Supporting Information Available.

S.1 Calculating method for heating value calculation.

S.2 Detailed GC-MS results of upgraded oil from distillation residue (U-DR) from 100 mL batch reaction under different processing conditions.

S.3 Comparison of fresh and recovered Pt/SZr catalysts analyses using X-ray diffraction patterns and N_2 absorption/desorption isotherms after 300 mL batch reaction and calcination.

S.4 Elemental composition of crude bio-oil (CB), distillation residue (DR), upgraded oil from crude bio-oil (U-CB) and U-DR.

S.5 Mass balance of 300 mL batch reaction.

S.1 Calculating method for heating value calculation.

$$\mathrm{CHVS} = \frac{\mathrm{MHVS} - \mathrm{SC} \times \mathrm{HVS}}{1 - \mathrm{SC} - \mathrm{WC}}$$

CHVS: calculated heating value of sample

MHVS: measured heating value of sample

HVS: heating value of solvent

SC: solvent content

WC: water content

S.2 Detailed GC-MS results of U-DR from 100 mL batch reaction under different processing conditions.

Table S1. Organic composition and relative abundance of U-DR from 100 mL batch reaction in supercritical ethanol.

Compound Name	Relative Abundance			
	Pt/HZSM-5	Pd/HZSM-5	Pt/SZr	Pd/SZr
Acids				
Aldehydes				
Acetaldehyde	1.31%	0.84%		
*Vanillin	1.25%	3.61%		
Alcohols				
*3-Hexanol, 4-methyl-	1.82%			
1,2-Ethanediol		1.41%	2.72%	1.93%
Esters				
Formic acid, ethyl ester		2.30%	4.19%	3.02%
Ethyl Acetate	42.66%	36.21%	33.66%	32.74%
Butanoic acid, ethyl ester	1.34%	0.89%	1.27%	
Propanoic acid, 2-hydroxy-, ethyl ester	5.53%	2.73%	6.35%	5.83%
Butanoic acid, 2-hydroxy-, ethyl ester	1.10%		1.52%	1.47%
Acetic acid, hydroxy-, ethyl ester	4.53%	4.38%	11.17%	7.50%
Pentanoic acid, 4-oxo-, ethyl ester	1.97%		1.37%	
*2-Furancarboxylic acid, ethyl ester	0.89%			
*Diethyl methylsuccinate			1.72%	
Butanedioic acid, diethyl ester	1.46%	1.14%	2.51%	2.22%
Ketones				
2-Butanone, 3-hydroxy-		1.17%	1.56%	1.58%
2-Propanone, 1-hydroxy-		2.55%	1.95%	1.94%
Phenols				
Phenol, 2-methoxy-	2.51%	1.36%	2.92%	2.67%
*Phenol, 2-methoxy-4-methyl-	1.99%	1.25%	1.60%	1.53%
*Phenol	5.73%	3.91%	4.22%	3.90%
*Phenol, 4-ethyl-2-methoxy-	1.19%	0.76%		
Phenol, 2-ethyl-	1.00%			
*Phenol, 4-methyl-	4.06%	1.42%	1.38%	1.45%
Phenol, 2-methoxy-4-propyl-	1.48%	1.00%		
*Phenol, 2-methoxy-6-(2-propenyl)-		0.95%		
Phenol, 2,6-dimethoxy-	1.66%	1.55%	1.56%	1.60%
*2,5-Dimethoxybenzyl alcohol	1.07%	1.29%	1.62%	
2-(Methylmercapto)-benzothiazol	0.85%			
Sugars				
*1,6-Anhydro-β-D-glucopyranose		1.90%	1.57%	
PAHs				
*Naphthalene			1.69%	

Others				
Ethyl ether	0.89%	5.76%		
Methane, diethoxy-	2.74%	12.17%	5.52%	5.52%
Ethane, 1,2-diethoxy-	2.37%	0.78%		
2-Ethoxytetrahydrofuran		2.63%	2.36%	2.44%
*(2,3,3-Trimethyloxiranyl)methanol	2.39%			
Ethanol, 2-ethoxy-	5.26%	1.44%		
*1-Propanol, 2-ethoxy-		0.88%	1.66%	1.54%
*Propane, 1,1,3,3-tetraethoxy-			2.32%	2.09%
*Heptaethylene glycol monododecyl ether	0.94%	2.31%		
*1,4-Dioxaspiro[4.5]decane-7-methanol		1.40%	1.60%	1.45%
*1,5-Di-p-tolyl-anthraquinone				1.90%
*17-(1,5-Dimethylhexyl)-10,13-dimethyl-2,3,4,5,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-4-ol				2.91%
1-Acetyl-2-amino-3-cyano-7-isopropyl-4-methylazulene				9.60%
Pregna-6,16-diene-11,20-diol, 3,9-epoxy-18-[N-methyl-N-[14-(2'-epoxyethyl)]amino]-				3.16%

Table S2. Organic composition and relative abundance of U-DR from 100 mL batch reaction in supercritical methanol.

Compound Name	Relative Abundance			
	Pt/HZSM-5	Pd/HZSM-5	Pt/SZr	Pd/SZr
Acids				
Aldehydes				
*Vanillin	3.64%	2.15%	0.00%	0.00%
Alcohols				
1,2-Ethanediol	1.33%	1.88%	1.78%	1.82%
Esters				
Acetic acid, methyl ester	10.89%	13.25%	14.96%	11.74%
Acetic acid, methoxy-, methyl ester	1.13%	1.42%		
Propanoic acid, 2-hydroxy-, methyl ester	3.36%	5.03%	5.91%	3.40%
Butanoic acid, 2-hydroxy-, methyl ester			1.79%	
Acetic acid, hydroxy-, methyl ester	5.16%	10.52%	8.79%	4.30%
Pentanoic acid, 4-oxo-, methyl ester	1.09%			
Butanedioic acid, dimethyl ester		1.52%	1.68%	
*Octanoic acid, 6-ethyl-3-octyl ester	1.76%	1.79%		
Ketones				
2-Butanone, 3-hydroxy-	1.56%	2.84%		2.13%
2-Propanone, 1-hydroxy-	2.38%	3.92%		2.98%
2-Cyclopenten-1-one, 2-hydroxy-3,4-dimethyl-			2.20%	
Phenols				
Phenol, 2-methoxy-	2.12%	3.40%	3.13%	1.73%

Phenol, 2-methoxy-4-methyl-	1.54%	2.33%	2.22%	1.34%
Phenol	5.26%	7.95%	4.97%	3.40%
*Phenol, 4-ethyl-2-methoxy-		1.47%		
*Phenol, 4-methyl-	1.96%	2.95%	1.75%	
Phenol, 2-methoxy-4-propyl-		1.96%		1.41%
*Phenol, 2-methoxy-6-(2-propenyl)-	1.27%	1.65%		
Phenol, 2,6-dimethoxy-	2.26%	3.34%	2.37%	1.66%
*2,5-Dimethoxybenzyl alcohol	1.51%	2.23%		
Phenol, 2,6-dibromo-4-(1,1-dimethylethyl)-			16.50%	
Phenol, 4,4'-(1-methylethylidene)bis-				34.19%
Sugars				
*1,6-Anhydro-β-D-glucopyranose	2.56%	2.68%		
*Flavone, 5,7-dihydroxy-6c-glucoside			2.80%	
PAHs				
Benzene, 1-ethyl-3-(phenylmethyl)-		1.90%		
Others				
Methane, dimethoxy-	5.93%	6.39%	3.30%	6.10%
Ethane, 1,1-dimethoxy-	1.60%	1.69%	1.63%	
2-Methoxytetrahydrofuran	1.46%	2.48%	6.05%	
2-Propanone, 1-methoxy-	4.79%			
*1,1,3-Trimethoxypropane	1.26%	1.55%		2.04%
Ethane, 1,1,2-trimethoxy-	20.63%	7.33%	1.87%	3.23%
Ethanol, 2-methoxy-	3.43%			
Furan, tetrahydro-2,5-dimethoxy-	1.35%			
*Propane, 1,1,3,3-tetramethoxy-	5.93%	2.19%	12.46%	14.23%
Hexanal dimethyl acetal				1.41%
*Heptaethylene glycol monododecyl ether	1.04%	2.21%		
Pregna-6,16-diene-11,20-diol, 3,9-epoxy-18-[N-methyl-N-[14-(2'-epoxyethyl)]amino]-			3.82%	2.91%
1,3-Diphenyl-1,1,3,3-tetramethyldisilazane	1.77%			

S.3 Comparison of fresh and recovered Pt/SZr catalysts analyses using X-ray diffraction patterns and N2 absorption/desorption isotherms after 300 mL batch reaction.

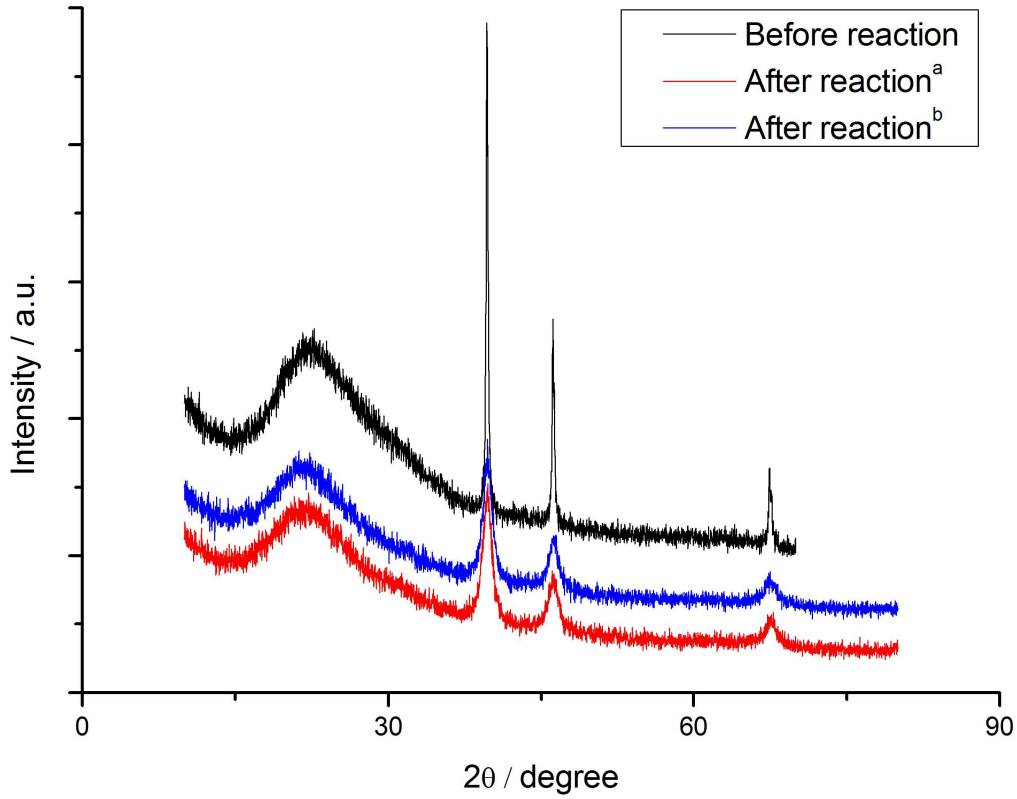

Figure S1. X-ray diffraction patterns of the fresh Pt/SZr catalysts and recovered catalysts after 300 mL batch reaction and calcination. [a] DR as feedstock, [b] CB as feedstock.

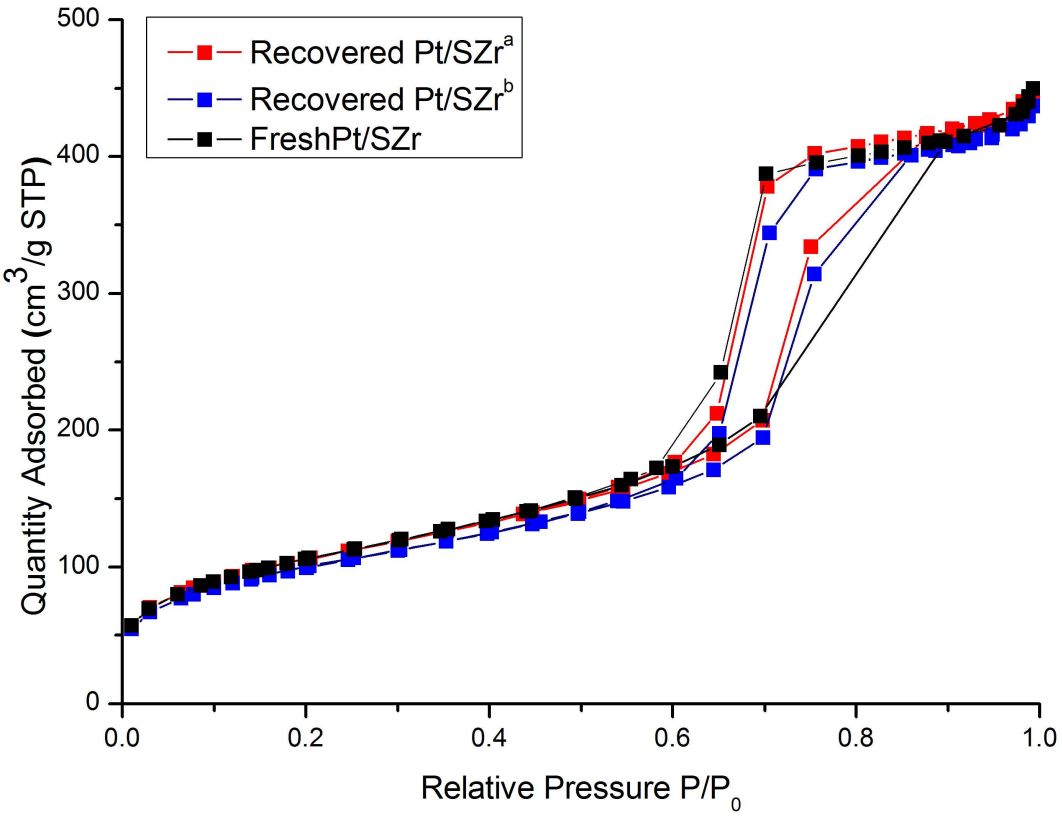

Figure S2. N_2 absorption/desorption isotherms of the fresh Pt/SZr catalysts and recovered catalysts after 300 mL batch reaction and calcination. [a] DR as feedstock, [b] CB as feedstock.

Table S3. Textural properties of the samples: fresh Pt/SZr, recovered Pt/SZr from 300 mL batch reaction.

Propoerties	Fresh Pt/SZr	Recovered Pt/SZr[a]	Recovered Pt/SZr[b]
BET Area (m^2/g)	385	361	383
Pore Volume (m^3/g)	0.667	0.649	0.667

[a] crude bio-oil as feedstock, [b] distillation residue as feedstock.

S.4 Elemental composition of CB, DR, U-CB and U-DR.

The elemental composition of crude bio-oil (CB), distillation residue (DR), upgrading products of 300 mL batch reaction from crude bio-oil and distillation residue (U-CB and U-DR) were analyzed using LECO-CHNS932. Since the instrument is not designed for the measurement of volatile liquid, the samples were dried at 75 degree centigrade under atmospheric pressure before analyzing. Oxygen content was calculated by difference. The hydrodeoxygenation performed effectively.

Table S4. Elemental composition of CB, DR, U-CB and U-CR.

Element	CB	DR	U-CB	U-DR
C (%)	39.00	52.60	58.48	54.00
H (%)	7.71	6.10	8.81	10.18
O (%)	53.29	41.30	32.71	35.82

S.5 Mass balance of 300 mL batch reaction.

The weight of gas products (excluding hydrogen) was calculated by difference. The weight of coke was calculated from the weight of catalysts added and the weight loss of solid mixture from TG/DTA. The total liquid recovery was about 85 %. Since there were certain amount of liquid products remained in the valve or other part of the apparatus that could not be collected, the total liquid recovery should be higher and the weight of gas products should be lower actually. For the same reason, the total liquid recovery was higher when we scaled up (70-80 % of total liquid recovery for 100 mL batch reactions, ~95 % of total liquid recovery achieved using 10 L batch reactor under similar reaction conditions). The weight of ethanol was calculated from the ethanol content of the upgrade products by GC-MS using external standard method. If we assume that all coke came from DR, all gas products came from ethanol, we may have the mass balance of 300 mL batch reaction. However, this assumption was not accurate; and we could not present the hydrogen consumption.

Table S5. Mass balance of 300 mL batch reaction.

		Feedstocks		Products
Gas		0 g		~15.6 g
Coke		0 g		~0.9 g
Liquid	Ethanol	100 g	Ethanol	~74.8 g
	DR	10 g	U-DR	~18.7 g

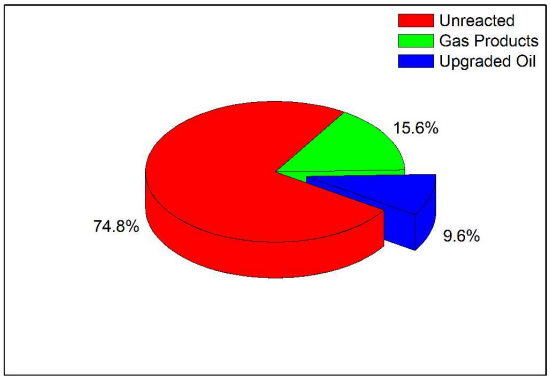

Figure S3. Mass balance of ethanol from 300 mL batch reaction.