Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information

Hydrocarbons from pre-hydrolysis liquors in two steps using heterogenous catalysis

Daria Lebedeva and Joseph S. M. Samec

Stockholm University, Department of Organic Chemistry, Stockholm, Sweden.

E-mail: joseph.samec@su.se

Contents

Experimental

General considerations

All chemicals were purchased in Sigma-Aldrich if not stated otherwise. Zeolites were purchased from Zeolyst. Birch sawdust was dried overnight before analysis and reactions. Furfural was distilled before use. For hydrodeoxygenation reactions, stainless steel reactor was assembled from Swagelok spare parts (SS-1610-C, SS-1611-PC, SS-811-PC-4, SS-1610-6-8, SS-3NBS4-G).

GC-MS/FID analyses were performed on a QP2020 system (SHIMADZU, Japan) equipped with two parallel HP-5MS columns (30 m × 0.25 mm × 0.25 µm).

HPLC analyses were performed on a Agilent 1200 Series HPLC system equipped with Aminex HPX-87P column (300 mm × 7.8 mm).

General procedure for prehydrolysis of birch sawdust

Birch sawdust (0.5 g) and 5 mL of DI water (water/wood (10:1)) were added to the autoclave and stirred at elevated temperatures (140-200 °C) for 20-60 min. After completion, the solids were filtered off, washed with DI water, dried overnight at 60 °C, and weighed. Pretreated wood samples were analyzed for sugar and lignin content as described below (see "Sugar and lignin content", ESI).

Hydrolysis liquor was analyzed by HPLC without any treatment to determine and quantify monosaccharides. For sugar quantification, calibration were done for D-(+)-glucose, D-(+)-xylose, D-(+)-galactose, D-(+)-arabinose, D-(+)mannose. The HPLC chromatogram for the sample pretreated under optimized conditions (200 °C, 40 min) is shown below (Figure S1).

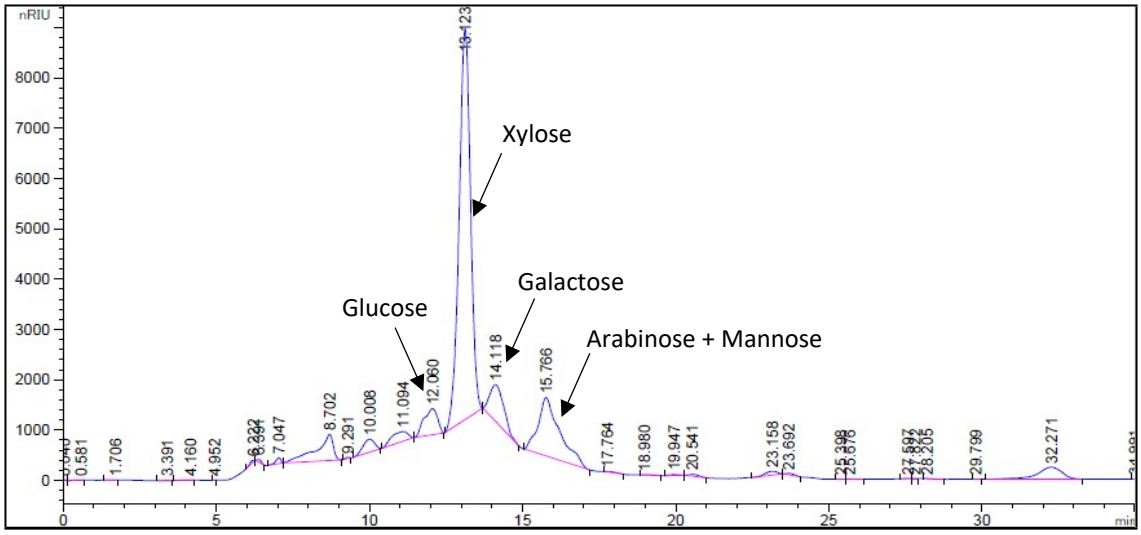


Figure S1. HPLC chromatogram of monosaccharides in hydrolysis liquor. Hydrolysis conditions: 200 °C, 40 min.

Sugar and lignin content

Initial wood and pretreated samples were analyzed for sugar and lignin content. Two-step hydrolysis was performed according to the standard NREL procedure described below.[1]

A sample (300 mg) was treated with 72% H_2SO_4 (3 mL) at 30 °C for 1 hour in the sealed pressure tube under stirring. After completion, the mixture was diluted with 84 mL of DI water, and heated at 120 °C for 1 hour in the sealed pressure tube under stirring. The mixture was cooled down to room temperature and filtered. After filtration, an aliquot of the filtrate was taken and neutralized by the addition of $CaCO_3$ to pH 6-7. An aliquot was filtered and subjected to HPLC analysis for sugar determination and quantification (Figure S2-6).

The solid residue was washed with DI water, dried overnight, weighed, and incinerated at 575 °C for ash determination. The ash was weighed, and the weight difference was acid insoluble lignin (AIL) content.

HPLC cromatograms

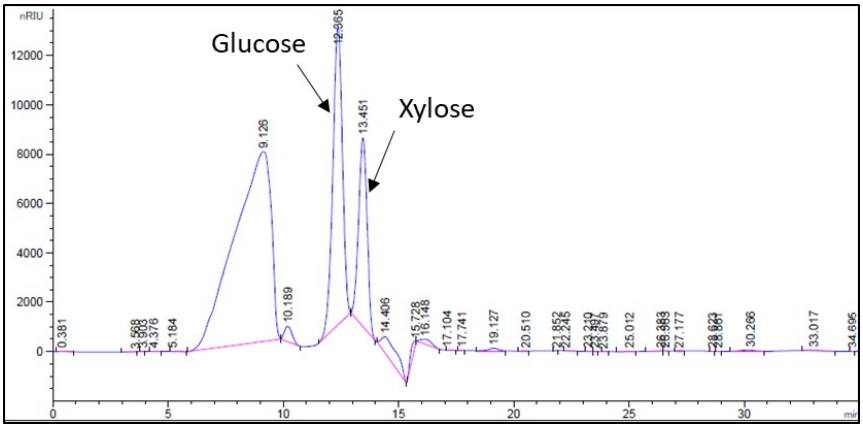
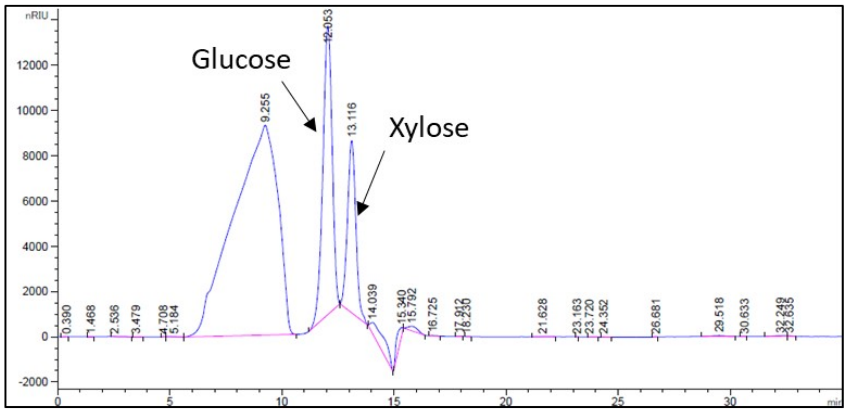


Figure S2. HPLC chromatograms of glucose and xylose found in birch sawdust raw material.

140°C, 40 min



140°C, 60 min

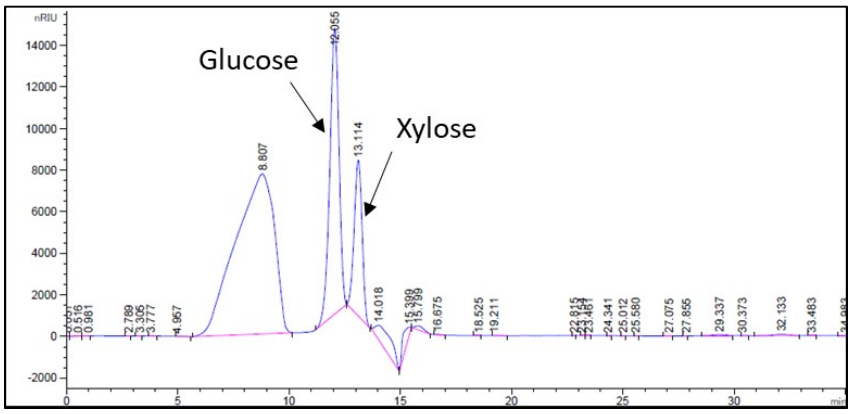
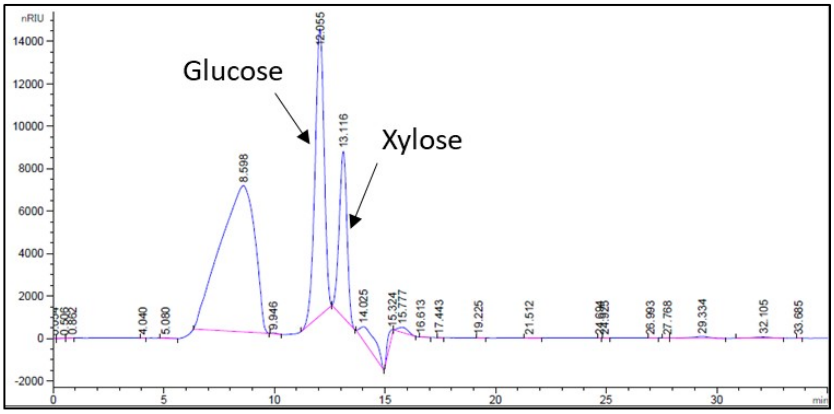
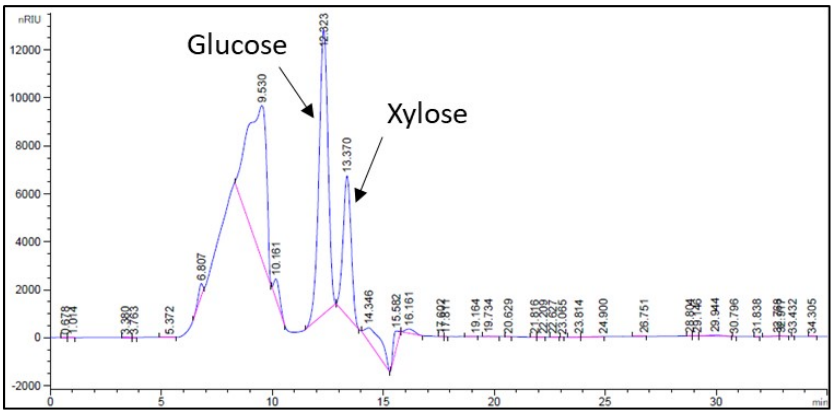


Figure S3. HPLC chromatograms of glucose and xylose found in wood samples pretreated at 140 °C.

160°C, 20 min



160°C, 40 min



160°C, 60 min

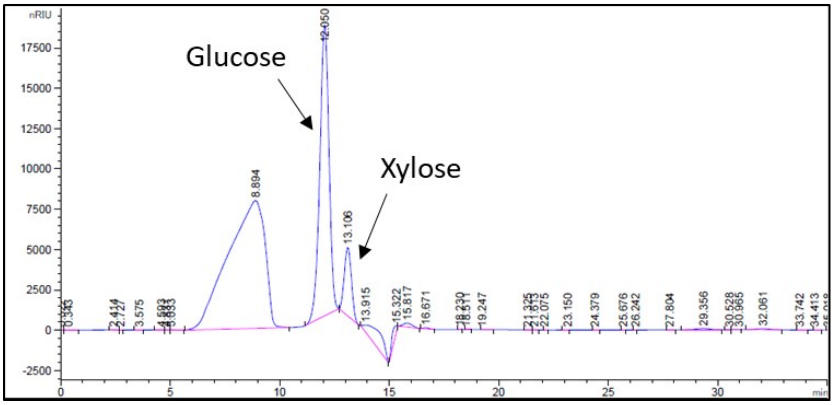
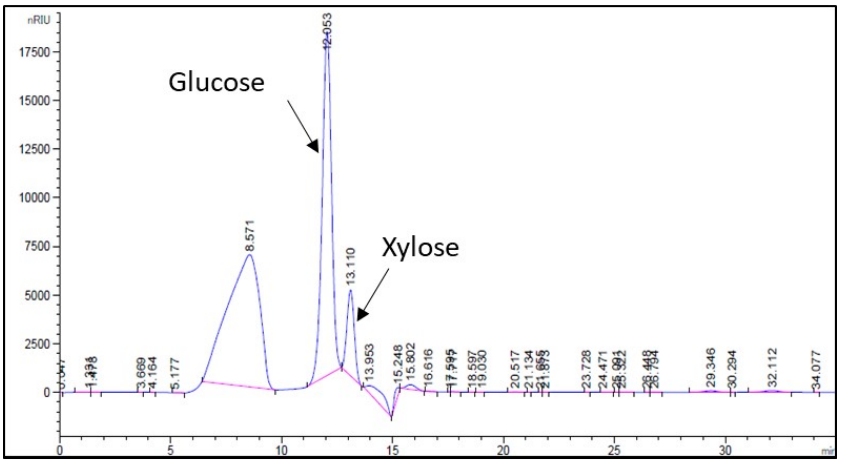
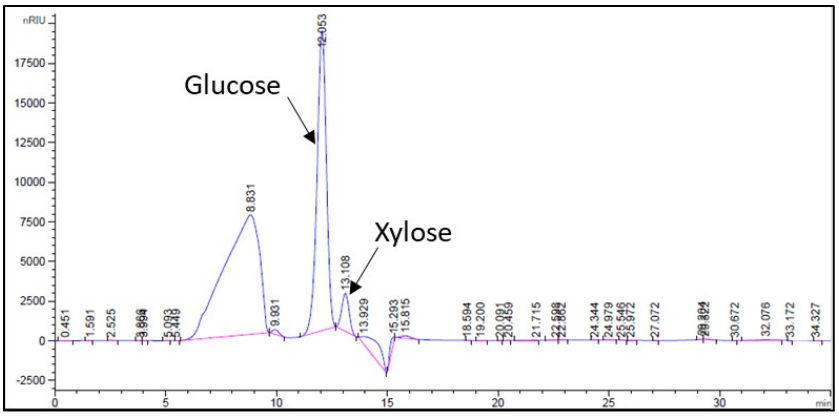


Figure S4. HPLC chromatograms of glucose and xylose found in wood samples pretreated at 160 °C.

180°C, 20 min



180°C, 40 min



180°C, 60 min

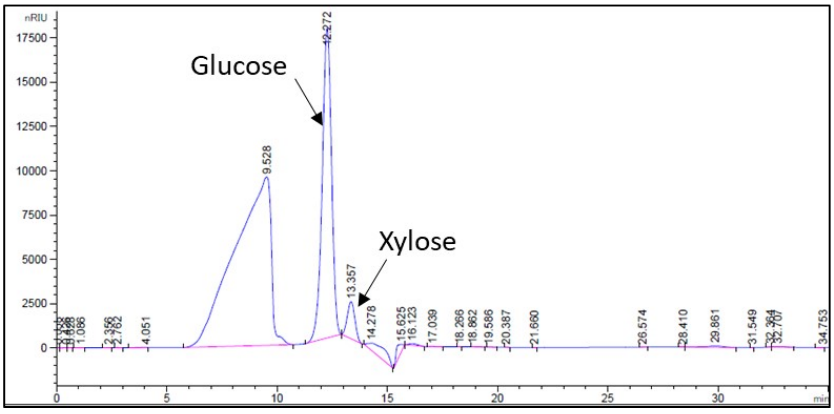
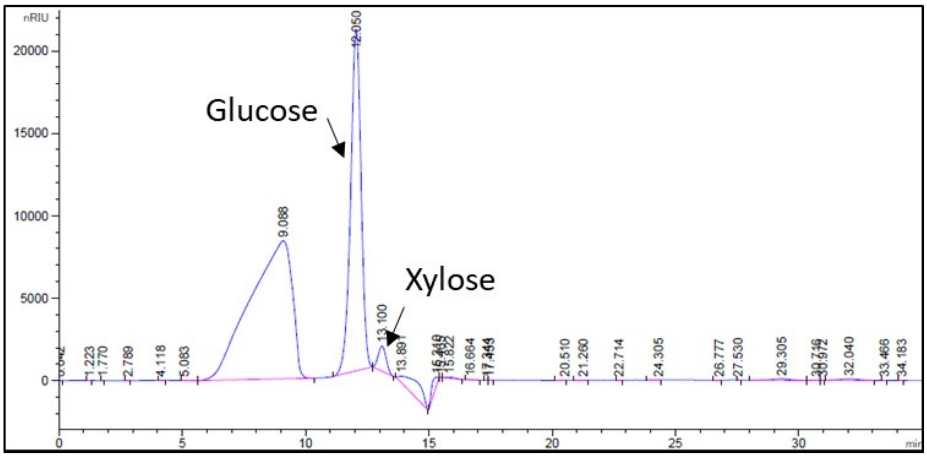


Figure S5. HPLC chromatograms of glucose and xylose found in wood samples pretreated at 180 °C.

200 °C, 20 min



200 °C, 40 min

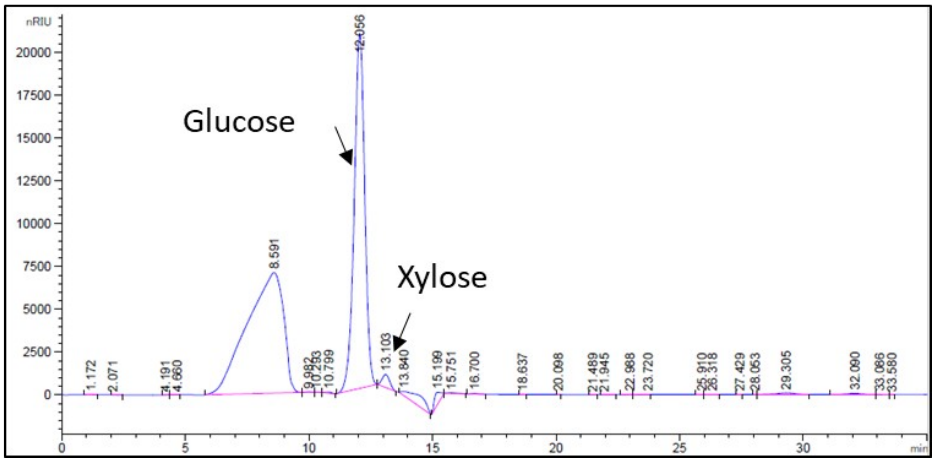


Figure S6. HPLC chromatograms of glucose and xylose found in wood samples pretreated at 200 °C.

Zeolite-assisted dehydration of xylose into furfural

Reaction with xylose. Reactions were performed in an autoclave. D-(+)-xylose (75 mg) was added to the H_2O/dioxane mixture (1:20), followed by the addition of a zeolite catalyst (25 mg). Reactions were performed at elevated temperatures for 1 hour. After completion, the standard (dodecane) was added. A reaction mixture was filtrated and subjected to GC-MS/FID analysis. The yields were quantified by GC-FID using the calibration curve for furfural (Figure S7). The calibration curve was built for furfural with dodecane as an internal standard.

GC method: Injection temperature was 250 °C; The column temperature program: 40 °C was held for 5 min, then increased to 260 °C with the rate of 20 °C·min^{-1}, and 260 °C was held for 4 min. Helium was a carrier gas. Column flow was 1.49 mL·min^{-1}.

Reaction with hydrolysis liquor (hydrolysis conditions: 200 °C, 40 min, 0.5 g of wood). After the hydrolysis completion, the mixture was filtered and washed with approx. 1 mL of DI water, giving 5 mL of hydrolysate liquor. Dioxane (5 mL) was added to 5 mL of hydrolysate liquor resulting in a 1:1 dioxane/water solution. H-Beta zeolite (50 mg) was added to the mixture. The reaction was performed at 180 °C for 2 h. After completion, the standard (dodecane) was added. The product was extracted by EtOAc (3 x 10 mL). The EtOAc layers were combined and dried over Na_2SO_4. An aliquot was taken, filtered, and subjected to GC-MS/FID analysis.

The yield of furfural in hydrolysis liquor was calculated by GC-FID considering the xylose content in the hydrolysate of 7.6% based on initial wood loading and determined by HPLC (see Figure S1).

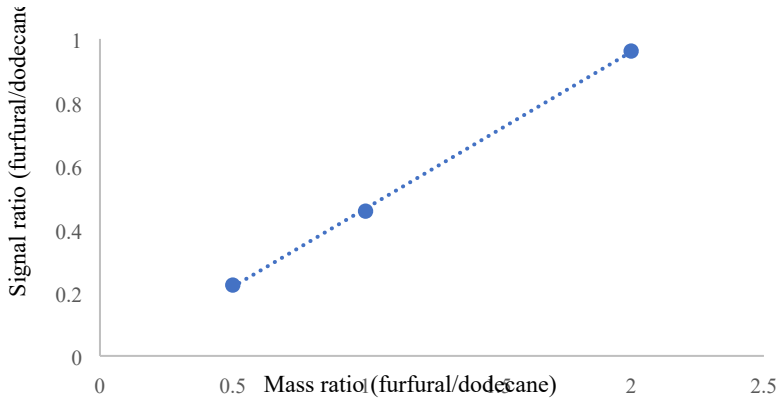


Figure S7. Calibration curve for furfural.

Hydrodeoxygenation of furfural

General procedure. Freshly distilled furfural (200 mg, 2.08 mmol), transition metal catalyst (20 mg, Pd content of 5 wt%; 0.45 mol%), co-catalyst (ZSM-5, 100 mg), and 5 mL of carrier liquid (pentane or cyclohexane) were loaded in the reactor (Figure S8). The reactor was thoroughly flushed with nitrogen for to remove any oxygen. The initial hydrogen pressure was applied (10-25 bar). The reactions were running in the sand bath at elevated temperatures (340-400 °C, the temperature of the sand bath). After reaction completion, the reactor was cooled down to room temperature, and pressure was slowly released through the pressure valve. Dodecane was added as an internal standard. The crude mixture was dried over $NaSO_4$, filtered, and subjected to GC-MS/FID analysis. Characterization of the products was done by GC-MS. Mass fragmentation patterns of detected molecules were compared to the molecules from the NIST MS database.

Quantification of the product yields. The quantification of hydrogenation products was performed by GC-FID using effective carbon number (ECN) of the molecules (Figures S9–S17). The following equations were used to determine GC yields:

$$RRF_x = \frac{MW_{std}}{MW_{sample}} \times \frac{ECN_{sample}}{ECN_{std}}; \quad \text{[Eq. 1]}$$

$$m_x = \frac{A_{sample}}{A_{std}} \times \frac{m_{std}}{RRF_x}; \quad \text{[Eq. 2]}$$

Where RRF – relative response factor, A – integrated peak area, m – mass, ECN – effective carbon number. ECN = carbon atoms – oxygen atoms.

GC method: Injection temperature was 2[illegible]40 °C was held for 5 min, then increased to 260 °C with the rate of 20 °C·min^{-1}, and [illegible]rrier gas. Column flow was 1.49 mL·min^{1}.

Figure S8. Reactor for hydrotreatment.

GC-FID chromatograms of HDO product mixtures.

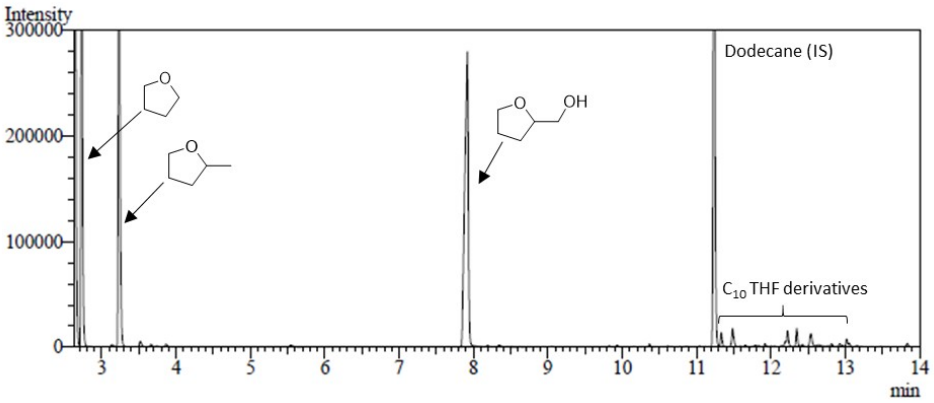


Figure S9. GC-FID chromatogram of the HDO product mixture (Pd/C, Table 3, Entry 1).

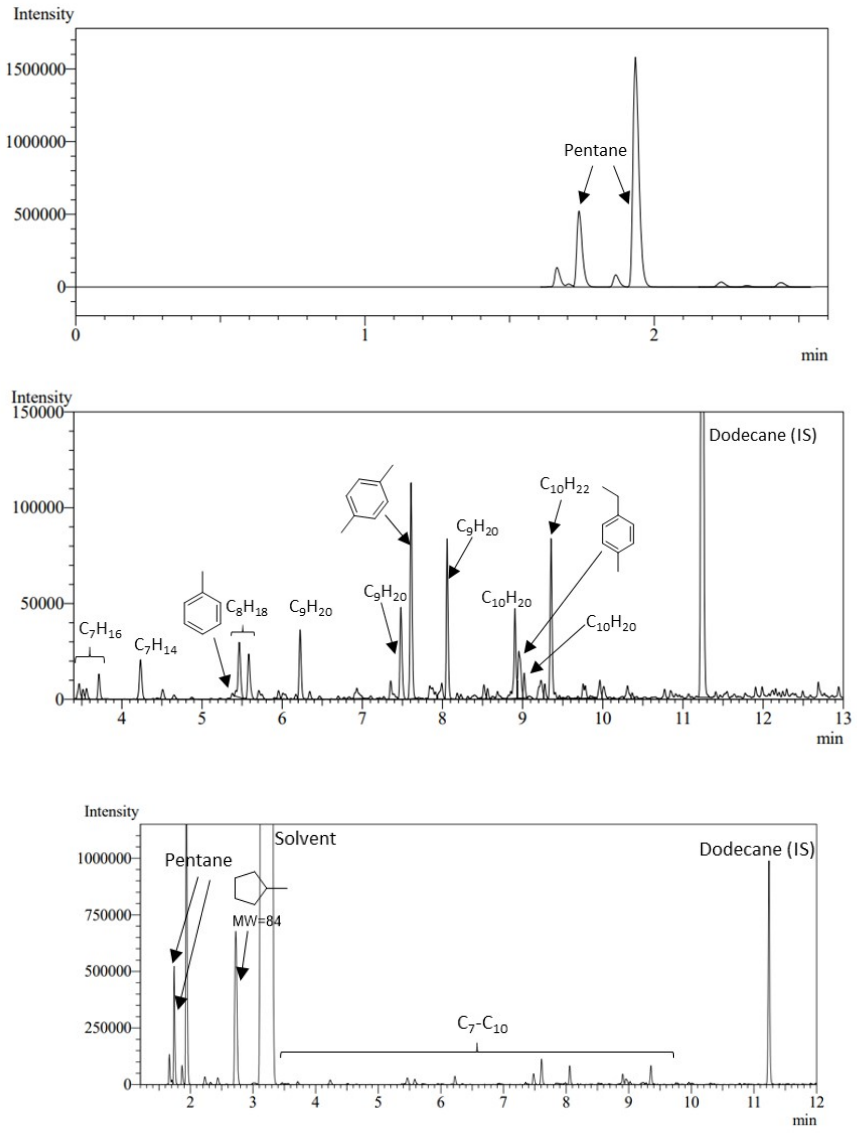


Figure S10. GC-FID chromatogram of the HDO product mixture (Pd/C + zeolites, reaction performed in cyclohexane, Table 3, Entry 2).Top chromatogram: enlarged area of chromatogram to demonstrate pentane detected in the product mixture; Middle chromatogram: enlarged area of chromatogram to show C7-C10 products; Bottom chromatogram: Full-size chromatogram.

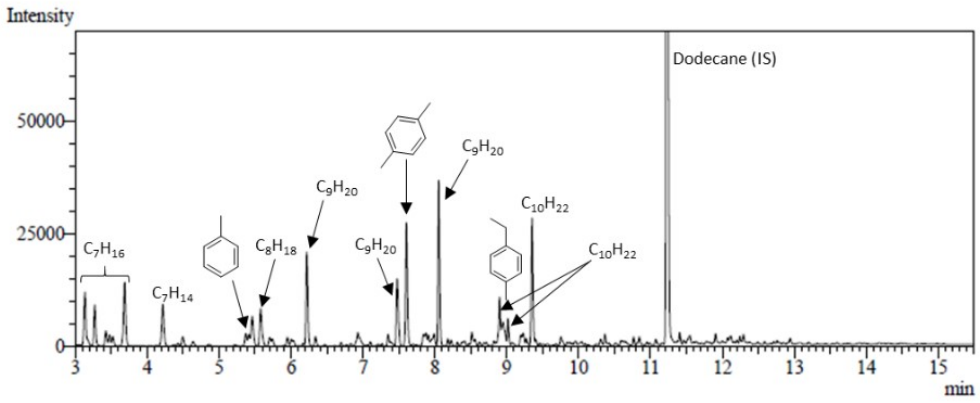


Figure S11. GC-FID chromatogram of the HDO product mixture (Pd/C+zeolite, rection performed in pentane, Table 3, Entry 3).

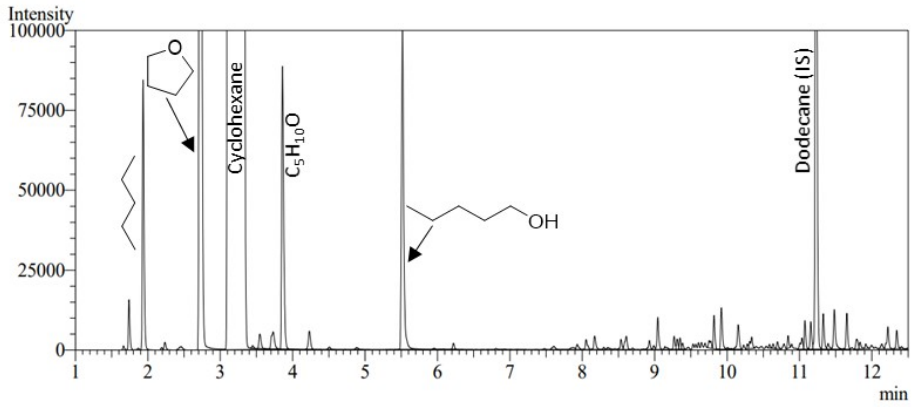


Figure S12. GC-FID chromatogram of the HDO product mixture (Pd/C+zeolite (reduces catalyst loading), Table 3, Entry 4).

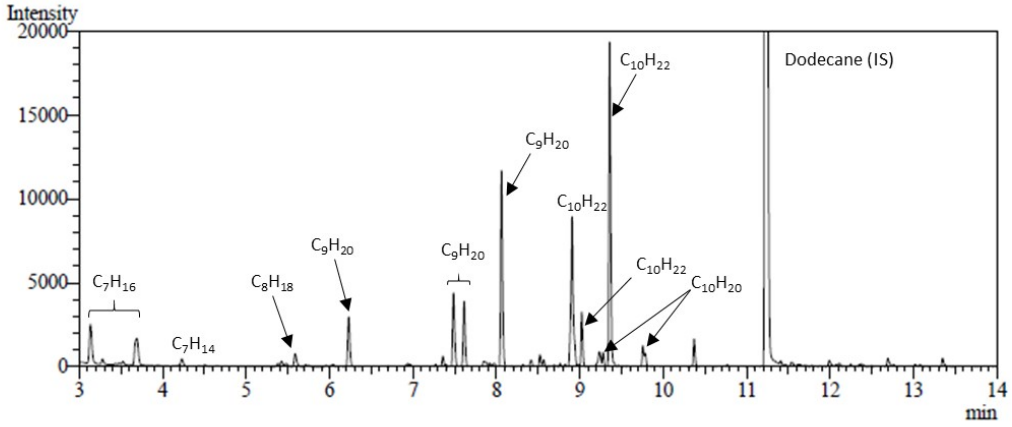


Figure S13. GC-FID chromatogram of the HDO product mixture (Pd/C+zeolite, reaction performed at 340 °C, 25 bar, Table 3, Entry 5).

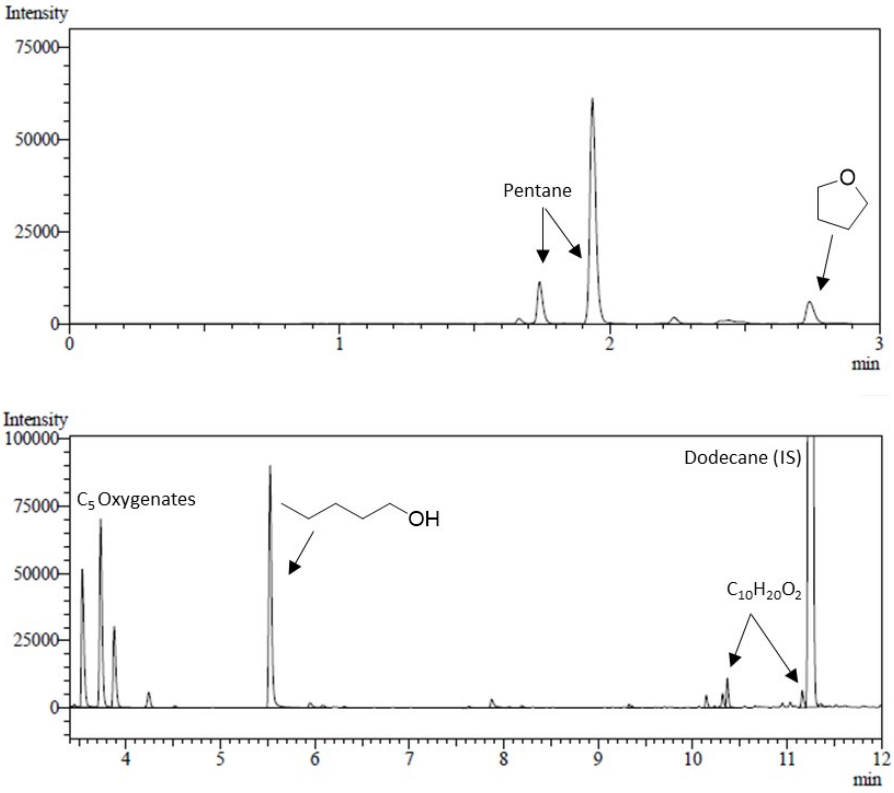


Figure S14. GC-FID chromatogram of the HDO product mixture (Pt/Al_2O_3, Table 3, Entry 6).

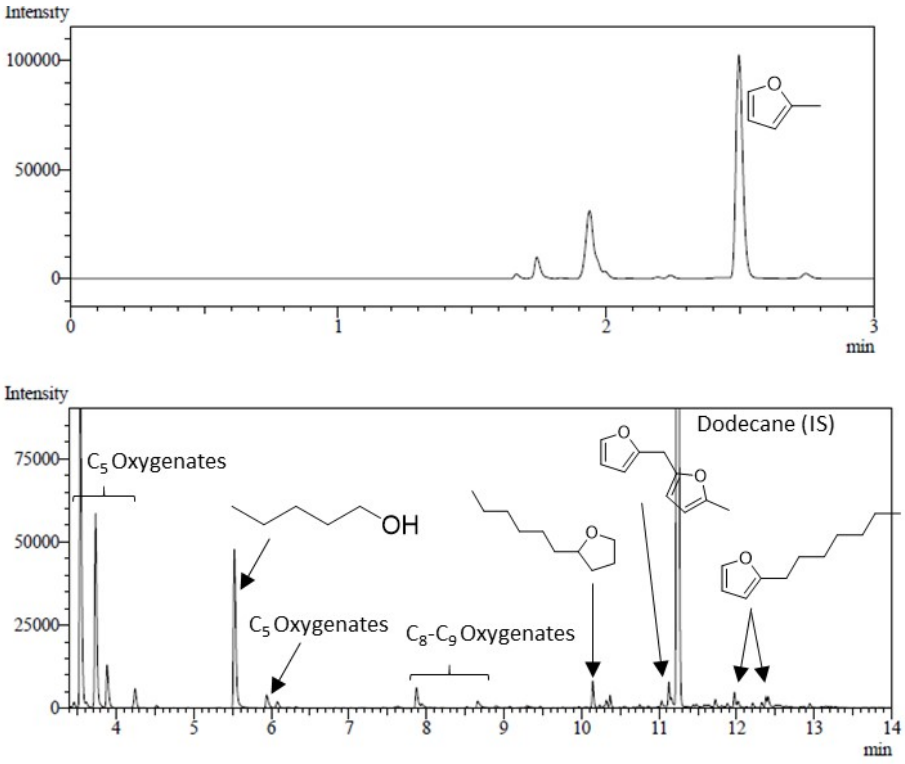


Figure S15. GC-FID chromatogram of the HDO product mixture ($Pt/Mo/TiO_2$, Table 3, Entry 7).

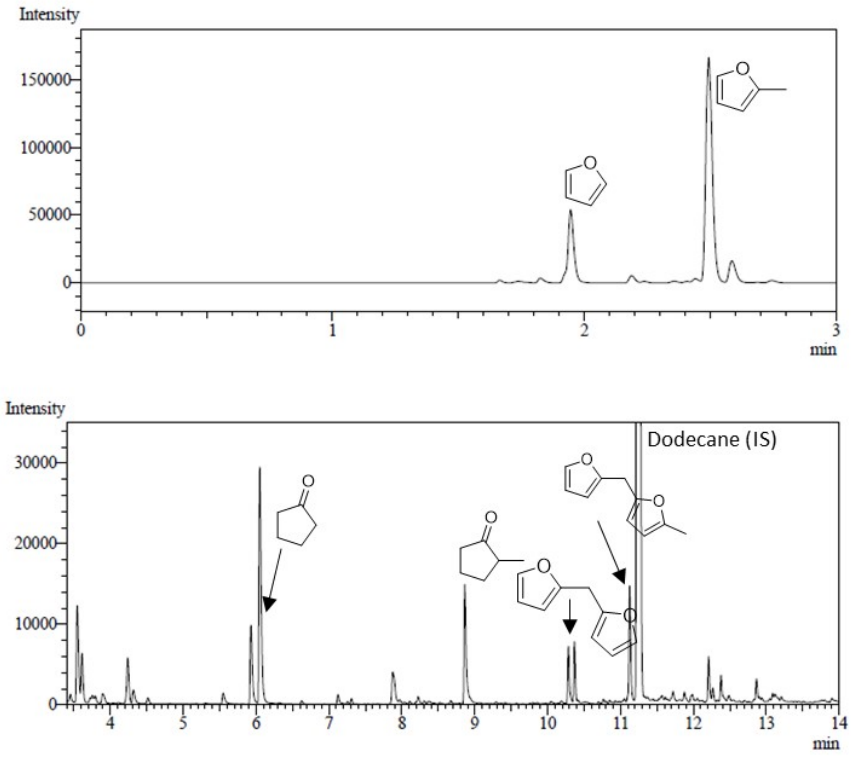


Figure S16. GC-FID chromatogram of the HDO product mixture (Ni/Al_2O_3, Table 3, Entry 8).

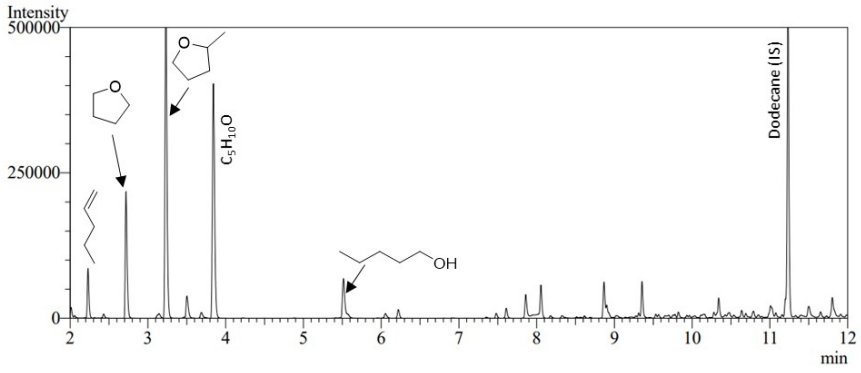


Figure S17. GC-FID chromatogram of the product mixture in 2-hour HDO reaction.

References

1 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, and D. Crocker, *Laboratory Analytical Procedure (LAP). National Renewable Energy* Laboratory, 2008