Conceptual Process Design and Techno-Economic Assessment of *Ex Situ* Catalytic Fast Pyrolysis of Biomass: A Fixed Bed Reactor Implementation Scenario for Future Feasibility

—Supplementary Material—

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This Supplementary Material provides details and data as called by the main text.

A. Catalyst Cost Calculations

The cost of each catalyst was determined using the following series of equations to take into consideration materials and processing costs. All prices were converted into 2011 base year US dollars ($ USD) using chemical cost indices.[A1]

The total catalyst cost $\boldsymbol{C_{cat}}$ is expressed as

$$\boldsymbol{C_{cat} = C_{pro} + C_{mat}} \qquad \text{Eq. A1}$$

where C_{pro} is the sum of all processing costs and C_{mat} is the sum of all materials in $ USD/lb catalyst. The price assumptions of each processing step are listed in Table A1 and were estimated using a graded scale based on the severity of the process. Process steps that only involve the active phase precursor (e.g., dissolution of metal salts) are scaled by the active phase weight percent of the final catalyst.

Table A1. Processing costs for a variety of different processing steps.

Process	Process severity range	Standard cost ($/lb catalyst)
Mixing	water or alcohol solvents	1
Ramping	(< 250 °C)	3
Ramping	(> 250 °C)	4
Heating	(< 350 °C)	2
Heating	(> 350 °C)	3
Cooling		1
Filtration		3
Supporting		2
Drying		1
Passivation		1

The price per lb of most raw materials was estimated from values obtained from the IHS Process Economics Program (PEP) yearbook, as shown in Table A2.[A2] A cost estimate for silica was obtained from the IHS Chemical Economics Handbook (CEH) report on Silicates and Silicas (2013 price of precipitated silica used for catalyst applications).[A3] The materials cost of $RuCl_3$ x H_2O (assumed for this study to be $RuCl_3$ x 3 H_2O) was estimated using publicly available consumer pricing for the reagent from Sigma-Aldrich. A plot of cost per lb for all available quantities of $RuCl_3$ x H_2O was fit to a power curve, and the cost determined at a quantity of 2000 lbs was used as the bulk cost of this material. The price for a 10% solution of $Pd(NH_3)_4(NO_3)_2$ was similarly obtained using publicly available consumer pricing from Sigma-Aldrich. This method was also used to determine a price for $Pd(NO_3)_2$ x 2 H_2O with consumer pricing from Fisher Scientific; however, this yielded comparatively high cost so an additional price was determined from the trading price of palladium. In short, the cumulative London Fix price[A4] of Pd from calendar year 2014, was used as the price of Pd and the fraction of Pd in the $Pd(NO_3)_2$ x 2 H_2O was

defined as the metal-based cost of $Pd(NO_3)_2$ x 2 H_2O. The price of H-ZSM5 was assumed to be $5/lb, and the price of H-BEA was assumed to be the cost of NH_4-BEA obtained from a bulk quote from Zeolyst with the addition of calcination processing steps to prepare the proton form.

Table A2. Sources for materials costs.

Material	IHS PEP Report
Water	PEP Review 2013-15 (MK)
Titania	PEP Review 99-6 (TFM)
Alumina	PEP Report 270 SEC 6 (RGB) PEP Report 223 SEC 7 (JLLM/MFH)
Nickel Nitrate Hexahydrate	PEP Report 153 P.166-175 (GER/LAW)
Methane	PEP Report 111A SEC 4 (MAC)
Hydrogen	PEP Review 2003-10 (BAW)
Nitrogen	PEP Report 225 SEC 5 (SNN)
Molybdenum Trioxide	PEP Report 22D SEC 7 (GJA)
Oxygen	PEP Report 37C SEC 7 (SNN)
Ammonia	PEP Report 259 SEC 5 (RGB)
Zirconia	PEP Report 196 SEC 7 (JJLM)
Diammonium Phosphate	PEP Report 127 P.151-186
Ammonium Paramolybdate	PEP Report 2H SEC 4 (SHW)

The amount of each raw material ($\boldsymbol{M_{mat}}$) to prepare a final catalyst was determined from reaction stoichiometries and general incipient wetness and ion exchange procedures. This value was then scaled by using Equation A2:

$$\boldsymbol{Q_{mat}} = \frac{\boldsymbol{M_{mat}}}{\boldsymbol{M_{cat}}} * \boldsymbol{Q_{basis}} \qquad \text{Eq. A2}$$

to give $\boldsymbol{Q_{mat}}$, the quantity (in lbs) of a raw material required for purchase. Here, $\boldsymbol{M_{cat}}$ is the mass of the final catalyst and $\boldsymbol{Q_{basis}}$ is the basis for materials purchase (assumed to be 19,178 lbs on 7 day frequency of purchase; or 1,000,000 lbs. catalyst per year). Multiplying $\boldsymbol{Q_{mat}}$ by the price per lb of a given raw material gives the total price per purchase of that material. The sum of $\boldsymbol{Q_{mat}}$ for all raw materials required to make a catalyst gives the total material cost $\boldsymbol{C_{mat}}$.

The amount of support material ($\boldsymbol{M_{sup}}$) used in these calculations was a function of active phase weight loading (a user defined variable) and was determined from Equation A3:

$$\boldsymbol{M_{sup}} = \frac{\boldsymbol{M_{ap}}}{\boldsymbol{wt\%/100}} - \boldsymbol{M_{ap}} \qquad \text{Eq. A3}$$

where $\boldsymbol{M_{ap}}$ is the mass of catalyst active phase. Thereby, the cost of various weight loadings was determined by adjusting the amount of support material without adjustments to the preparation of the active phase. For all catalysts, the volume of solvent was adjusted as a function of $\boldsymbol{M_{sup}}$, where the ratio of solvent:$\boldsymbol{M_{sup}}$ was determined from analogous literature procedures except in the case of MoO_3 where

the solvent volume was fixed at the room temperature solubility of MoO_3. The total catalyst mass ($\boldsymbol{M_{cat}}$) is then simply the sum of $\boldsymbol{M_{sup}}$ and $\boldsymbol{M_{ap}}$. The cost of various active phase weight loadings was determined. The yield of catalysts prepared via incipient wetness and ion exchange methods was assumed to be 100% and no attempt was made to account for processing losses. Reagent masses and catalyst preparation scale were chosen to be within the range of proven bench-scale literature procedures, e.g., incipient wetness.

Supplementary Material Section A References

A1. Producer Price Index Industry Data for Chemical mfg., Bureau of Labor Statistics, Series ID: PCU325---325--- . http://data.bls.gov/cgi-bin/srgate

A2. IHS / SRI 2014 Process Economics Program (PEP) Yearbook. Accessed June 9, 2015. http://chemical.ihs.com/PEP/

A3. IHS Chemical Economics Handbook Reports. SRI Consulting, Subsidiary of SRI International. http://chemical.ihs.com/CEH/available_reports.html.

A4. Historical Palladium Charts and Data – London Fix. http://www.kitco.com/charts/historicalpalladium.html

B. Additional Process and Economic Information

Table B1. Summary of process configurations and operating conditions by process area

Area 100: Feed Handling	
Feed type	Woody composition formulation
Feed rate	2,000 dry metric tonnes per day

Area 200: Fast Pyrolysis & Vapor Upgrading	
Fast Pyrolysis	
Configuration	Dual circulating fluidized bed (CFB)
Fast pyrolysis reactor conditions	500 °C, 8.3 bar
Bed material	Sand
Ratio of sand to dry biomass	7.9 w/w
Fluidization gas to dry biomass	0.79 w/w
Fluidized bed char combustor conditions	720 °C, 8.1 bar
Ex situ fixed bed upgrading reactors	
H_2 concentration	61 mole % at inlet of #1
Number of reactors in series	2
Reactor #1	
External configuration	2 online/1 regenerating
Internal configuration	3 catalyst beds with 2 intercoolers
Operating pressure	8.1 bar
Inlet & outlet temp.	350 °C & 400 °C
Catalyst type (for cost)	Non-precious metal based
Reactor #2	
External configuration	2 online/1 regenerating
Internal configuration	3 catalyst beds, no intercoolers
Operating pressure	7.2 bar
Inlet & outlet temp.	275 °C & 293 °C
Catalyst type (for cost)	Precious metal based

Area 300: Vapor Quench & Condensation	
Heavy fraction absorber-condenser	
Overhead conditions	178 °C, 6.7 bar
Light fraction absorber-condenser	
Overhead conditions	12 °C, 5.9 bar
Overhead light gas	65 mole % H_2, 68% to recycle

Area 400: Hydroprocessing & Product Separation	
Hydrotreater	
Inlet & outlet temp.	375 °C & 403 °C
Reactor inlet pressure	106.5 bar
Hydrocracker	
Inlet & outlet temp.	392 °C & 420 °C
Reactor inlet pressure	134.1 bar
Product separation	
Configuration	2 distillation columns
Product streams	(1) Gasoline and (2) diesel blendstock

Area 500: Hydrogen Production	
Gas source	Process off gases
Natural gas feed	Not required
Production methods	Water-gas shift, steam reforming

Areas 600, 700: Steam System & Utilities	
Configuration	2-stage steam turbine with intermediate reheat
Steam generation heat source	Excess heat from process streams
Configuration for cooling water	Mechanical draft cooling tower

Area 800: Wastewater Management	
Aqueous carbon waste from A300	Processed by Regenerative Thermal Oxidizer
Other aqueous waste	Cleanup includes reverse osmosis & aerobic digestion

Table B2. Total project costs including total direct costs, total indirect costs, and total capital investment.

		Fluidized bed[1]	Fixed bed (this study)
Total purchased equipment cost (TPEC)		**$141,180,000**	**$162,320,000**
Aggregate installation factor		2.249	2.134
Total installed cost (TIC)		**$317,540,000**	**$347,370,000**
Other direct costs			
Land (not depreciated)		$1,610,000	$1,610,000
Warehouse	4.0% of ISBL	$7,230,000	$7,940,000
Site development	10.0% of ISBL	$18,070,000	$19,840,000
Additional piping	4.5% of ISBL	$8,130,000	$8,930,000
Total direct costs (TDC)		**$350,970,000**	**$384,080,000**
Indirect costs	% of TDC (ex land)		
Prorated expenses	10.0%	$35,100,000	$38,410,000
Home office and construction fees	20.0%	$70,190,000	$76,820,000
Field expenses	10.0%	$35,100,000	$38,410,000
Project contingency	10.0%	$35,100,000	$38,410,000
Other costs (start-up and permits)	10.0%	$35,100,000	$38,410,000
Total indirect costs	**60.0%**	**$210,580,000**	**$230,450,000**
Fixed capital investment (FCI)		**$561,550,000**	**$614,520,000**
Working capital	5.0% of FCI (ex land)	$28,080,000	$30,730,000
Total capital investment (TCI)		**$589,630,000**	**$645,250,000**
TCI/TPEC		4.177	3.975
FCI Lang Factor = FCI/ISBL TPEC		8.023	7.176
TCI Lang Factor = TCI/ISBL TPEC		8.424	7.534

[1] Dutta, A.; Sahir, A.; Tan, E.; Humbird, D.; Snowden-Swan, L.; Meyer, P.; Ross, J.; Sexton, D.; Yap, R.; Lukas, J. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels - Thermochemical Research Pathways With *In Situ* and *Ex Situ* Upgrading of Fast Pyrolysis Vapors. NREL/TP-5100-62455, PNNL-23823, 2015.