Biomass valorization by heterogeneous catalysis: Ethylene glycol production via hydrogenolysis of cellulose using Pd-W_XC/C catalyst

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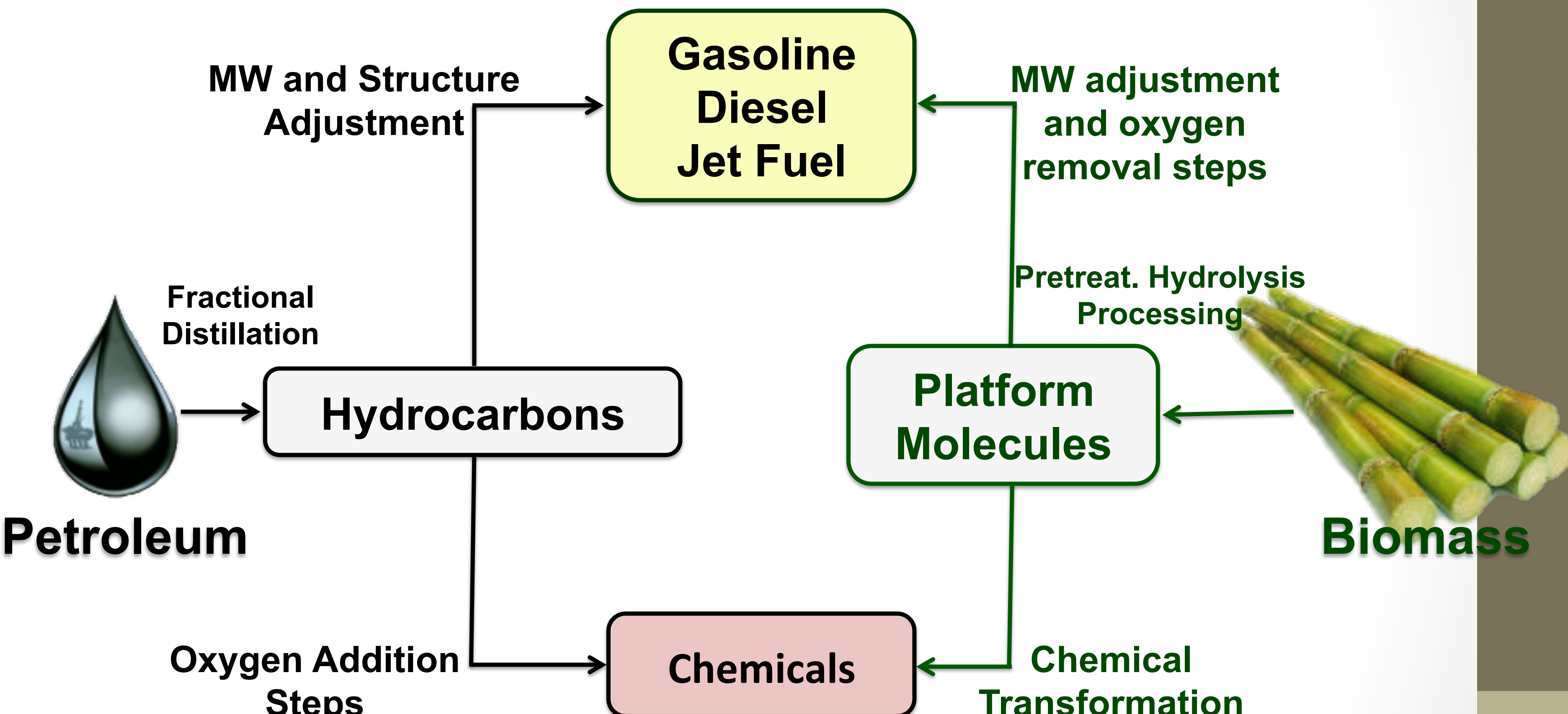
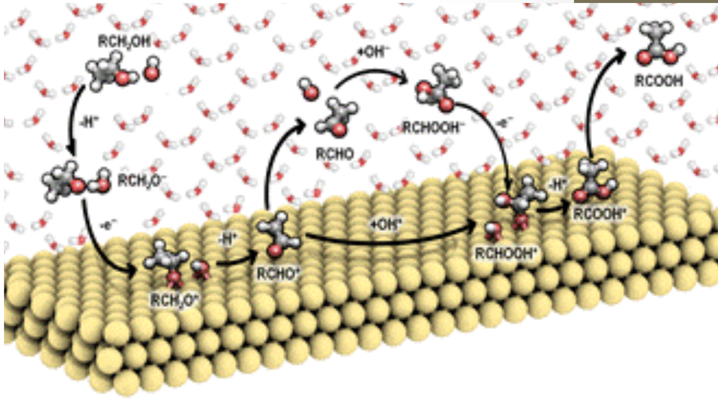
Introduction



Scheme 1: Relationship between petroleum and biomass in the production of fuels and chemicals. (Chem. Soc. Rev., 2011, 40, 5266-5281)

Design of Heterogeneous Catalysts

- Potential way to promote biomass transformation;
- Ease separation between products from catalyst as they are in different phases;
- Design of a catalyst in order to modulate the catalytic activity;
- Production of sugar alcohols from cellulose through; hydrogenation/hydrogenolysis of the glucose monomer; [1-2]



1 Yamaguchi, A.; Sato, O.; Mimura, N.; Hirosaki, Y.; Kobayashi, H.; Fukuoka, A. *Catal. Commun.* **2014**, 54, 22–26.
2 Li, Y.; Liao, T.; Cao, X.; Wang, T.; Ma, L.; Long, J. *Biomass and Bioenergy.* **2015**, 74, 148–161.

Tungsten Carbide

- Carbon atoms incorporated into the metal structure provides catalytic properties similar to noble metals.[1]

Reduction ($WO_3 \rightarrow WO_x\ (3>x>2) \rightarrow WO_2 \rightarrow W$) — **Introduction of C atoms** ($W \rightarrow \beta\text{-}W_2C \rightarrow h\text{-}WC$)

$$WO_3 \rightarrow WO_x\ (3>x>2) \rightarrow WO_2 \rightarrow W \rightarrow \beta\text{-}W_2C \rightarrow h\text{-}WC$$

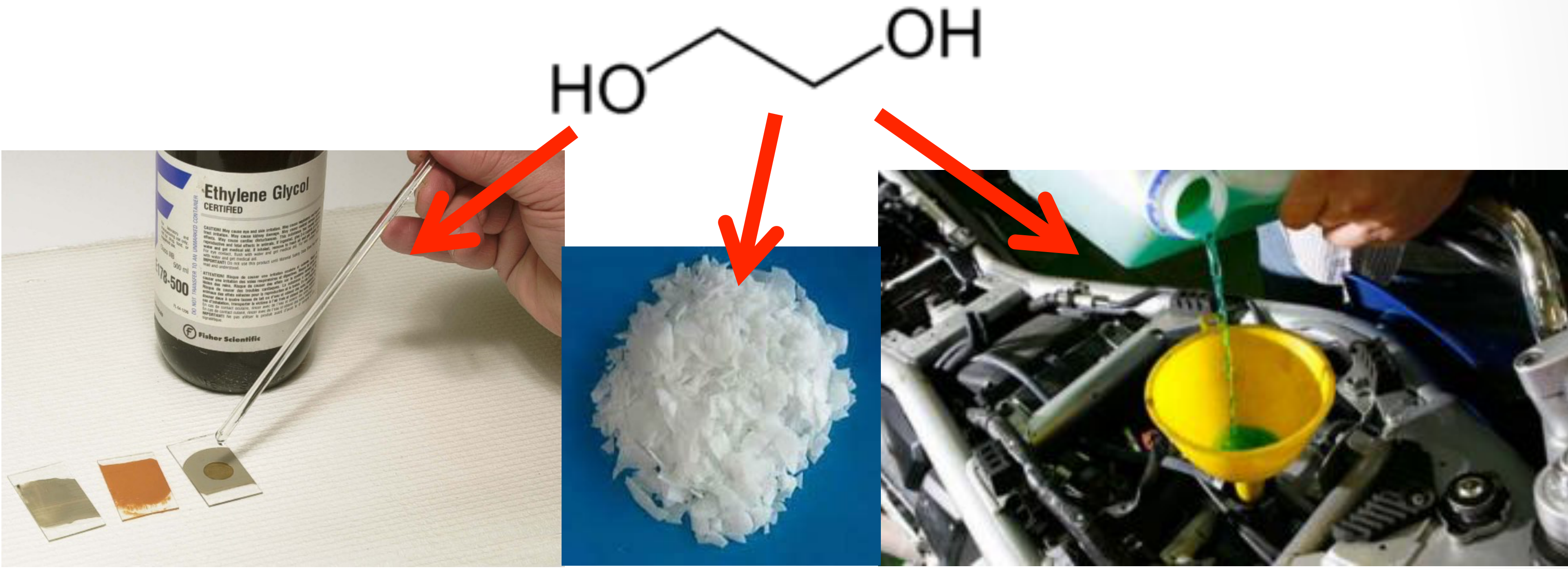
- Cheaper catalyst in comparison with noble metals to be applied in reactions of cellulose conversion using hydrogen, especially hydrogenolysis.[2-4]

- Use of promoters to improve the catalytic properties.

1 Levi, R. B.; Boudart, M. Platinum-like behaviour of tungsten carbide in surface catalysis. **Science**, v. 181, p. 547, 1973.
2 R. Rinaldi, F. Schuth, ChemSusChem. **2009**, 3, 1096-1107.
3 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J. G. Chen, Angew. Chem. Int. Ed. **2008**, 47, 8510-8513.
4 L. Zhou, A. Wang, C. Li, M. Zheng, T. Zhang, ChemSusChem **2012**, 5, 932-938.

Ethylene glycol

- Around 20 million tons/year produced using ethylene oxide in the petrochemical industry. [1]



- Producing ethylene glycol from biomass, is a step forward for the chemical industry independence from petroleum.

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1 Kobayashi, H.; Komanoya, T.; Guha, S. K.; Hara, K.; Fukuoka,A. Conversion of cellulose into renewable chemicals by supported metal catalysis. *Applied Catalysis A: General*, **2011**, 409, 13-20.

Aims

- Synthesis and characterization of tungsten carbide catalyst supported on activated carbon and promoted with palladium.
- Application of these catalysts into cellulose conversion reactions using hydrogen.

Experimental

- Catalyst Preparation

$(NH_4)_{10}W_{12}O_{41}.5H_2O$ + Activated Carbon → W/C —($PdCl_2$)→ Pd-W/C

850 ^oC — 40 min — CH_4/H_2 (10:90 mL min^{-1})

8 ^oC min^{-1}

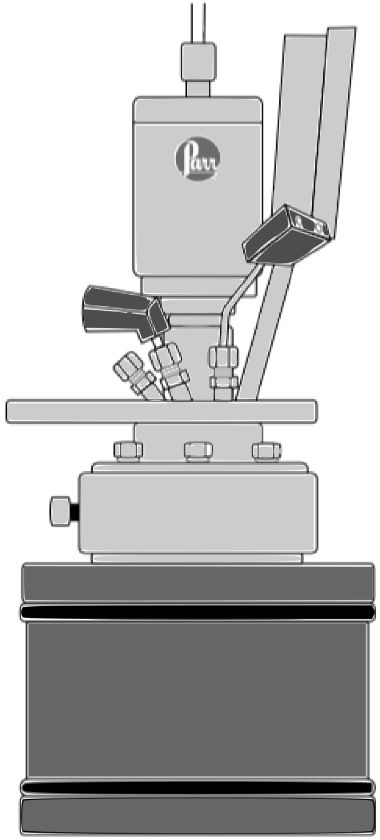
R.T. — Pd-W/C → $Pd\text{-}W_XC/C$

$Pd\text{-}W_XC/C$ → Crystalline Structure; Surface Area; Surface Chemical Composition

Catalyst Composition
2% Pd
30% W
68% C

Cellulose Conversion Reactions

- 1,50 g Avicel cellulose
- 0,50 g Pd-W_XC/C
- 150 mL H_2O
- 800 psi H_2
- Stirring 1000 rpm
- Temperature (^oC): 190, 220 e 250
- Time (min): 30 – 120



➢ **After Reaction**

Solid Phase:
Pd-W_XC/C + Cellulose

TGA[1]

Liquid Phase:
Products

GC e HPLC

Yield (%) = $(n_{Carbon\ Product}/n_{Carbon\ Cellulose})$. 100

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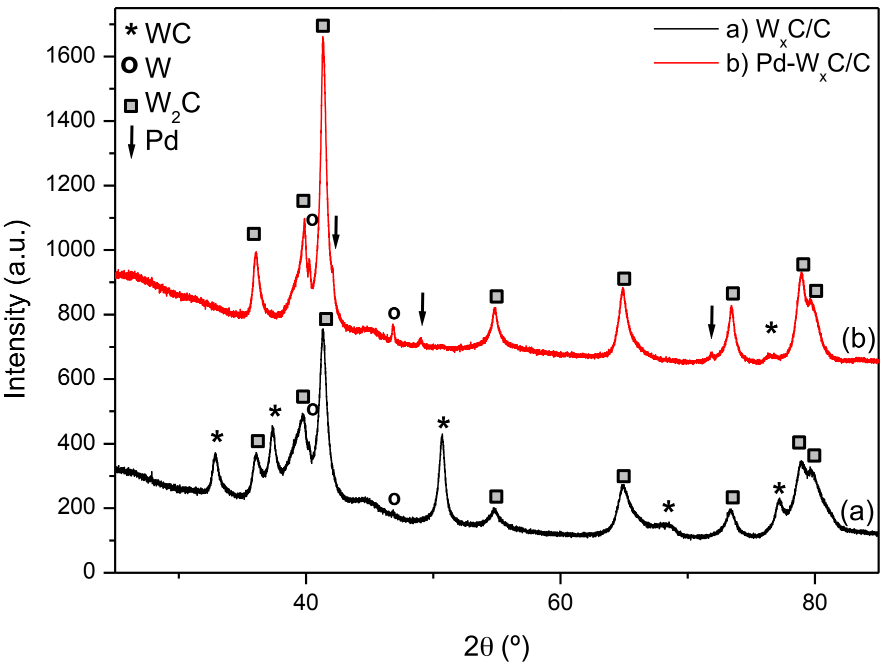
1 Leal, G. F.; Ramos, L. A.; Barrett, D. H.; Curvelo, A. A. S.; Rodella, C. B. *Thermochim. Acta.* **2015**, 616, 9-13.

Catalyst characterization

Structural Characterization



X ray diffraction analysis

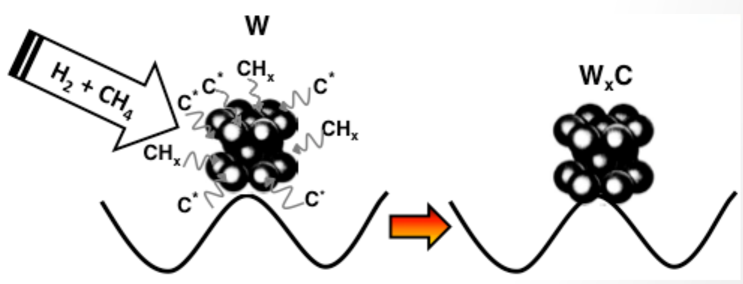
$WO_3 \rightarrow WO_x\ (3>x>2) \rightarrow WO_2 \rightarrow W \rightarrow \beta\text{-}W_2C \rightarrow h\text{-}WC$

Surface chemical composition, surface area and porosity

Catalyst	W/C (%)	BET Surface Area ($m^2\ g^{-1}$)	Total Pore Volume ($cm^3\ g^{-1}$)
W_XC/C	2,9	709	0,70
Pd-W_XC/C	3,8	366	0,30

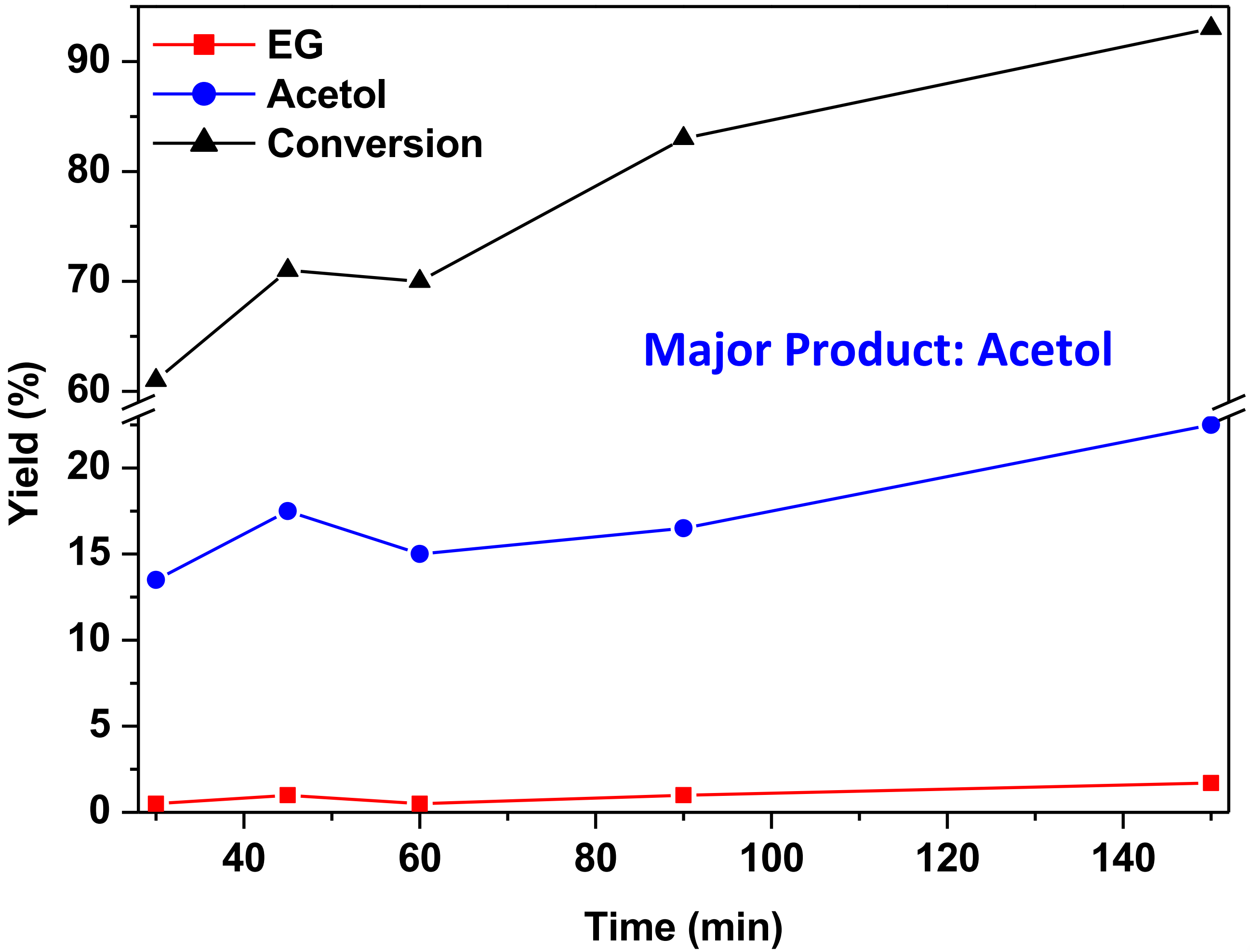
W on surface Increased 31%

Surface area decreased 48% and porosity 57%



Catalytic Reactions

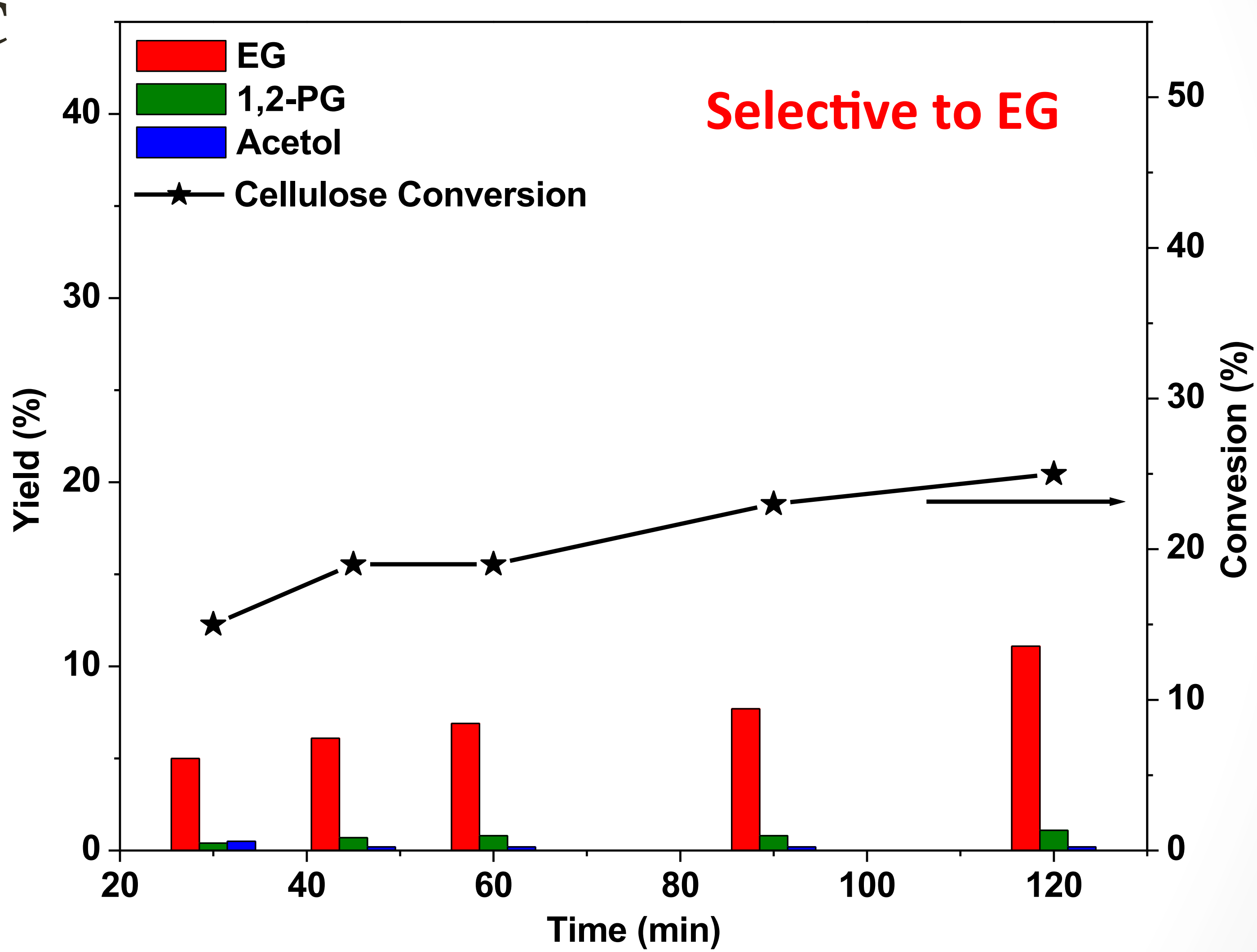
- W_XC/C



Catalytic performance of W_XC/C in cellulose conversion at 220°C.

Pd-W_XC/C – Temperature and Time Effect

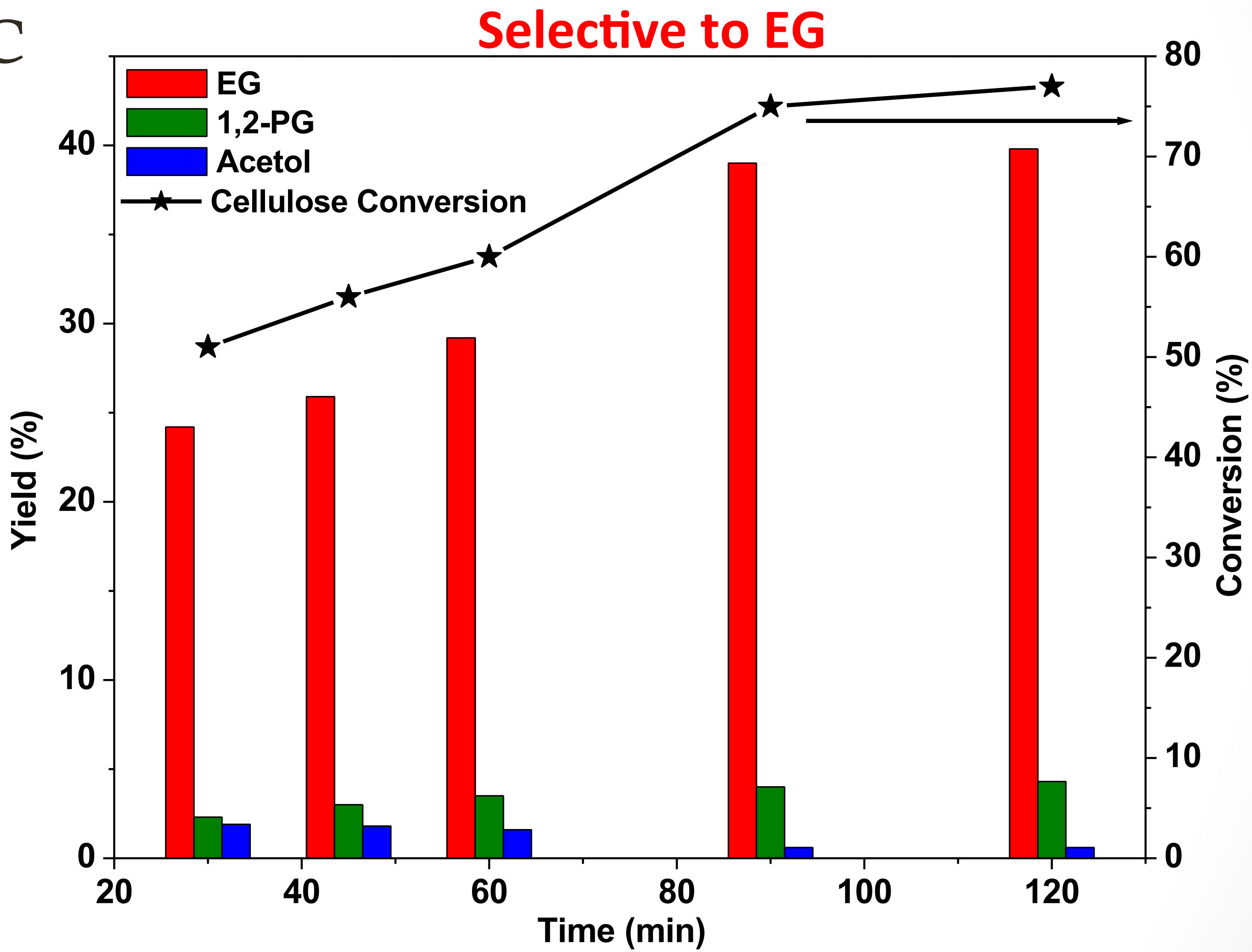
190°C



Catalytic performance of Pd-W_XC/C in cellulose conversion at 190°C.

Pd-W_XC/C – Temperature and Time Effect

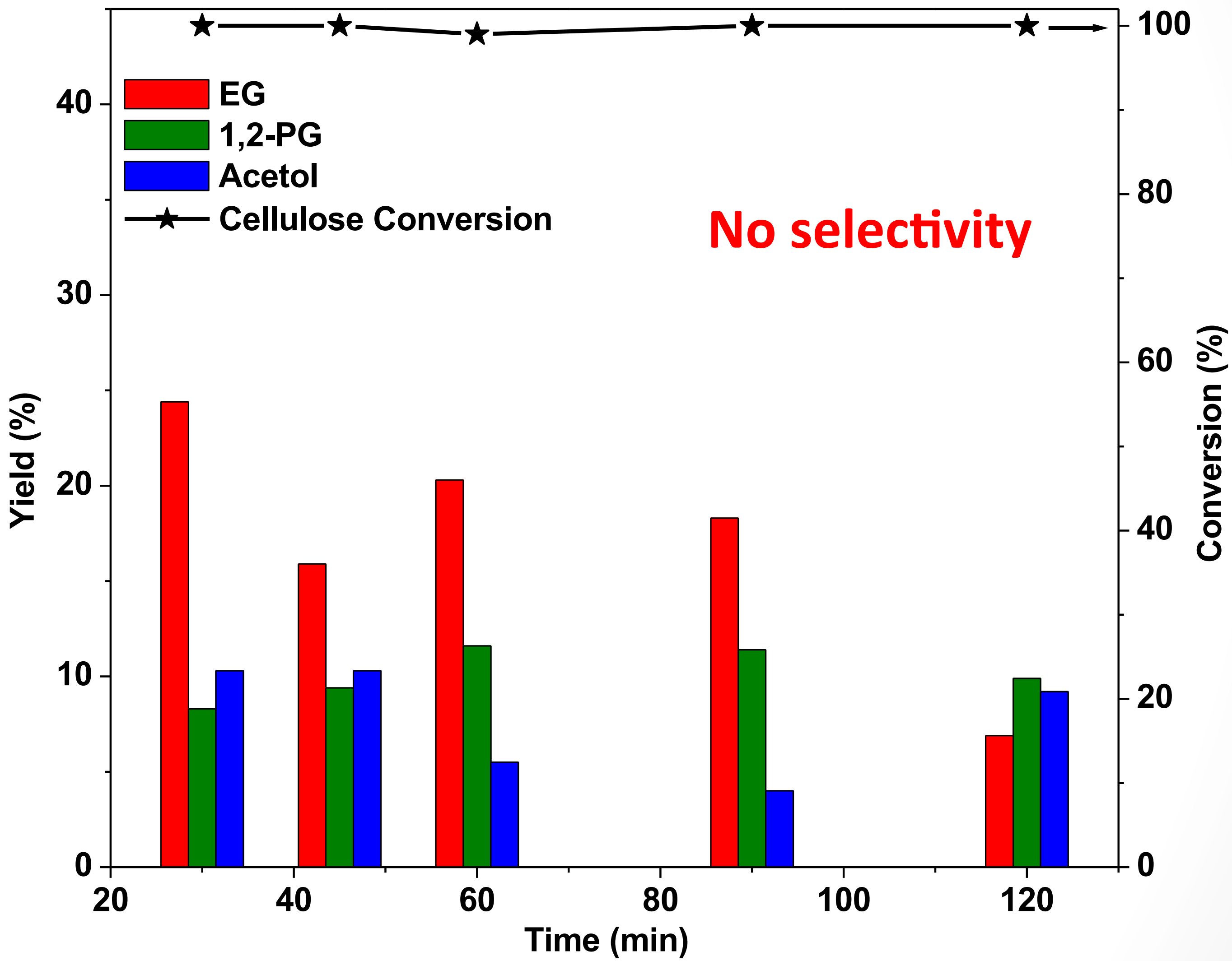
220°C



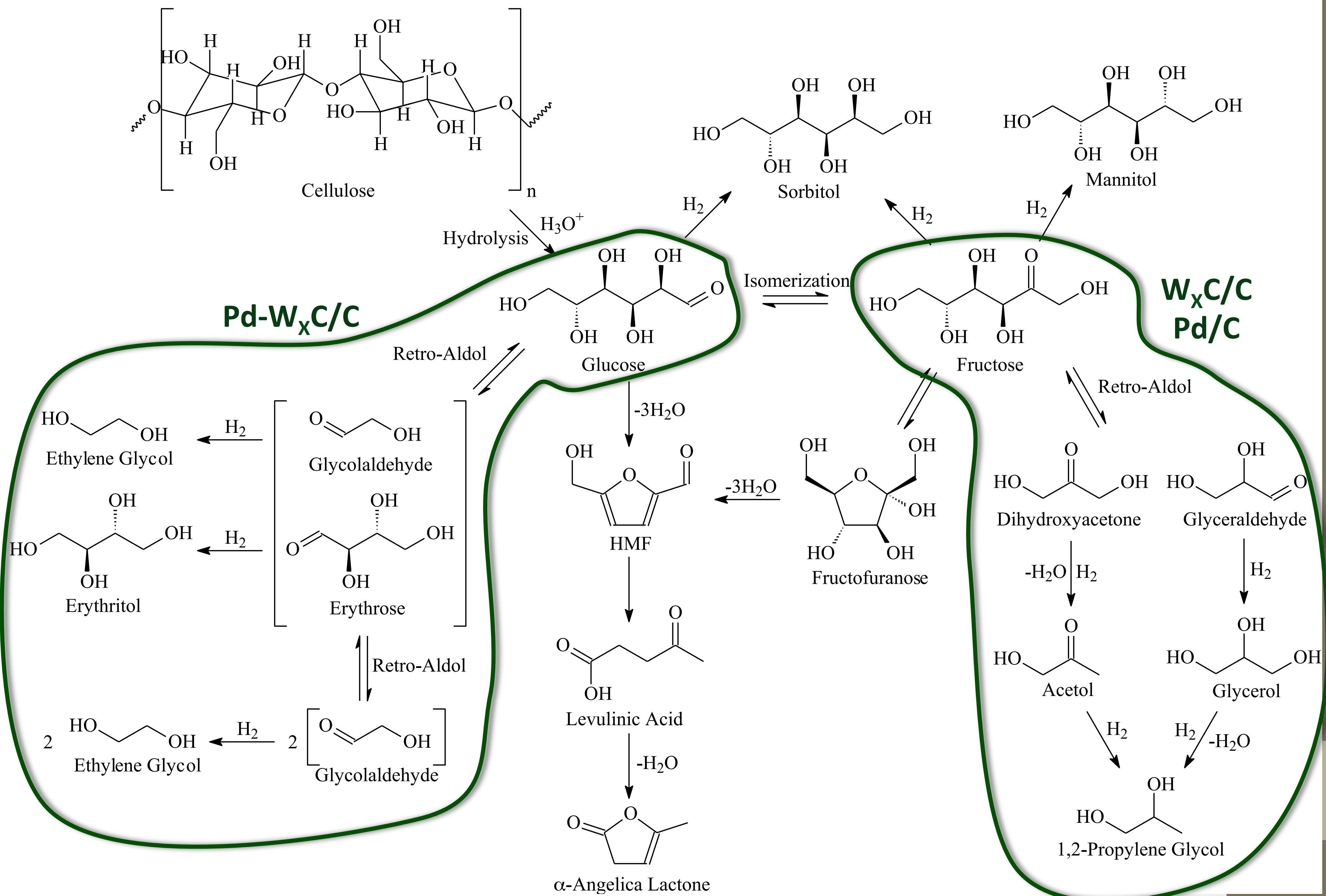
Catalytic performance of Pd-W_XC/C in cellulose conversion at 220°C.

Pd-W_XC/C – Temperature and Time Effect

250°C



Catalytic performance of Pd-W_XC/C in cellulose conversion at 250°C.



Cellulose
Hydrolysis
H_3O^+
H_2
Sorbitol
Mannitol
Glucose
Isomerization
Fructose
Pd-W_XC/C
W_XC/C
Pd/C
Retro-Aldol
Ethylene Glycol
Glycolaldehyde
Erythritol
Erythrose
$-3H_2O$
HMF
Fructofuranose
Levulinic Acid
$-H_2O$
α-Angelica Lactone
Dihydroxyacetone
Glyceraldehyde
Acetol
Glycerol
1,2-Propylene Glycol
2 Ethylene Glycol
2 Glycolaldehyde

Conclusions

- Pd-WXC/C is an effective catalyst to produce ethylene glycol through hydrogenolysis of cellulose.
- The optimal conditions were 220°C and 120 min, where 77% of cellulose was converted, producing 40% of EG yield.
- The catalyst in absence of Pd produced acetol as major product.
- The interaction between Pd and W_XC seems to be important to produce EG.
- Heterogeneous catalysis which already play an important role in the petrochemical industry have great potential to be important in the biorefinery context.

Acknowledgements

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