Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Hydrodeoxygenation of Vegetable Oils over Biochar Supported Bimetallic Carbides for Producing Renewable Diesel under Mild Conditions

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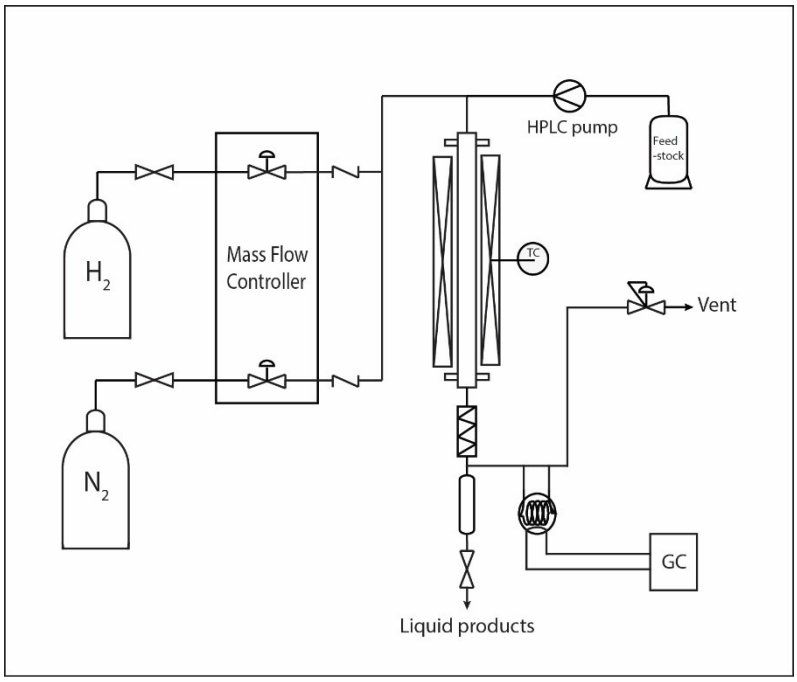

Figure S1. Continuous flow process diagram of HDO system

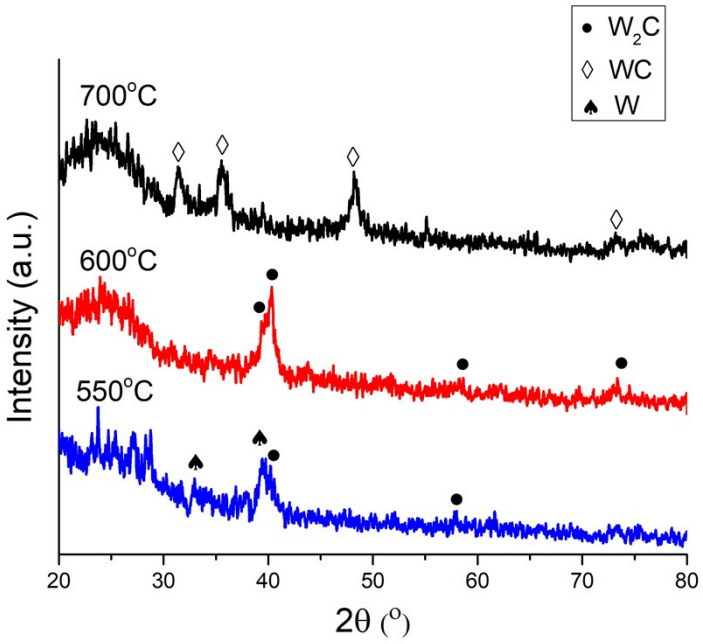

Figure S2. XRD diffractograms of biochar supported monometallic tungsten carbides WC/C prepared at different temperatures (550, 600, 700°C)

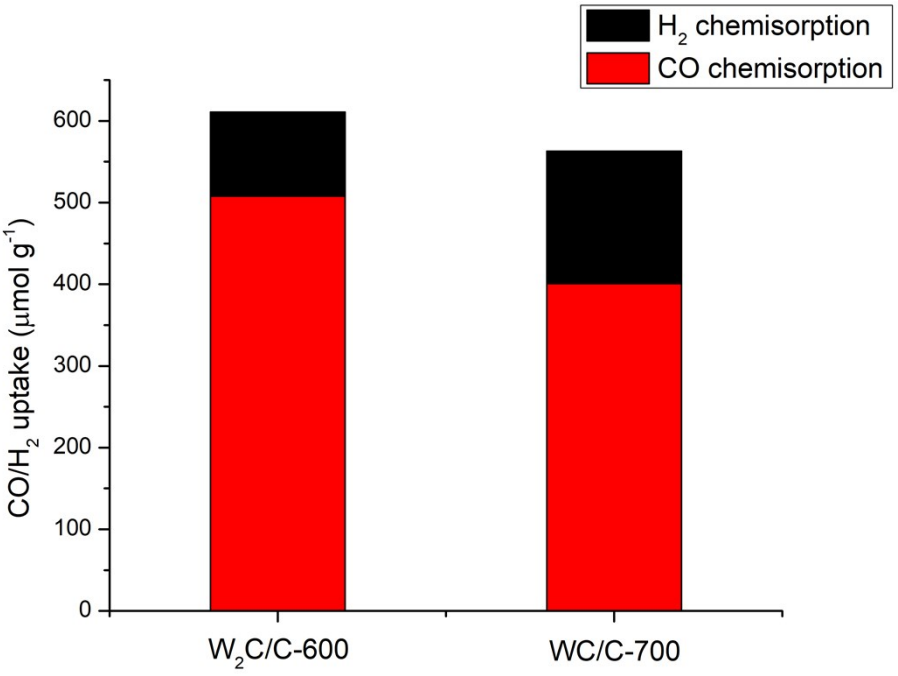

Figure S3. CO and H_2 uptake (μmol g^{-1}) of monometallic W carbides supported on biochar prepared at 600 and 700°C.

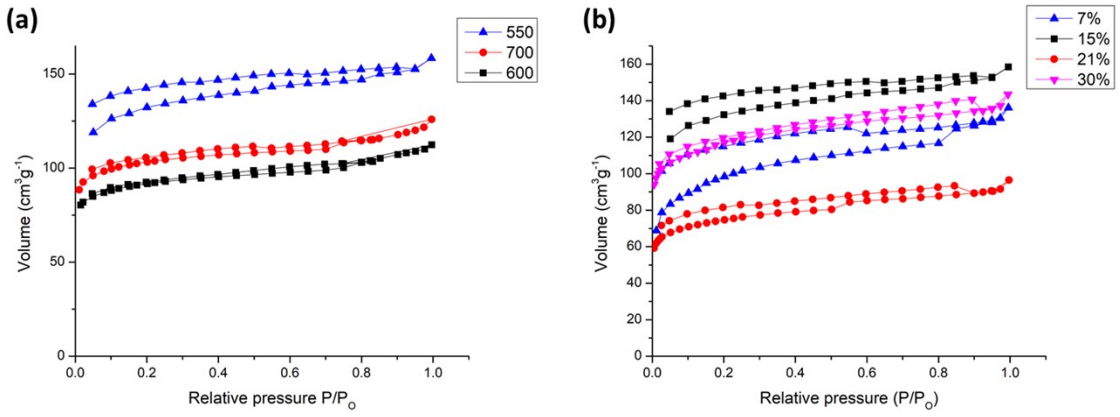

Figure S4. Physisorption isotherms of biochar supported bimetallic carbides synthesized at (a) different temperatures: 550, 600, and 700 ^{o}C; (b) different metal contents: 7, 15, 21, and 30 wt%.

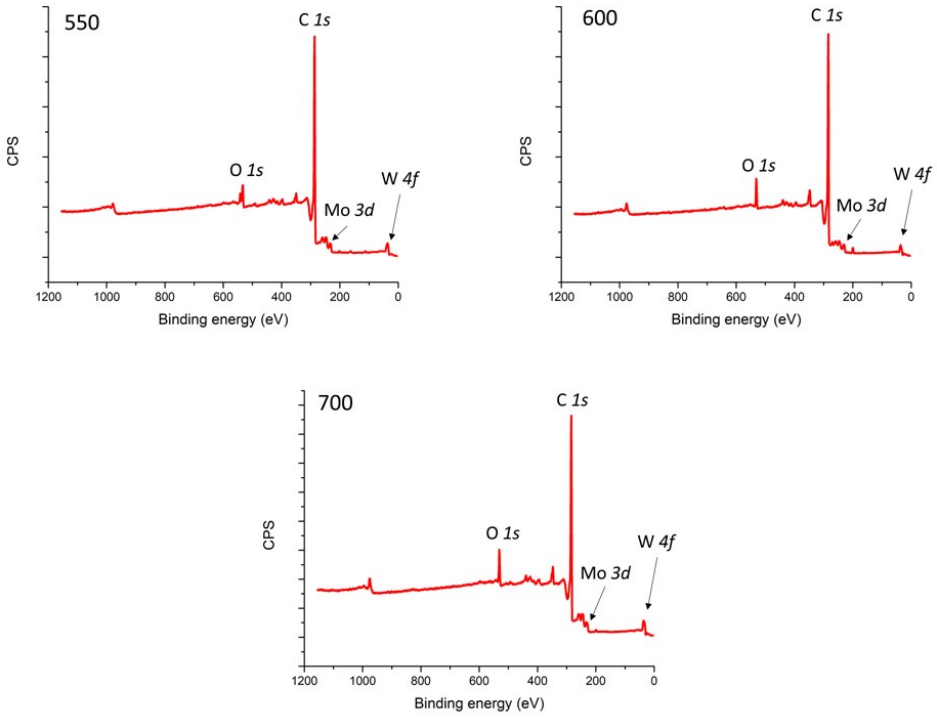

Figure S5. XPS survey spectra of MoWC/C carbides synthesized at 550, 600, and 700°C.

Table S1. Comparison of deoxygenation activity of vegetable oils and model compounds over various types of catalyst.

Catalysts	Reactant	Reaction conditions				Conversion [%]	Selectivity to hydrocarbons [%]	Ref
		T [°C]	P [psig]	LHSV[a] [h^{-1}]	Time[b] [h]			
Mo_2C/NMC	Oleic acid	350	435	-	3	91.0	83.4	[1]
α-MoC_{1-x}/CNF	Stearic acid	350	580	-	6	92.0	-	[2]
β-Mo_2C/CNF	Stearic acid	350	580	-	6	85.0	-	[2]
Mo_2C/AC	Fatty acids	360	435	-	3	96	☐85	[3]
Mo_2C/AC	Soybean oil	380	290	-	3	100	☐100	[4]
β-Mo_2C/Al_2O_3	Sunflower	360	725	5.0	-	100	90	[5]
W_2C/AC	Fatty acids	360	435	-	3	55	☐53	[3]
NiMoC/ZSM5	Soybean	360-450	650	1.5	-	100	☐50	[6]
NiMoC/Al-SBA-15	Soybean	400	600	1.0	-	96	97	[7]
MoCx/Al_2O_3	Rapeseed oil	350-390	797	1,2,4	-	-	☐73-80	[8]
MoS_2/Al_2O_3	Soybean oil	380	290	-	3	83.5	-	[4]
NiMoS/Al_2O_3	Canola	350	450	1.0	-	100	77	[9]
CoMoS/Al_2O_3	Canola	375	450	1.0	-	100	79	[9]
NiP/Al_2O_3	Soybean oil	380	290	-	3	48.7	-	[4]
MoPx/Al_2O_3	Rapeseed oil	350-390	797	1,2,4	-	-	-	[8]
Nitride NiMo/ZSM5	Soybean	360-450	650	1.5	-	100	☐50	[6]
MoNx/Al_2O_3	Rapeseed oil	350-390	797	1,2,4	-	-	-	[8]
MoO/Al_2O_3	Soybean oil	380	290	-	3	85.6	-	[4]
Mo/Al_2O_3	Soybean oil	380	290	-	3	68	-	[4]
Ni/Al_2O_3	Canola	400	500	0.5	-	☐80	92	[10]
Ni/Al_2O_3	Soybean oil	380	290	-	3	18.1	-	[4]
Pd/C-biphasic	Stearic acid	260	400	-	6	100	☐99	[11]
Pt/C	Oleic acid	350	435	-	3	79.8	69.1	[1]
MoWC/C	Canola oil	250	450	5.0	-	100	☐ 87	Present work

[a] liquid hourly space velocity (h^{-1}) for continuous reactor.
[b] time of reaction (h) for batch reactor.

References

1. Wang, F.; Jiang, J.; Wang, K.; Zhai, Q.; Long, F.; Liu, P.; Feng, J.; Xia, H.; Ye, J.; Li, J., Hydrotreatment of lipid model for diesel-like alkane using nitrogen-doped mesoporous carbon-supported molybdenum carbide. *Applied Catalysis B: Environmental* **2019,** *242*, 150-160.
2. Macedo, L. S.; Oliveira Jr, R. R.; van Haasterecht, T.; da Silva, V. T.; Bitter, H., Influence of synthesis method on molybdenum carbide crystal structure and catalytic performance in stearic acid hydrodeoxygenation. *Applied Catalysis B: Environmental* **2019,** *241*, 81-88.
3. Wang, F.; Jiang, J.; Wang, K.; Zhai, Q.; Sun, H.; Liu, P.; Feng, J.; Xia, H.; Ye, J.; Li, Z., Activated carbon supported molybdenum and tungsten carbides for hydrotreatment of fatty acids into green diesel. *Fuel* **2018,** *228*, 103-111.
4. Wang, F.; Xu, J.; Jiang, J.; Liu, P.; Li, F.; Ye, J.; Zhou, M., Hydrotreatment of vegetable oil for green diesel over activated carbon supported molybdenum carbide catalyst. *Fuel* **2018,** *216*, 738-746.
5. Sousa, L.; Zotin, J.; da Silva, V. T., Hydrotreatment of sunflower oil using supported molybdenum carbide. *Applied Catalysis A: General* **2012,** *449*, 105-111.
6. Wang, H.; Yan, S.; Salley, S. O.; Ng, K. S., Hydrocarbon fuels production from hydrocracking of soybean oil using transition metal carbides and nitrides supported on ZSM-5. *Industrial & Engineering Chemistry Research* **2012,** *51* (30), 10066-10073.
7. Wang, H.; Yan, S.; Salley, S. O.; Ng, K. S., Support effects on hydrotreating of soybean oil over NiMo carbide catalyst. *Fuel* **2013,** *111*, 81-87.
8. Horáček, J.; Akhmetzyanova, U.; Skuhrovcová, L.; Tišler, Z.; de Paz Carmona, H., Alumina-supported MoNx, MoCx and MoPx catalysts for the hydrotreatment of rapeseed oil. *Applied Catalysis B: Environmental* **2020,** *263*, 118328.
9. Taromi, A. A.; Kaliaguine, S., Green diesel production via continuous hydrotreatment of triglycerides over mesostructured γ-alumina supported NiMo/CoMo catalysts. *Fuel processing technology* **2018,** *171*, 20-30.
10. Taromi, A. A.; Kaliaguine, S., Hydrodeoxygenation of triglycerides over reduced mesostructured Ni/γ-alumina catalysts prepared via one-pot sol-gel route for green diesel production. *Applied Catalysis A: General* **2018,** *558*, 140-149.
11. Xie, S.; Jia, C.; Prakash, A.; Palafox, M. I.; Pfaendtner, J.; Lin, H., A generic biphasic catalytic approach for producing renewable diesel from fatty acids and vegetable oils. *ACS Catalysis* **2019**.