

Hydrodeoxygenation of Lignin-Derived Phenols into Alkanes over Carbon Nanotubes Supported Ru Catalysts in Biphasic Systems

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Table S1. Chemisorption of supported-Ru catalysts

Catalysts	Metal Dispersion/ %	Metallic Surface Area/ m ² /g metal
5%Ru/CNT	27.2102	99.5614
5%Ru/C	77.6735	284.2050
5%Ru/ZrO ₂	34.6094	126.6350
5%Ru/CeO ₂	0.3265	1.1948

Table S2. N₂ adsorption and desorption of supported-Ru catalysts

Catalysts	Surface Area/ m ² /g ^a	Pore Volume/ m ³ /g ^b	Pore Size/ Å ^c
5%Ru/CNT	201.6027	0.725084	138.560
5%Ru/C	1245.1460	1.222686	42.568
5%Ru/ZrO ₂	98.8010	0.270289	91.374
5%Ru/CeO ₂	5.2126	0.026519	179.750

a. BET Surface Area; b. BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter; c. BJH Desorption average pore diameter (4V/A)

Table S3. XPS Ru 3p analysis for supported-Ru catalysts and used Ru/CNT

Catalysts	Ru ⁰ Area (462.2 ± 0.2 eV)	Ru(IV) Area (464.2 ± 0.3 eV)	Ru(IV) (Hydrate) Area (466.5 ± 0.5 eV)	Ru ⁰ /(Ru(IV)+Ru(IV) Hydrate)
Ru/CNT	1937	1057	863	1.01
Ru/C	2343	1168	875	1.15
Ru/ZrO ₂	3842	1229	927	1.78
Ru/CeO ₂	3097	1169	851	1.53
Ru/CNT(used)	1564	523	395	1.70

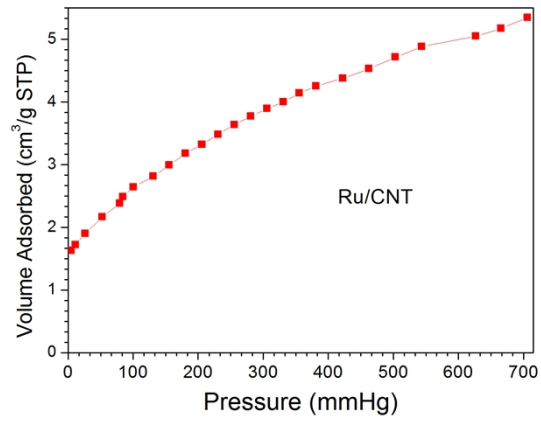


Figure S1. Chemisorption of Ru/CNT

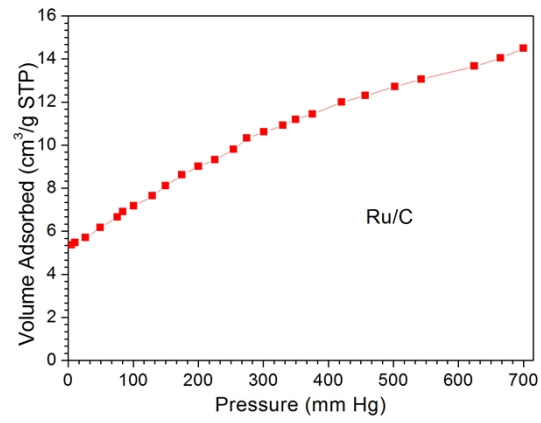


Figure S2. Chemisorption of Ru/C

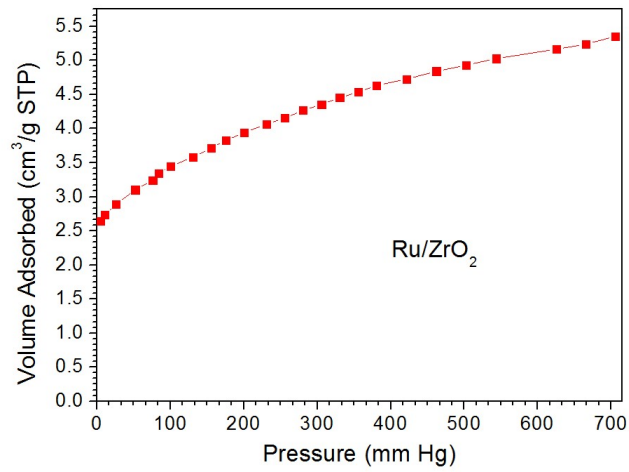


Figure S3. Chemisorption of Ru/ZrO₂

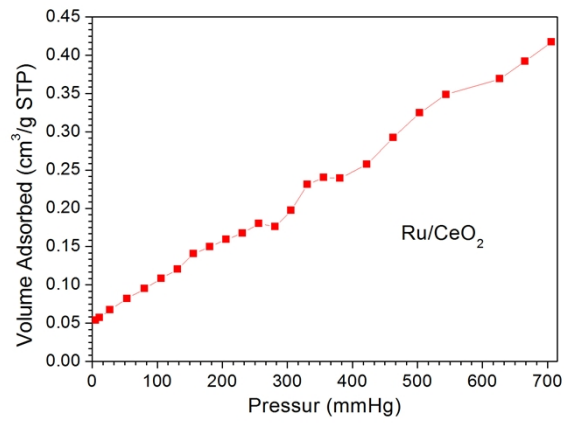


Figure S4. Chemisorption of Ru/CeO₂

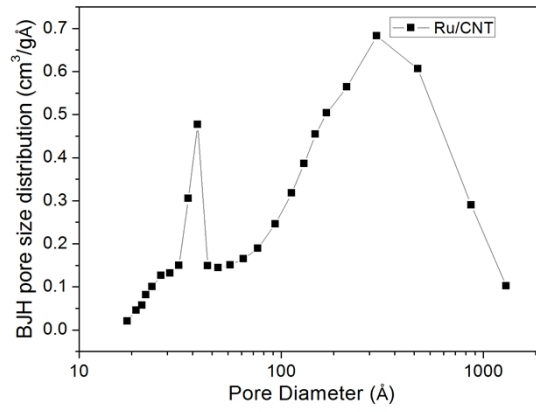


Figure S5. BJH pore size distributions for Ru/CNT

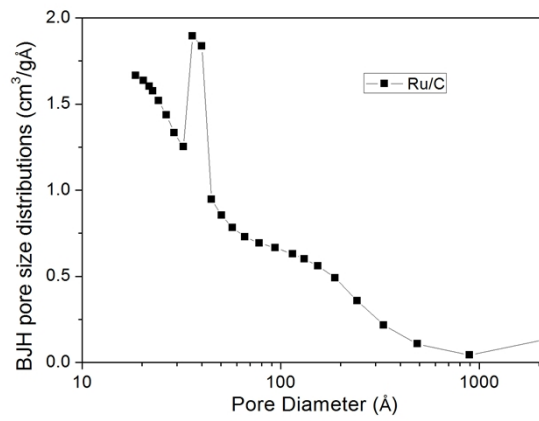


Figure S6. BJH pore size distributions for Ru/C

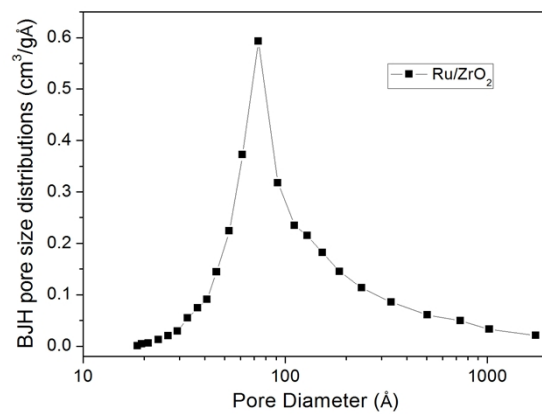


Figure S7. BJH pore size distributions for Ru/ZrO₂

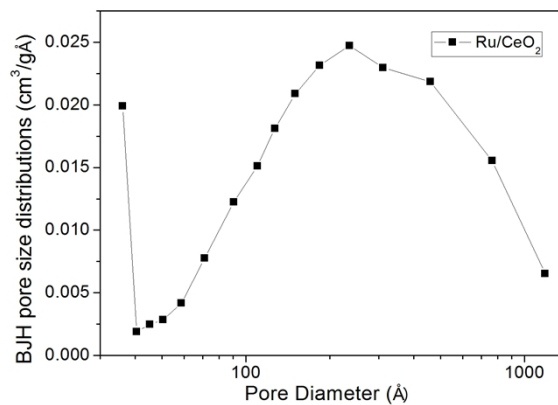


Figure S8. BJH pore size distributions for Ru/CeO₂

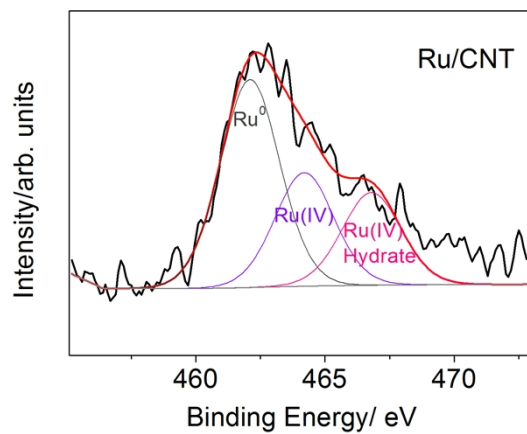


Figure S9. XPS Ru 3p spectra for Ru/CNT

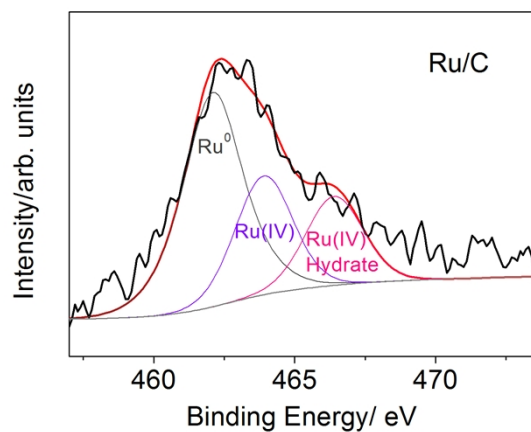


Figure S10. XPS Ru 3p spectra for Ru/C

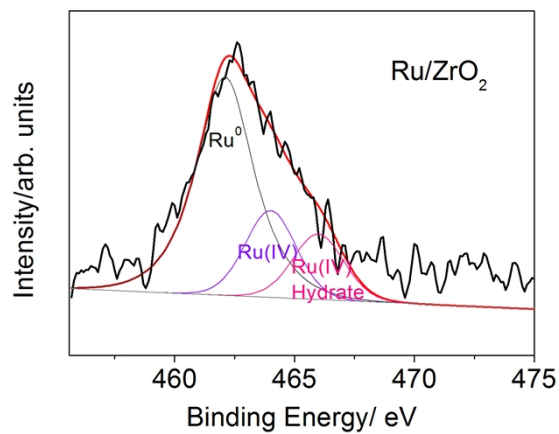


Figure S11. XPS Ru 3p spectra for Ru/ZrO₂

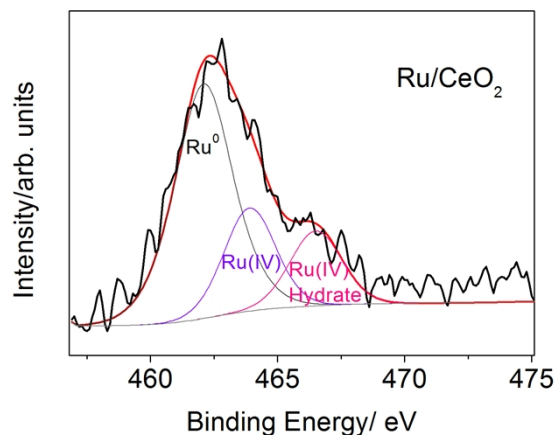


Figure S12. XPS Ru 3p spectra for Ru/CeO₂

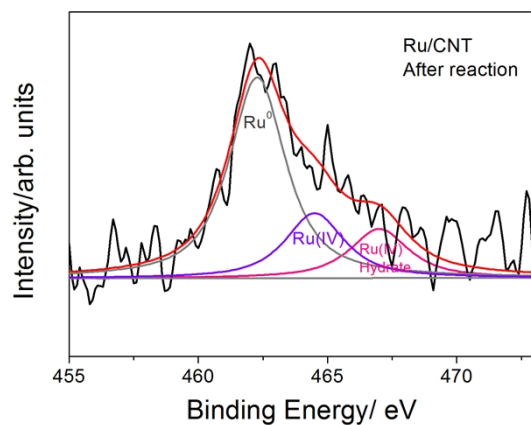


Figure S13. XPS Ru 3p spectra for the used Ru/CNT

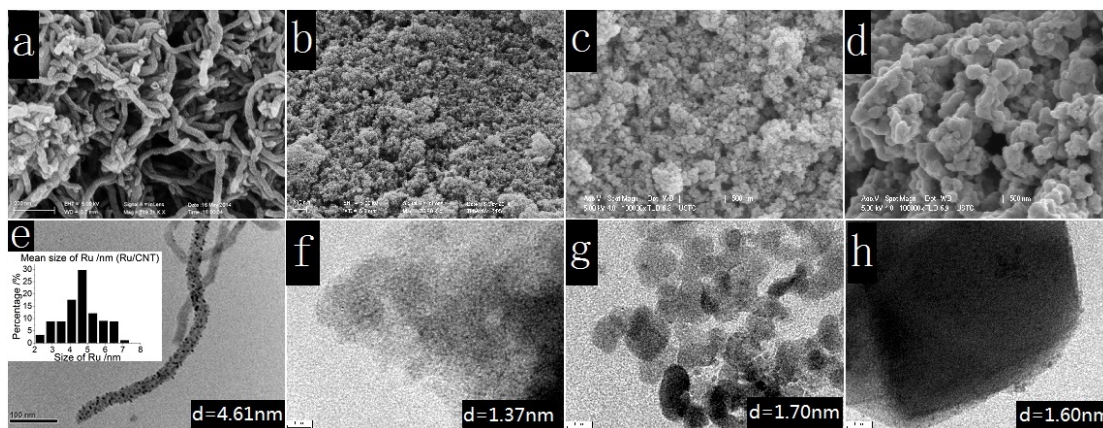


Figure S14. SEM and TEM micrographs of 5%Ru/CNT, 5%Ru/C, 5%Ru/ZrO₂ and 5%Ru/CeO₂

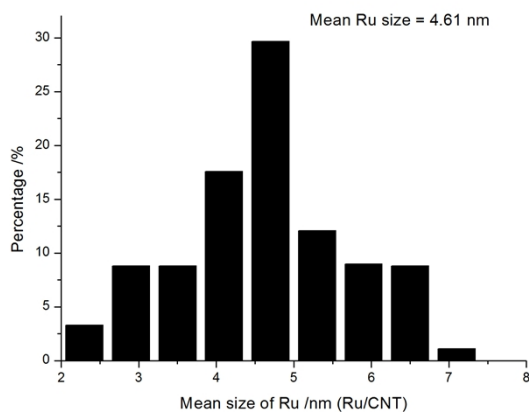


Figure S15. Ru particle size distribution for Ru/CNT

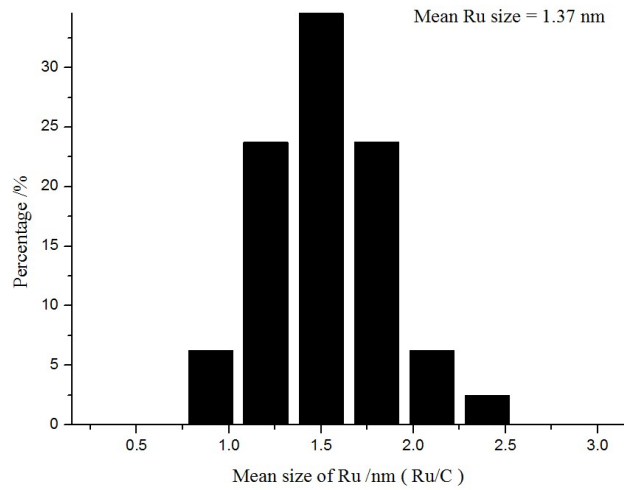


Figure S16. Ru particle size distribution for Ru/C

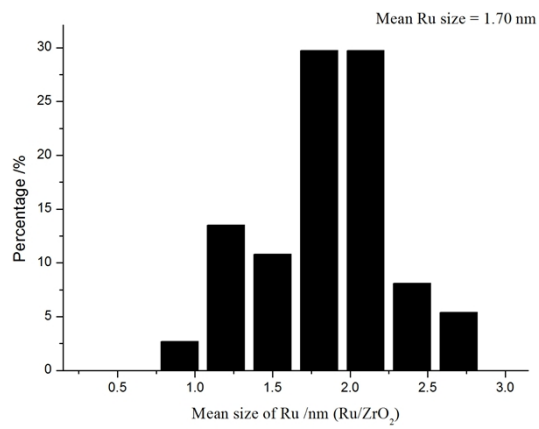


Figure S17. Ru particle size distribution for Ru/ZrO₂

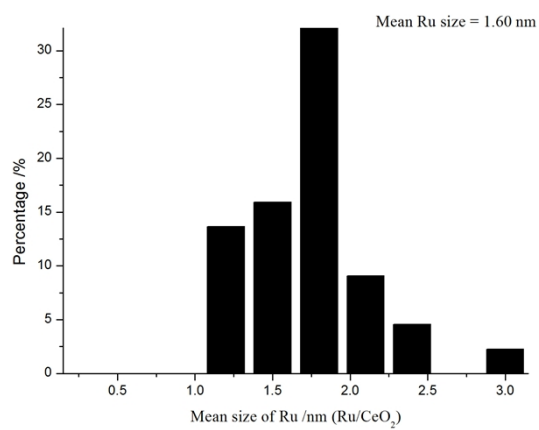


Figure S18. Ru particle size distribution for Ru/CeO₂

3. Discussion

Catalyst characterization

Table S1 summarizes the metal dispersion and metallic surface area achieved from the chemisorption of Ru/CNT, Ru/C, Ru/ZrO₂ and Ru/CeO₂.

The CO adsorption curves for Ru/CNT, Ru/C, Ru/ZrO₂ and Ru/CeO₂ are shown in Figure. S1-S4. It can be confirmed from these figures that Ru/C showed a better adsorbing capacity than the others. The adsorbing capacity of Ru/CNT was similar to that of Ru/ZrO₂, while Ru/CeO₂ showed the least adsorption performance.

Table S2 shows the BET surface area (S_{BET}), pore volume (V_p) and pore size (D_p) of Ru/CNT, Ru/C, Ru/ZrO₂ and Ru/CeO₂.

The BJH pore size distributions for Ru/CNT, Ru/C, Ru/ZrO₂ and Ru/CeO₂ are shown in Figure. S4-S7. All these four supported-Ru catalysts shows characteristic of mesoporous materials. However, the N₂ adsorption and desorption curves of Ru/C (not shown here) indicates the presence of partial micropores which are not dominating in Ru/C. Ru/C shows the maximum surface area which is 1245 m²/g, in the cases of Ru/CNT, Ru/ZrO₂ and Ru/CeO₂, 202 m²/g, 99 m²/g and 5 m²/g are achieved, respectively.

The XPS Ru 3p analysis for supported-Ru catalysts and used Ru/CNT in Table S3 and Figures. S9-S13 indicates the presence of Ru⁰, Ru (IV) and Ru (IV)(hydrate) simultaneously, and the ratio of Ru⁰ / (Ru (IV)+ Ru (IV)(hydrate)) are calculated through the peak area in Table S3. The ratio showed a higher content of Ru⁰ than Ru (IV) and Ru (IV)(hydrate) existed in all the supported-Ru catalysts. The XPS analysis of the used catalysts showed that Ru (IV) and Ru (IV)(hydrate) particles were further reduced into Ru⁰ particles under the reductive reaction condition.

Figure. S14 shows the scanning electron microscopy (SEM) microphotographs and transmission electron microscopy (TEM) microphotographs of Ru/CNT, Ru/C, Ru/ZrO₂ and Ru/CeO₂. The SEM and TEM microphotographs indicates that the Ru particles were dispersed on all the supports homogeneously. And the Ru particle size distribution for all the supported-Ru catalysts (Figure. S15-S18) were calculated from the TEM microphotographs (Figure. S14).

The HDO of phenols extracted from bio-oil.

The crude bio-oil was obtained by flash pyrolysis of rice husk at 550-600°C according to the previous work [1]. Phenols were separated from the crude bio-oil by a modified glycerol-assisted distillation technology [1]: a mixture of 10 g glycerin and 100 g bio-oil was distilled. The first distillate under 120°C was about 60 g. The second distillate (about 10 g), mainly consisted of phenols was obtained under 0.1 atm at 120°C. The mixture of the second distillate was washed by NaHCO₃ and the organic layer was extracted by hexane. The hexane was removed by a rotary evaporation. And the mixture of phenols for the hydrodeoxygenation reaction was collected as a light yellow liquid.

The reaction conditions for the HDO of the bio-oil was as follow: bio-oil 200 mg, 5 wt% Ru/CNT 50 mg, n-C₁₂H₂₆/H₂O= 6/6 ml, 5.0 MPa H₂, 270°C, 20 h. The products after the reaction were extracted by ethyl acetate and analyzed by GC and GC-MS (Figure. 4). All the phenols

were converted into alkanes in the biphasic systems.

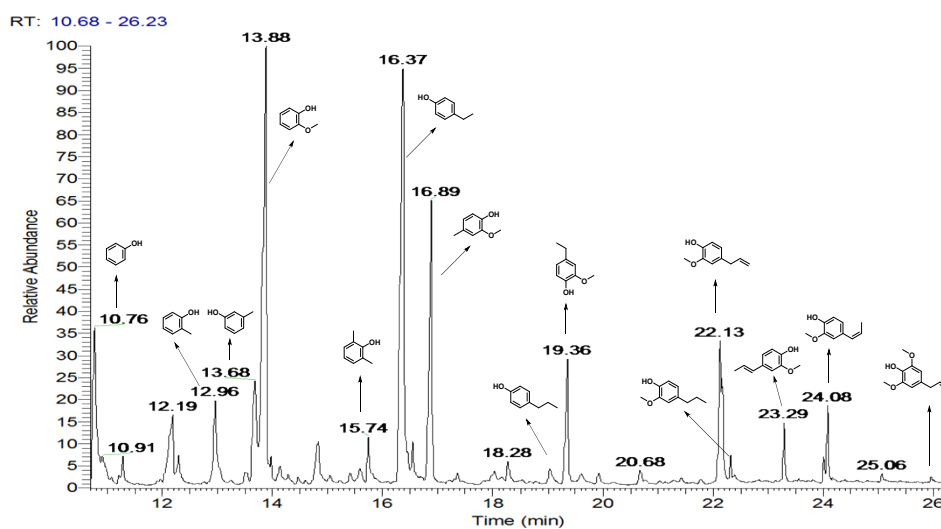


Figure. S19 GC-MS analysis of the mixture of phenols from bio-oil

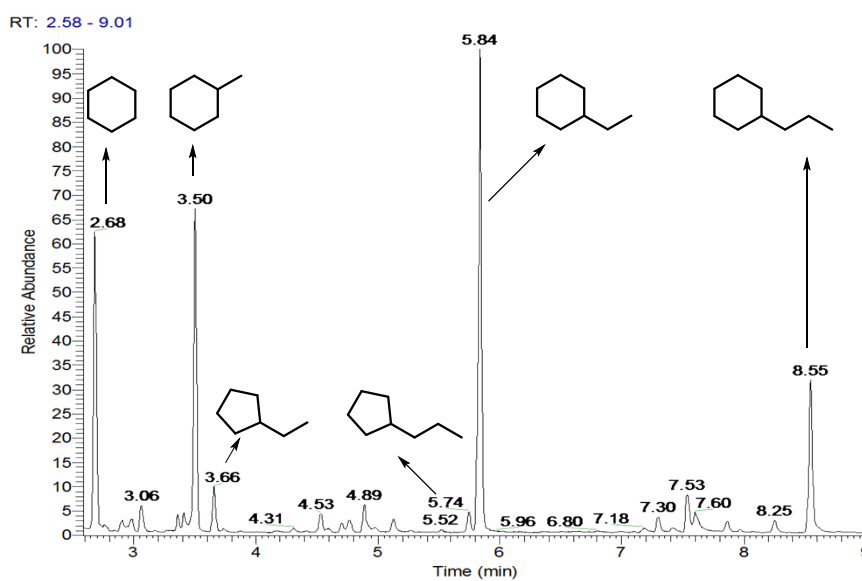











Figure. S20 GC-MS analysis of the mixture of the alkanes products after the hydrodeoxygenation of bio-oil

Table S4. The weight of alkane products from the HDO of bio-oil. (Extracted phenols 200mg)

Entry	Alkane	Retention Time/ min	Weight/ mg
1	<chem>C1CCCCC1</chem>	2.68	13.47

2		3.50	9.28
3		3.66	1.43
4		4.53	0.88
5		4.70	0.72
6		5.74	0.78
7		5.84	15.56
8		7.30	0.66
9		8.25	0.62
10		8.55	5.74
Total		-	49.14

[1] J. Guo; R. Ruan, Y. Zhang, *Ind. Eng. Chem. Res.* **2012**, *51*, 6599.