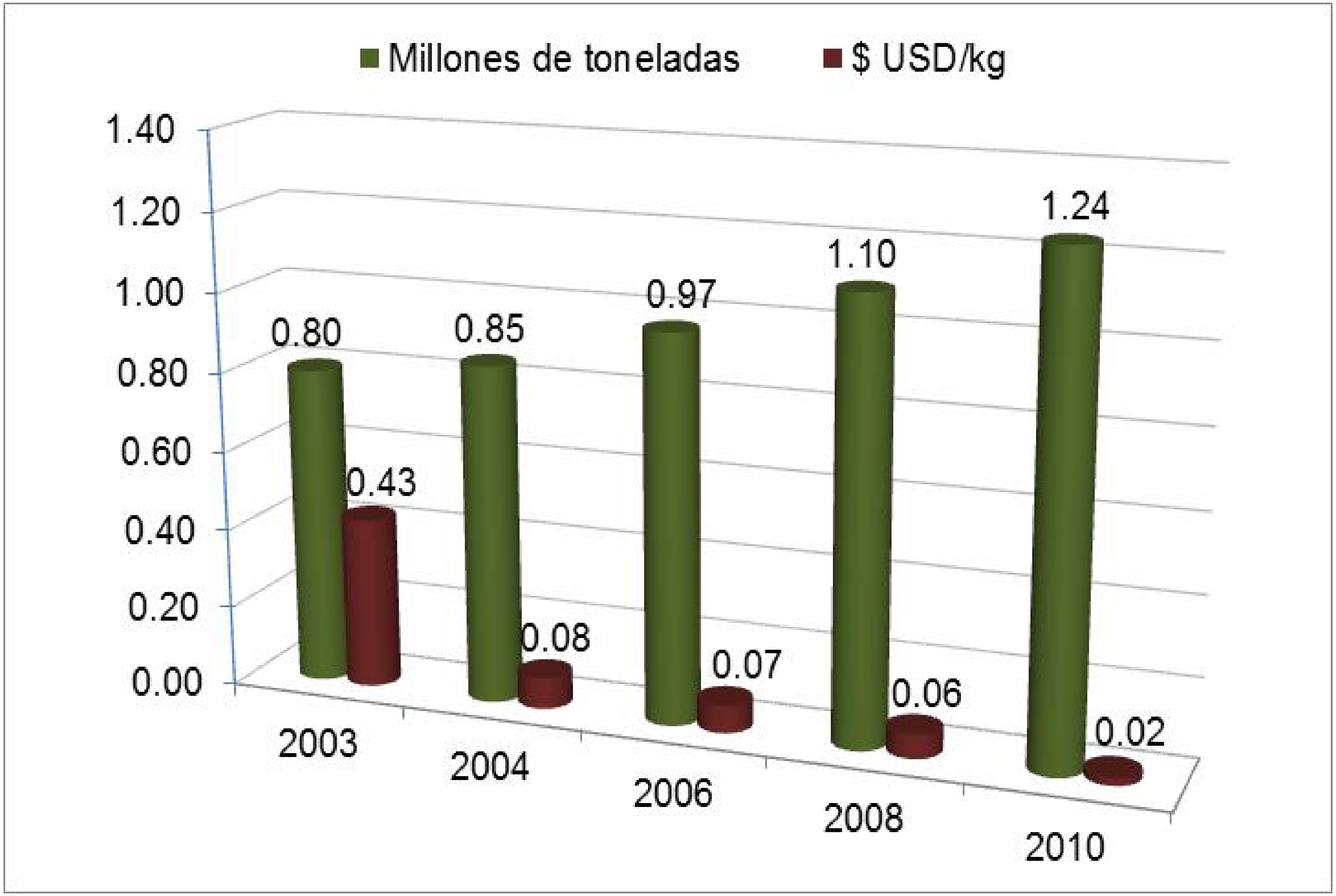
Biodiesel

- Production of biodiesel involves relatively simple chemistry, the transesterification of triglycerides (vegetable oils or animal fat).



- 1 mol of glycerol is produced for every 3 moles of methyl esther.
- **Roughly 1 ton per each 9 tons of biodiesel.**

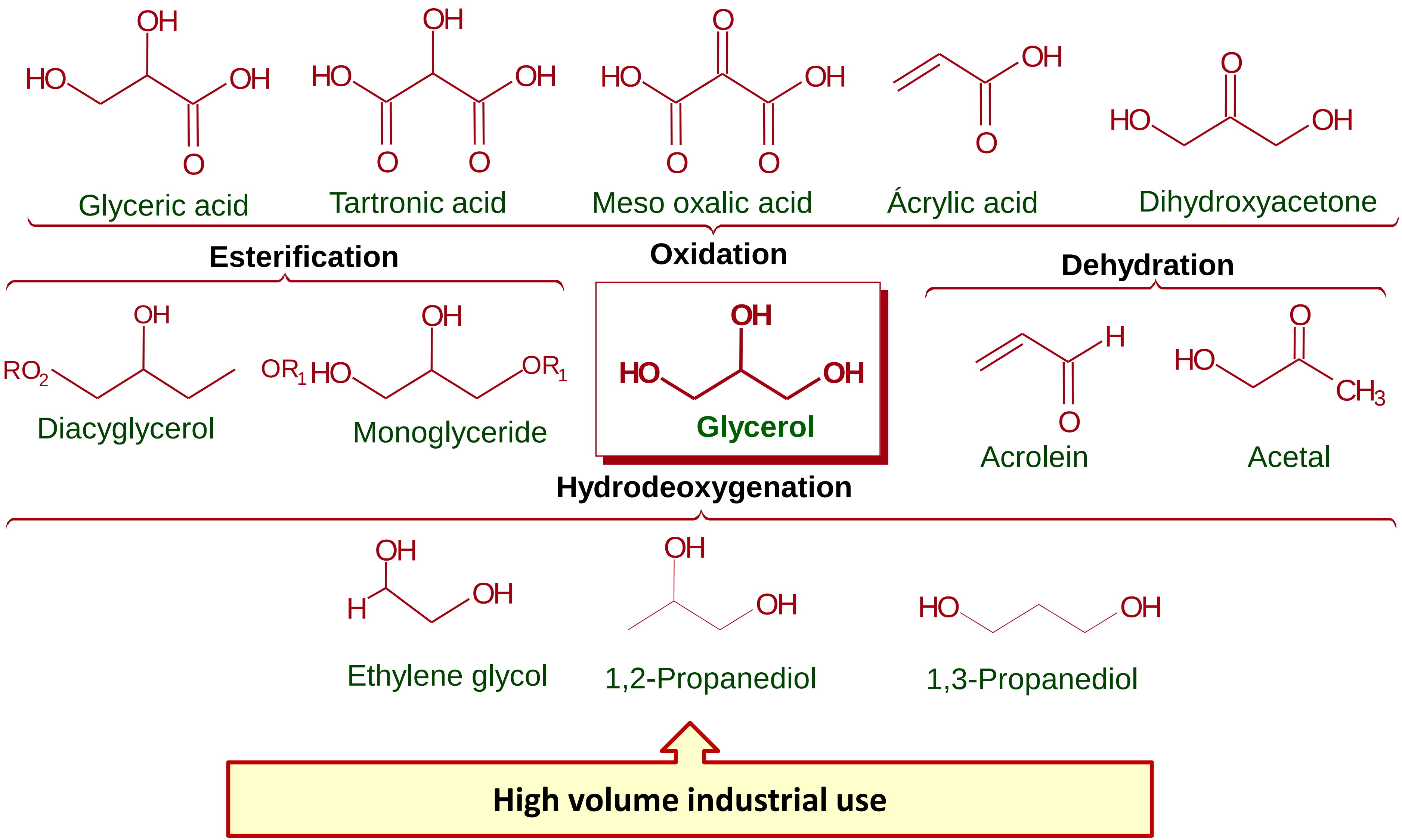
Glycerol glut



Glycerol as a platform chemical

- Highly functionalized molecule.
- Purity of crude glycerol is a key economic factor in its utilization.
- Present in a mixture with methanol, water, inorganic salts, free fatty acids, methyl esters, mono-, di- and triglycerides.
- Synthetic strategy: preserve as much oxygen and carbon as possible.

Glycerol-derived industrial products

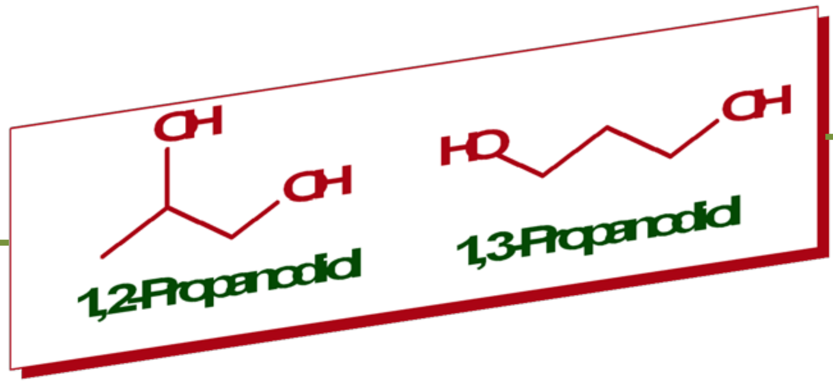


A. Bevilacqua. et al. *Renew. Energ.* 45 **(2012)** 138. Muhammad et al. *Renew. Sust. Energ. Rev*. 16 **(2012)** 2671. A. Corma et al. *J. Catal.* 257 **(2008)** 163. B. Peng, C. Zhao, I. Mejía-Centeno, G. Fuentes, A. Jentys, J. Lercher. *Catal. Today* 183 **(2012**) 3.

Glycerol Hydrodeoxygenation

Hydration of propylene oxide
Selective oxidation of propylene

Hydrolysis of acrolein
Hydroformylation of ethylene oxide



Used as a Solvent - Moistener - Lubricant

- 180,000 t/year
- Polyesthers
- Detergents and antifreeze agents

Monomer in polycondensations

- 120,000 t/year
- 499 patents 1970-2006
- Polymers and solvent
- Refrigerant and paints

Xiaoyuan Liao et al. *J. Ind. Engin. Chem.* 18 **(2012)** 818-821. I. Jiménez-Morales et al. *App. Catal. B: Environ*. 117 **(2012)** 253. Shuixin Xia et al. *Bio. Tech.* 104 **(2012)** 814–817. Zhiwei Huang et al. *Catal. Today* 183 **(2012)** 42.

Reaction Coupling at the catalyst level

Processing usually requires high H_2 pressures and temperatures. We are exploring the coupling of H_2 production and hydrodeoxygenation by having different active sites on the catalyst surface. That reduces external H_2 requirements and improves the overall economics of the process.

We are using Pd-Cu on a basic support such as Na-TiO_2 or MgO.

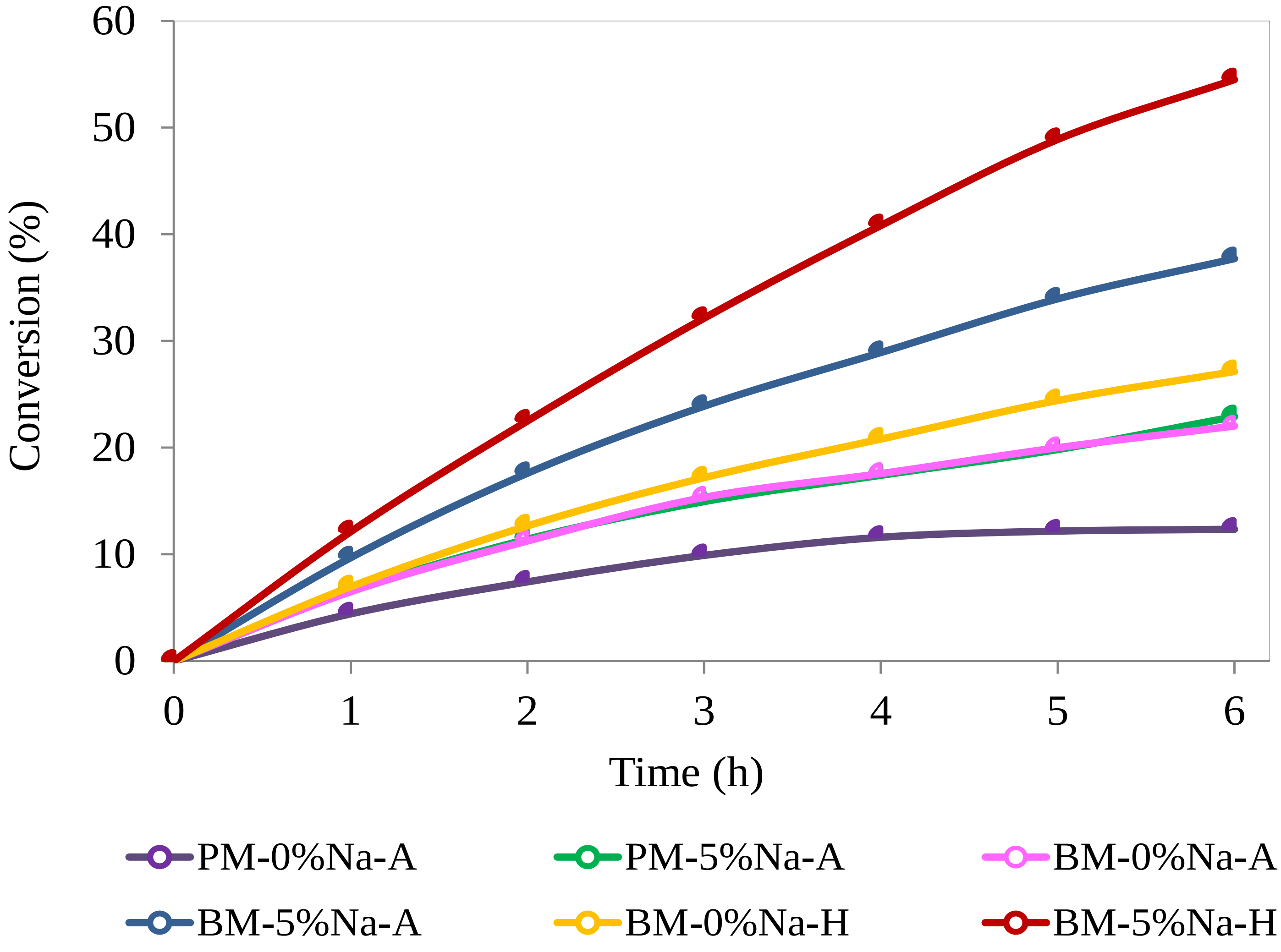
$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$$ **Reforming**

$$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$$ **Hydrodeoxygenation**

↓

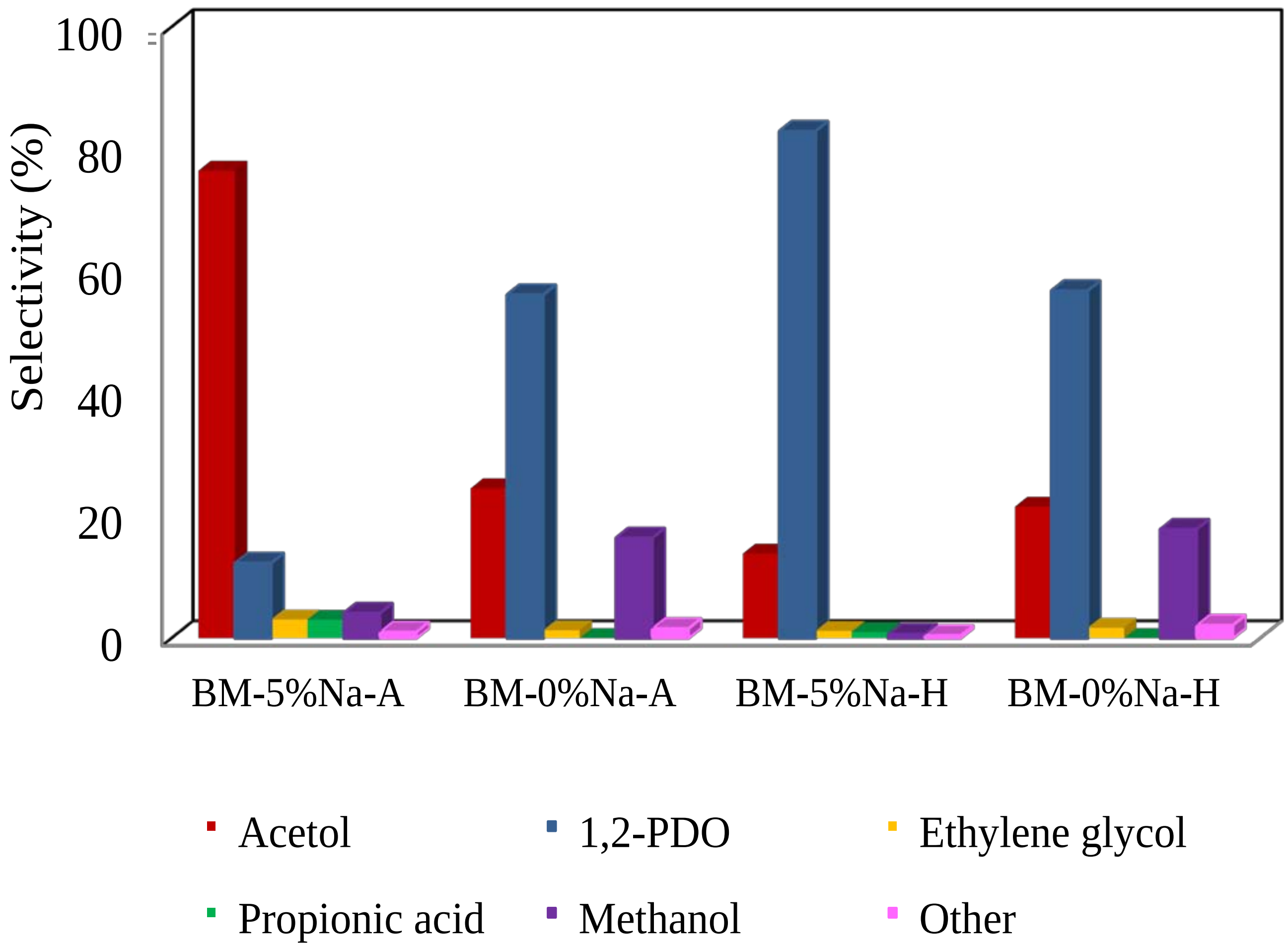
Selective Hydrodeoxygenation of Glycerol to Propanediols

There is a synergistic effect when Cu and Pd are combined in the same material at 220 C

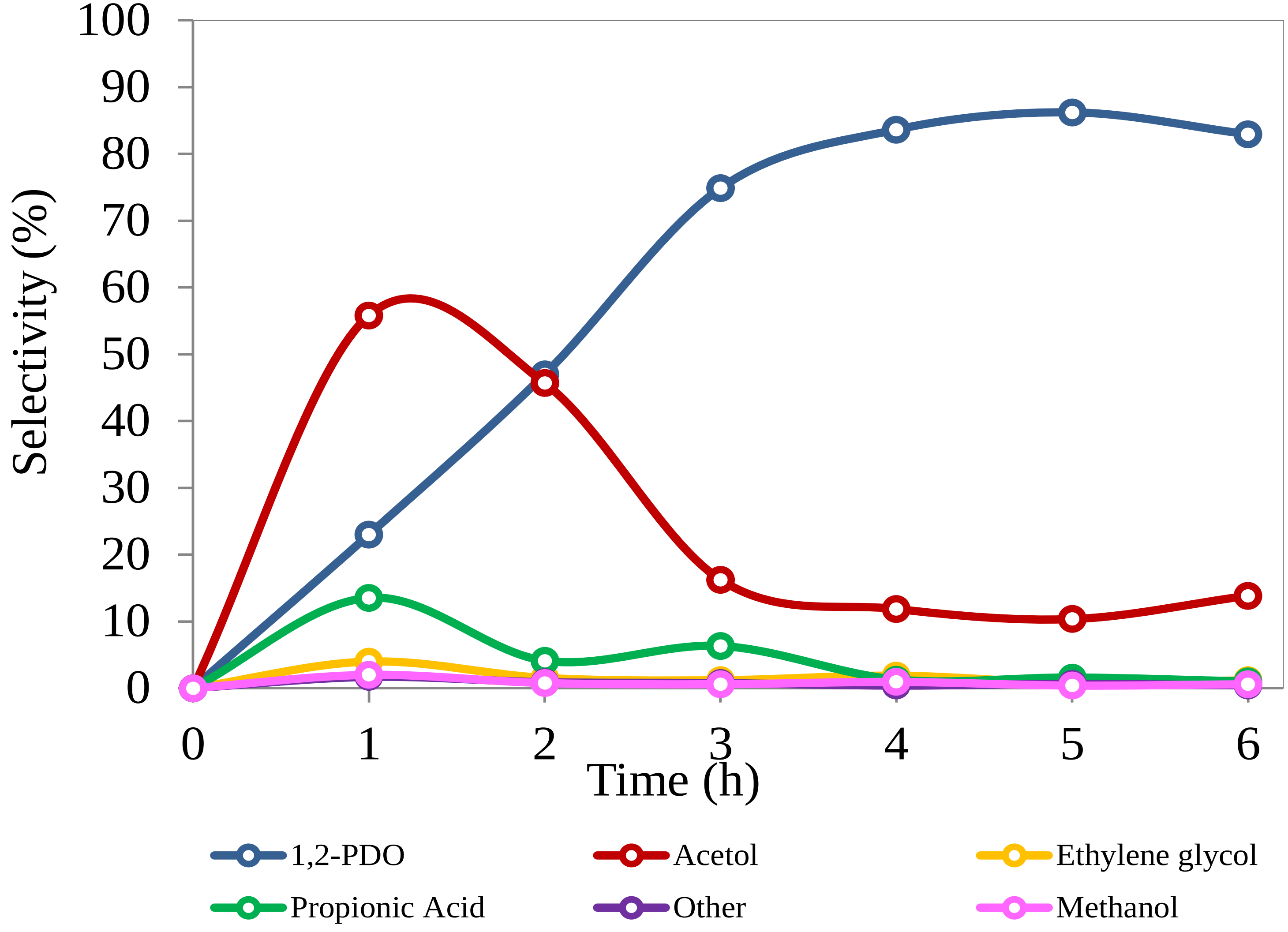


Stéphanie Lambert et al. *Appl. Catal. A Gen.* 270 **(2004)** 201;Wenliang Gao et al. *Appl. Catal. B Environ.* 46 **(2003)** 341.

Selectivity to 1,2-PDO increased with the use of both Na and H_2 at 220 C

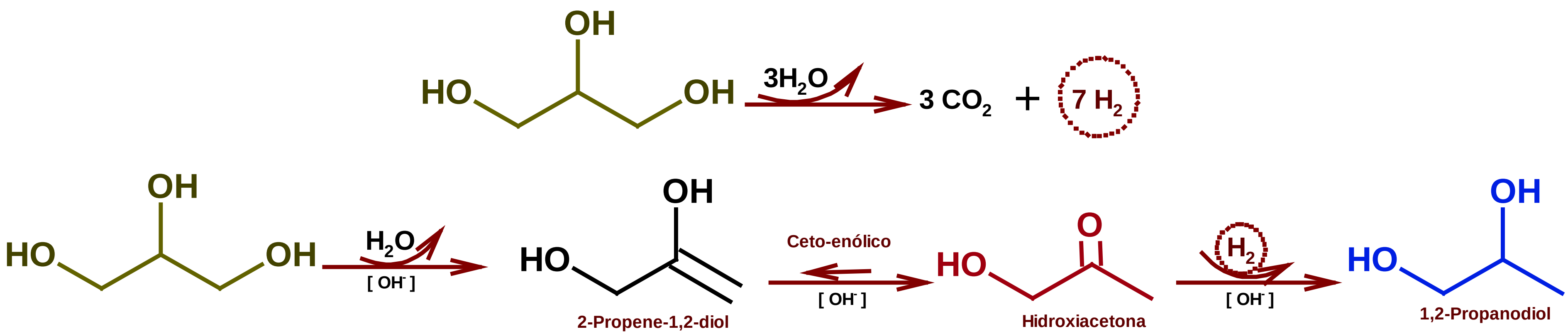


Production of 1,2-PDO with high selectivity on Cu-Pd/TiO_2-5.0%Na and pressure low H_2 at 220 C



There is leaching, so the reaction probably has both homogeneous and heterogeneous contributions

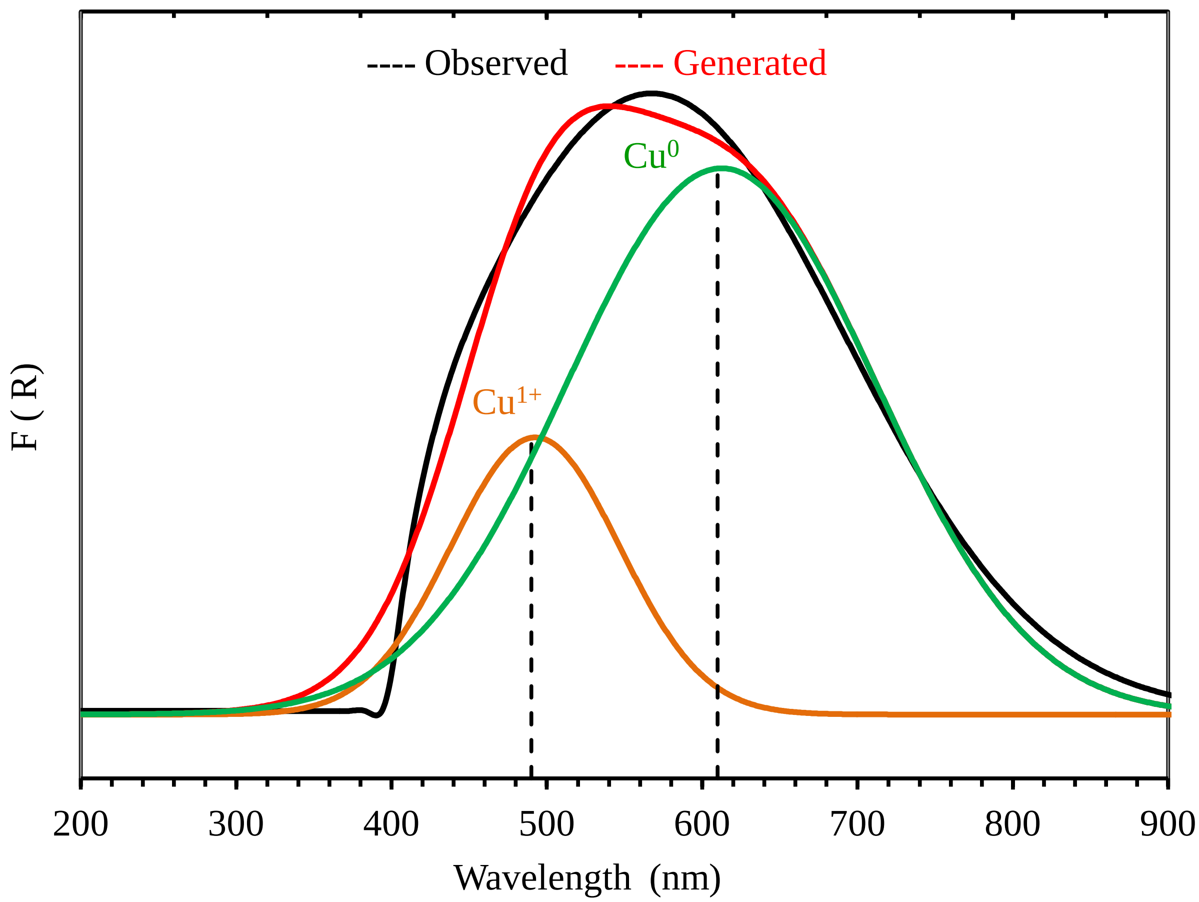
Catalyst	Sodium Amount (%)			Sodium leaching (%)	TEM average size Cu-Pd (nm)	Specific Area (m^2/g)
	Fresh	Solution	Used			
Cu-Pd/TiO_2-0%Na	0	0	0	0	20.3	46.4
Cu-Pd/TiO_2-5%Na	4.8	2.4	2.4	50	15.4	42.3



The mechanism involves dehydration followed by keto-enol tautomerization and hydrogenation

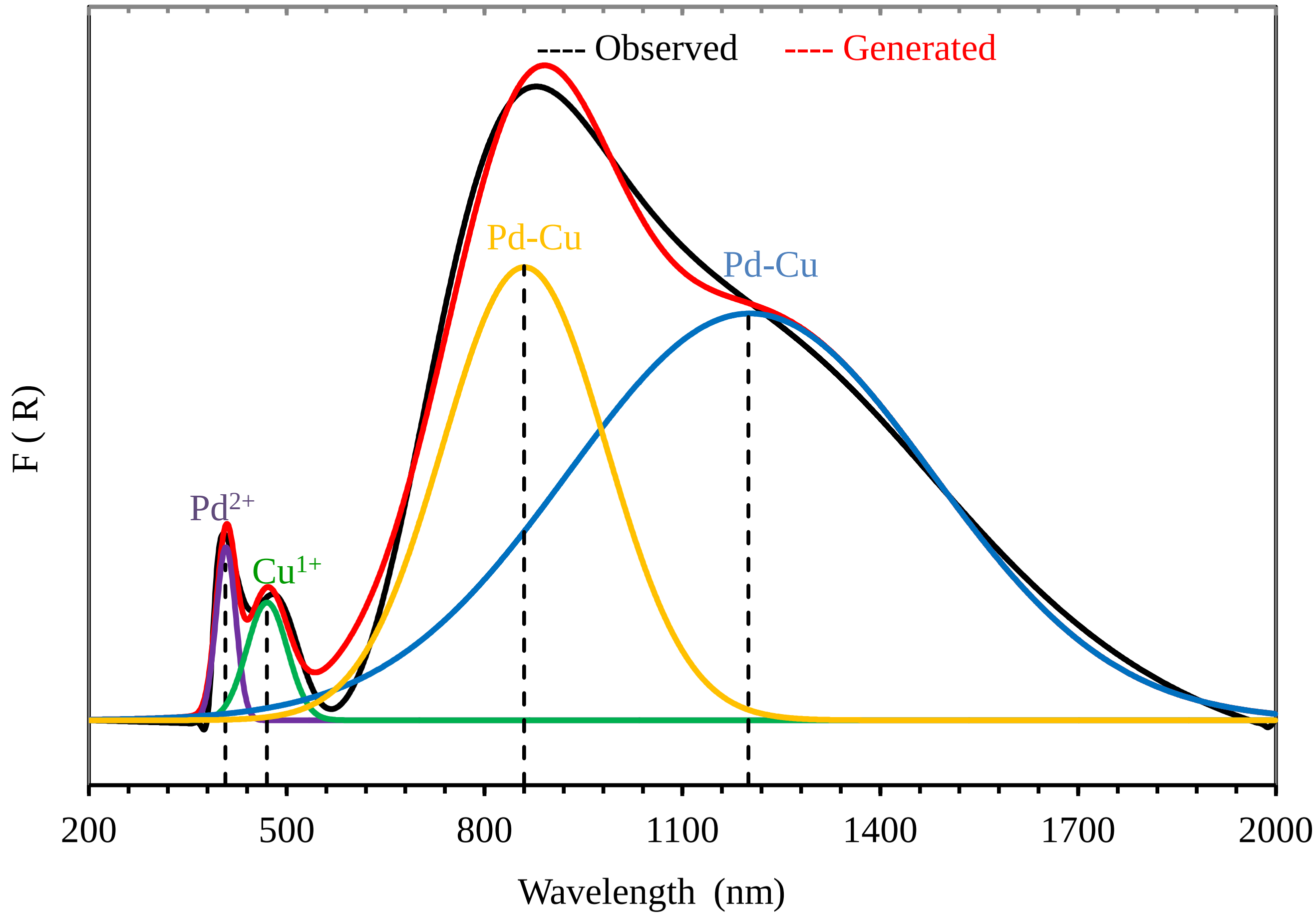
Stéphanie Lambert et al. *Appl. Catal. A Gen.* 270 **(2004)** 201;Wenliang Gao et al. *Appl. Catal. B Environ.* 46 **(2003)** 341.

There are oxidized species and metallic copper in the Cu monometallic catalyst



Lei Huang et al. *Catal. Commun.* 10 **(2009)** 1839; Y. Bessekhouad et al. *Catal. Today.* 101 **(2005)** 315.

Formation of Pd-Cu alloy in the bimetallic catalyst



Sue V. Myers et al. *Chem. Mater.* 21 **(2009)** 4824.

Highlights

- We observed a synergistic effect in the production of 1,2-PDO and acetol when Cu and Pd were combined in the same material. The monometallic materials and their physical mixture showed lower activity under the conditions of our study.
- Glycerol in basic aqueous solution, produces 1,2-PDO + acetol with high yield and selectivity and very low amounts of ethylene glycol, indicating that C-C breaking is almost suppressed.
- This system may be a promising alternative for industrial applications. Our results are better or comparable with reports in the literature, but we use lower H_2 pressure.

What is required to detonate the use of RE?

Enhanced scientific and engineering knowledge should lead to performance improvements and cost reductions in RE technologies. Additional knowledge related to RE and its role in GHG emissions reductions remains to be gained in a number of broad areas including [for details, see Table 1.1]:

- Future cost and timing of RE deployment;
- Realizable technical potential for RE at all geographical scales;
- Technical and institutional challenges and costs of integrating diverse RE technologies into energy systems and markets;
- Comprehensive assessments of socioeconomic and environmental aspects of RE and other energy technologies;
- Opportunities for meeting the needs of developing countries with sustainable RE services; and
- Policy, institutional and financial mechanisms to enable cost-effective deployment of RE in a wide variety of contexts.

Knowledge about RE and its climate change mitigation potential continues to advance. The existing scientific knowledge is significant and can facilitate the decision-making process [1.1.8].

Acknowledgements

- Alba N. Ardila
- Fernando Bernal
- Victor Rivera A.
- Guillermo Rivera
- Víctor M. Sánchez

Primary references

- Special Report on Renewable Energy Sources and Climate Change Mitigation – Intergovernmental Panel on Climate Change Mayo 2011
- Sustainable Energy without the Hot Air, DJC MacKay, 2009