# HYDROGENOLYSIS OF CELLULOSE CATALYZED BY TUNGSTEN CARBIDE PROMOTED WITH PALLADIUM: EFFECT OF CATALYST AND REACTION PATHWAYS FOR ETHYLENE GLYCOL PRODUCTION


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## Introduc)on

### ➢Celulose

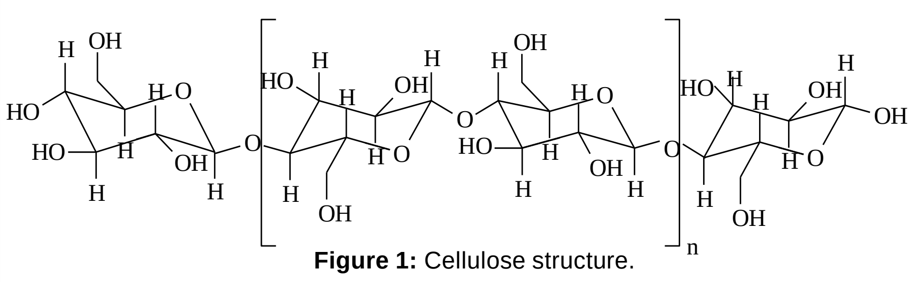


**Figure 1:** Cellulose structure.

### ➢Tungsten Carbide ($W_XC$)

Alternative to replace noble metals in cellulose conversion reactions which use hydrogen, especially hydrogenolysis[1-3].

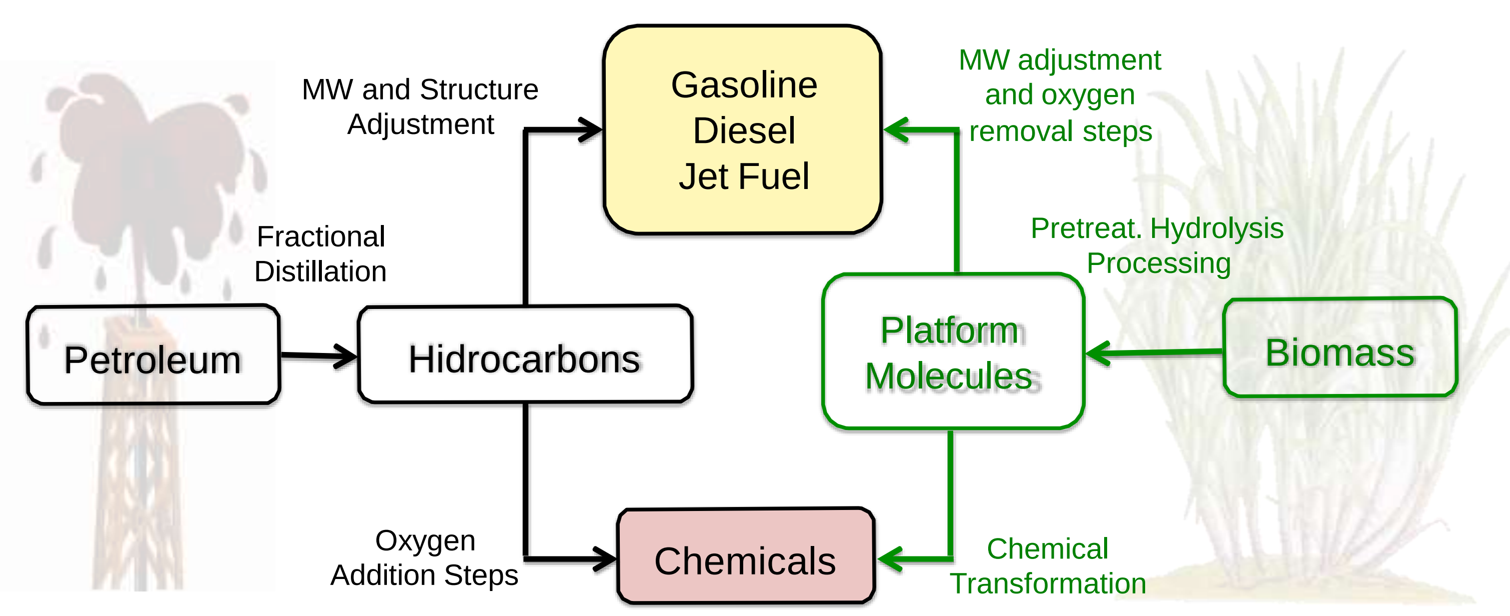



**Figure 2:** Relationship between petroleum and biomass in the production of fuels and chemicals. (*Chem. Soc. Rev.*, **2011**, 40, 5266-5281)

### ➢Goals

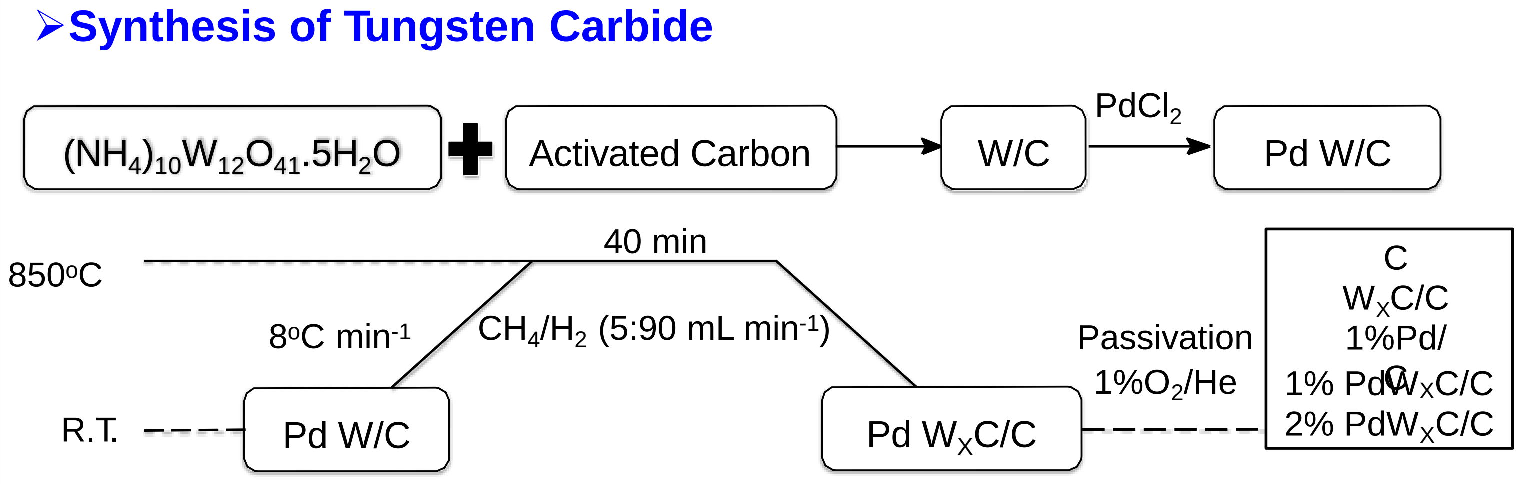
✓Optimization of reaction parameters for catalytic conversion of cellulose in order to maximize the production of ethylene glycol.

✓Comprehension of the role of each catalyst's components in the cellulose transformation.

✓Proposal of a reaction pathway for the hydrogenolysis of cellulose to ethylene glycol.

## Experimental

### ➢Synthesis of Tungsten Carbide




### ➢Catalytic Reactions

✓ 1.50 g Cellulose Avicel; 0.50 g catalyst; 150 mL $H_2O$; 800 psi $H_2$; 220ºC; 1000 rpm.

✓Another tested substrates: Glucose, fructose, sorbitol, acetol.

✓The quantification of reaction products were performed by GC and HPLC.

## Results

### ➢Catalytic Tests

➢Effect of reaction time and Pd loading on products distribution.

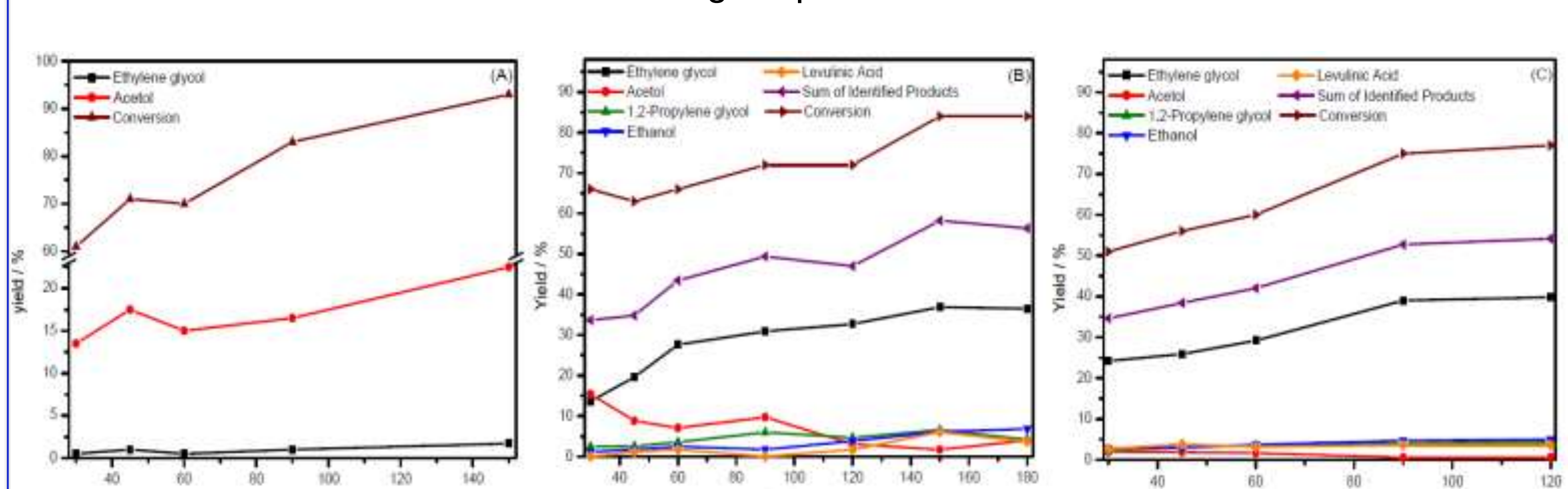



**Figure 3:** Effect of catalyst composition on products of hydrogenolysis of cellulose: (A) $W_XC$/C; (B) 1%Pd$W_XC$/C; (C) 2%Pd$W_XC$/C.

**Table 1:** Conversions and products for the hydrogenolysis of cellulose with different substrates and catalysts.

| Catalyst | Substrate | Conversion (%) | Carbon Yield (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | EG | Acetol | 1-PropOH | 1,2-Prop. Glycol | Levulinic Acid | Sorbitol |
| **C** | **Cellulose** | 26 | ND | 8.0 | ND | ND | 1.2 | ND |
| **1%Pd/C** | **Cellulose** | 73 | 1.7 | 20.5 | ND | 0.1 | 0.3 | ND |
| **$W_XC$/C** | **Cellulose** | 93 | 1.7 | 22.5 | ND | 0.3 | 0.6 | ND |
| **1%Pd$W_XC$/C** | **Cellulose** | 84 | 36.9 | 1.7 | ND | 6.6 | 6.0 | ND |
| **1%Pd$W_XC$/C** | **Glucose** | 100 | 3.7 | 3.4 | 1.7 | 7.3 | 7.3 | 1.7 |
| **1%Pd$W_XC$/C** | **Fructose** | 100 | 0.2 | 7.4 | 1.8 | 13.5 | 12.6 | 1.9 |
| **1%Pd$W_XC$/C** | **Sorbitol** | 41 | 0.4 | 0.2 | 0.1 | 0.3 | 0.9 | --- |
| **1%Pd$W_XC$/C** | **Acetol** | 71 | ND | --- | 3.1 | 55.4 | ND | ND |

### ➢Reaction Pathways

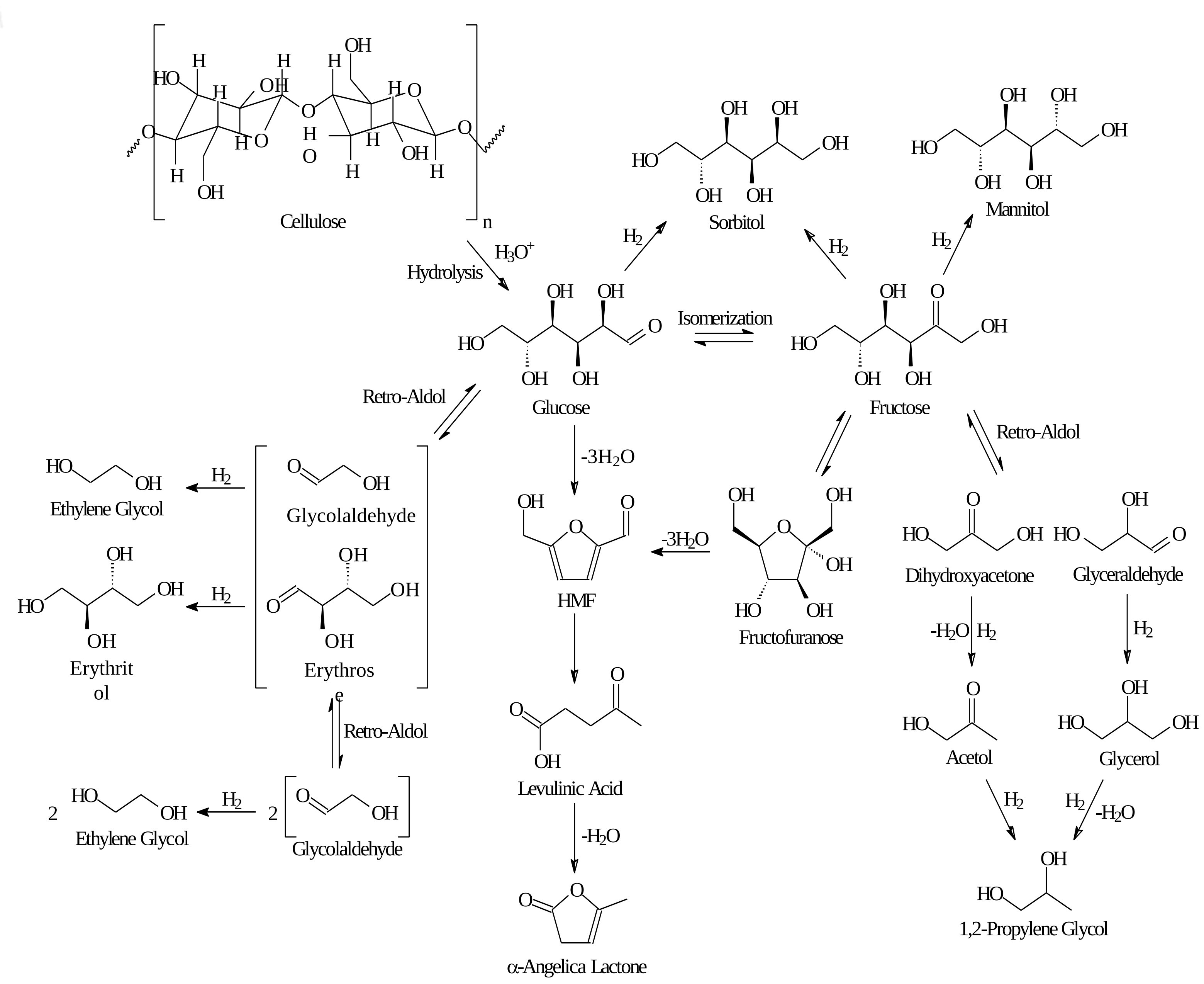



**Figure 4:** Reaction pathways for the hydrogenolysis of cellulose.

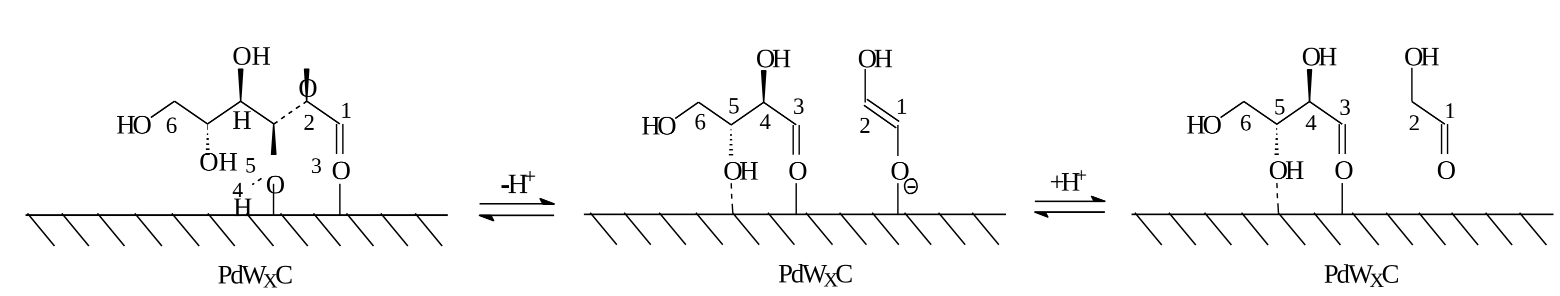



**Figure 5:** Interaction between substrate and catalyst surface.

## Conclusions

The catalyst based on tungsten carbide promoted with palladium showed catalytic activity for the hydrogenolysis of cellulose, directing the conversion to ethylene glycol as major product. The cellulose transformation pathway starts with hydrolysis of the polysaccharide and involves retro-aldol and hydrogenation steps.


## Acknowledgements



[1] R. Rinaldi, F. Schuth, ChemSusChem. **2009**, 3, 1096-1107.

[2] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J. G. Chen, Angew. Chem. Int. Ed. **2008**, 47, 8510-8513. [3] L. Zhou, A. Wang, C. Li, M. Zheng, T. Zhang, ChemSusChem **2012**, 5, 932-938.