2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

3.6.1.1, 3.6.1.3
Thermochemical Platform Analysis: Ex-Situ and In-Situ TEAs
(No Evaluation)

May 22, 2013

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Technology Area Review: Bio-Oils

Organizations: National Renewable Energy Laboratory, Pacific Northwest National Laboratory

Goal Statement

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- Enable technologies for improvement of the quality of vapors from the fast pyrolysis of biomass, prior to condensation
  - Facilitate easier downstream hydroprocessing and blending into transportation fuels infrastructure for use in gasoline, jet and diesel pools

- By providing techno-economic analysis, help the research and development efforts achieve cost-competitiveness with petroleum derived fuels
  - Help establish research targets
  - Track research progress based on experimental results
  - Provide feedback to the research and outline alternatives when there are deviations from established plans

Barriers and Project Management

- Barriers to be addressed (November 2012 MYPP)
  - Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
  - Tt-G. Fuel Synthesis and *Upgrading*
  - Tt-K. Bio-Oil Pathways Process Integration
- Managed by Annual Operating Plan and Project Management Plan before each fiscal year
  - Progress tracked by milestones and quarterly reports

Overview: Fast Pyrolysis

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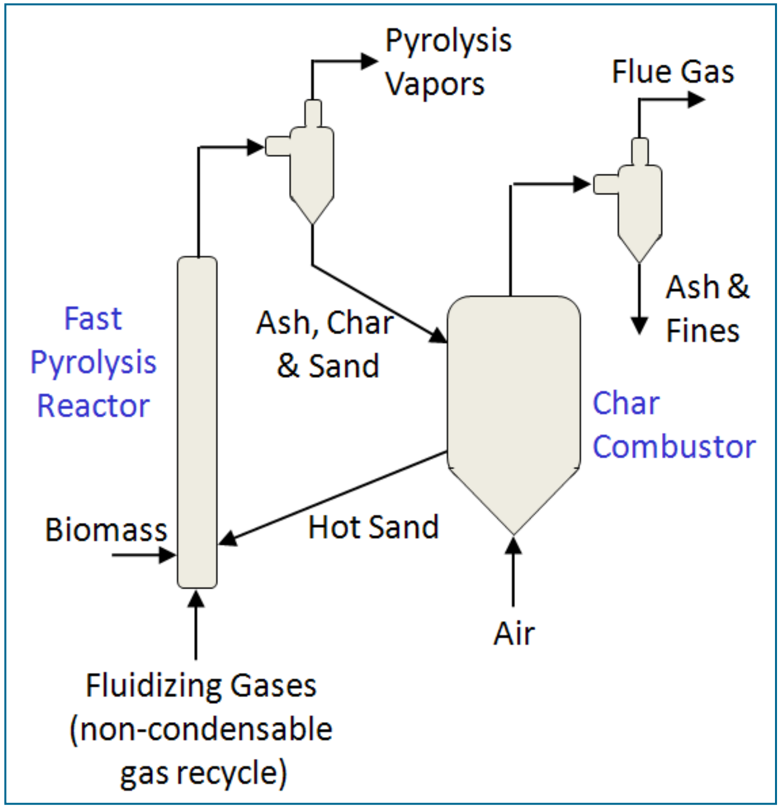


***Diagram represents one possible configuration**

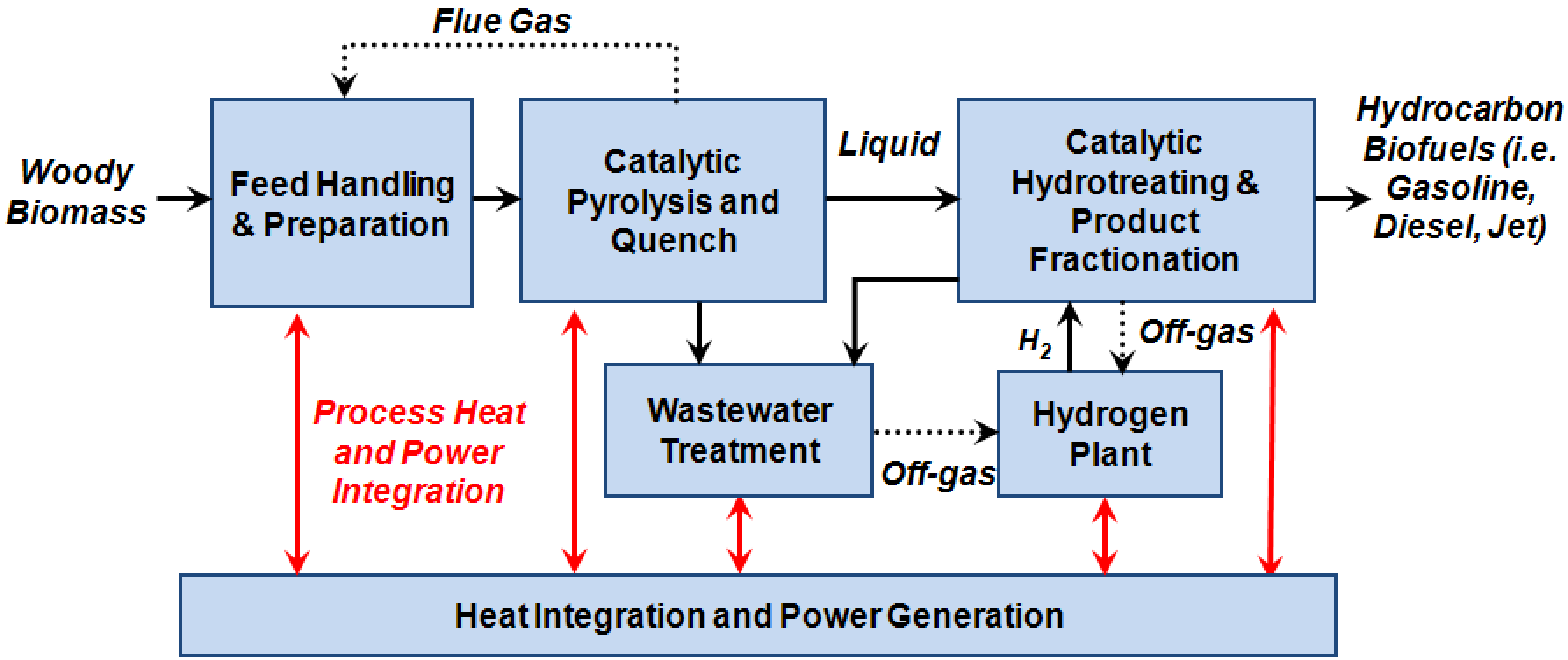
- Conditions: ~500°C, residence time <2s
- Products: (a) Non-condensable gases, (b) liquid, including water, (c) solids, char & ash
- Status: Commercial/pre-commercial (Ensyn)
- Scale: 400 tons/day (TPD), n^{th} plant scale of 1000 TPD possible
- Quality: Produced oil not suitable for transportation fuels: high oxygen, acidity and reactivity, needs hydroprocessing for upgrading to acceptable quality

Yield† (wt % dry biomass)	
Oil	59.9-64.9%
Water	10.8
Char & Ash	13.2-16.2
Gas	11.1-13.1

Oil Properties‡	
Carbon	54-58%
Hydrogen	5.5-7.0%
Oxygen	35-40%
pH	2-3

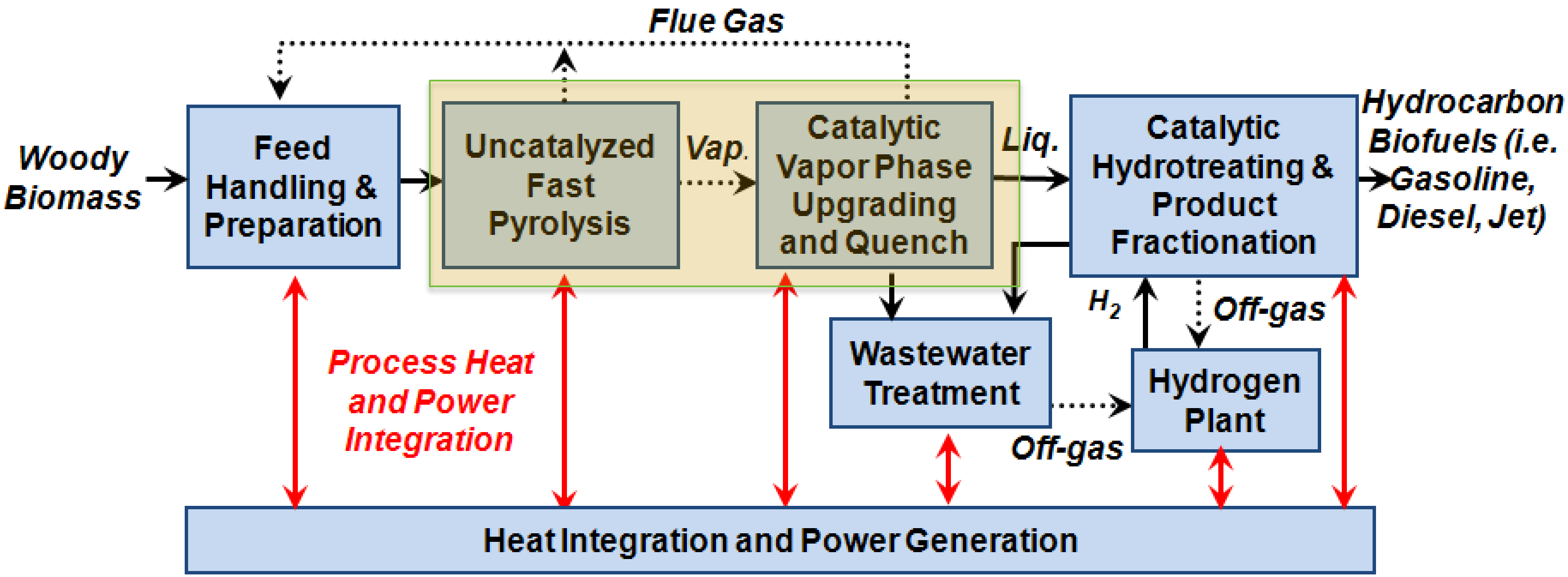
†Ren. & Sust. En. Rev.; Vol. 6, 2002; pp. 181-248 ‡Energy & Fuels 2004, 18, 590-598

Overview: In-situ Catalytic Upgrading



- Upgrading catalyst present in the fast pyrolysis reactor
- Potential reduction in capital cost over a separate (ex-situ) upgrading reactor
- Catalyst maintenance challenging because of mixing with char, ash and biomass at high temperatures

Overview: Ex-Situ Catalytic Upgrading



- Upgrades pyrolysis vapors in a separate reactor after solids separation
- Potential increase in capital cost over an in-situ upgrading reactor
- Catalyst maintenance and functionality can be better controlled (since catalyst will not mix with char, ash and biomass)

Approach and Accomplishments

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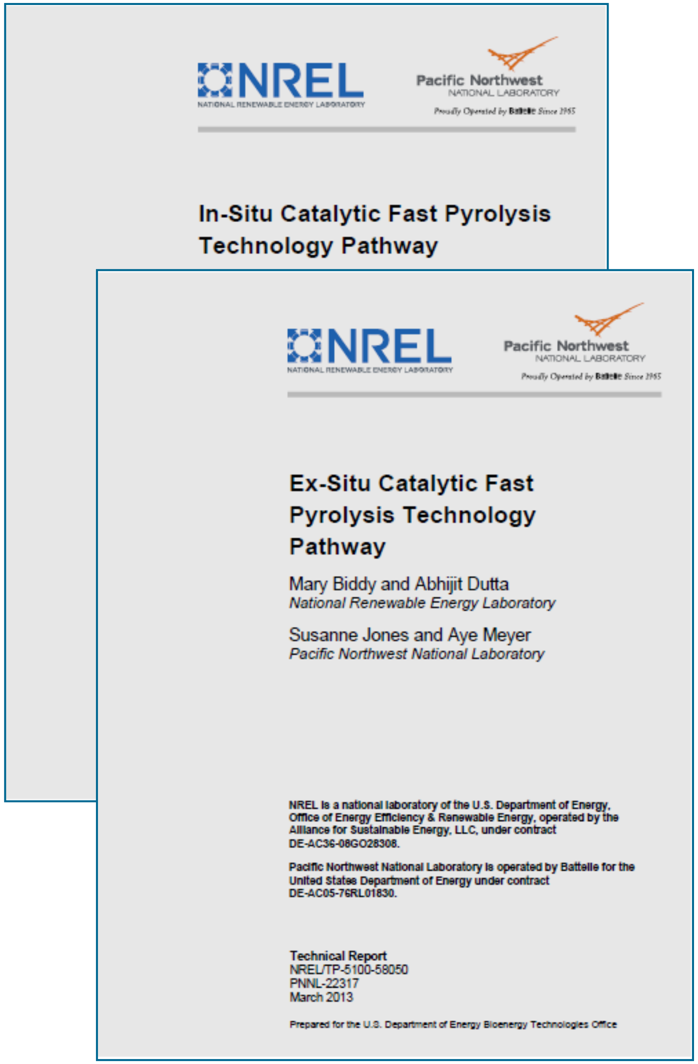
- Initial scoping techno-economic analysis (TEA)
  - Used public experimental data for key yield and quality (oxygen content) assumptions
  - Technical Memos published jointly with Analysis task
- Identified key data gaps and technology improvements to be addressed for cost competitiveness (focus of presentation)
- Concurrent initiation of experimental efforts to fill some of the identified data gaps
- More detailed TEA model in FY14 using new and existing data to establish possible pathways to cost competitiveness
- Beyond FY14: Assess research progress and cost reduction
  - Objective reevaluations, feedback and re-scoping of research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In-Situ Catalytic Fast Pyrolysis Technology Pathway

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Pacific Northwest NATIONAL LABORATORY
Ex-Situ Catalytic Fast Pyrolysis Technology Pathway
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Pacific Northwest National Laboratory is operated by Battelle for the United States Department of Energy under contract DE-AC05-76RL01830.

Technical Report
NREL/TP-5100-58050
PNNL-22317
March 2013

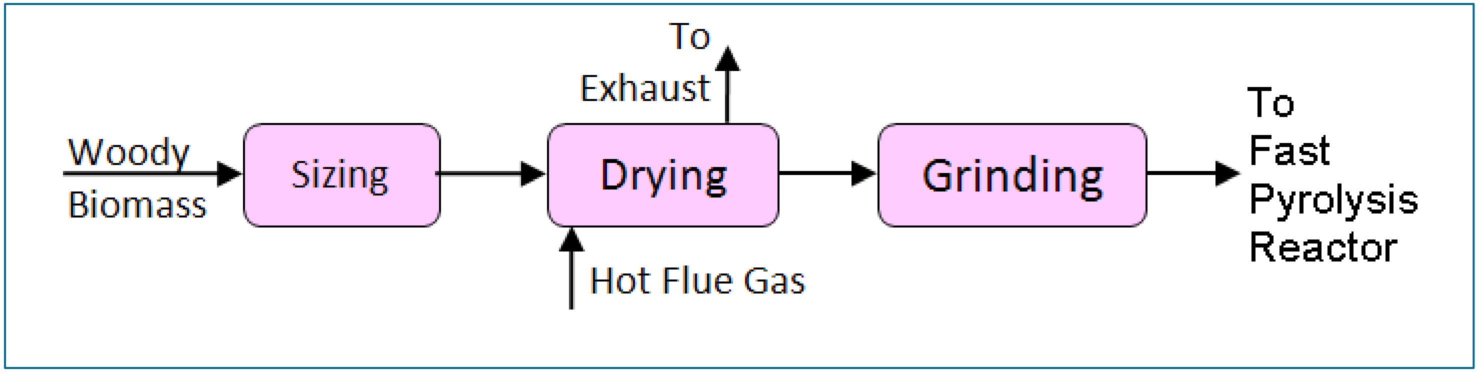
Prepared for the U.S. Department of Energy Bioenergy Technologies Office

***Available at NREL and PNNL websites. See additional slides for links**

Fast Pyrolysis Vapor Upgrading (In-Situ & Ex-Situ): Key Objectives

- Improve quality of fast pyrolysis condensable vapors
  - Lower oxygen and acidity in produced organic liquid compared to non-upgraded fast pyrolysis oils
  - Require less downstream hydrogen and hydroprocessing
  - More stable and can be fractionated if necessary
  - Vapors can be cooled in heat exchangers instead of direct quench, allowing process heat recovery and water savings
- Increase product yields through catalyst design
  - Reduce loss of carbon to the solid-phase
  - Acceptable catalyst stability, lifetimes & product yields to allow economical operations.
    - Develop through a combination of computational and experimental techniques
    - A fundamental understanding of detailed reaction mechanisms and kinetics can enable the design of catalysts
- Optimize reactor designs for catalyst, mass & heat transfer behavior

Feed Handling & Preparation



- Currently expected that process waste heat from flue gases will be used to dry biomass from 30 wt% to 10 wt% moisture content
- Size reduction to 2-6 mm required for rapid heating rates
- Moisture content of ~10 wt% at the pyrolysis reactor
- Challenges include providing low ash, low moisture, small size feed at a low cost. Effective solids handling methods will be important
- Initial assumption is to use woody feedstock for bio-oil pathways, although impacts of feedstock and quality variations are being studied
- Feedstock handling and preparation appropriate for bio-oil production being studied by the "Feedstock Interface" tasks at INL/NREL/PNNL

In-Situ Catalytic Fast Pyrolysis Reactor

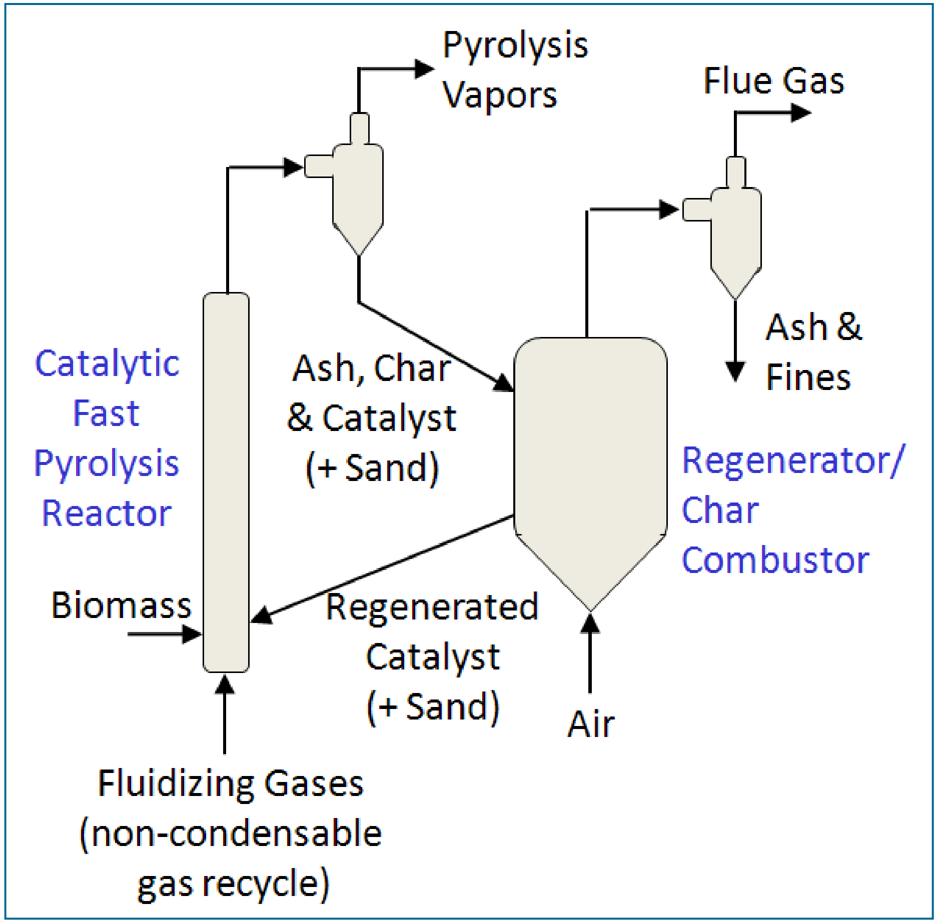


***Diagram represents one possible configuration**

- Fluid Catalytic Cracker (FCC) type circulation
- Catalyst life and regeneration challenges. Expected that char combustion, and regeneration via coke burn-off will happen in the same regenerator vessel
- Yields decrease with improvements in product quality. Catalyst functionality and activity need to be optimized for economic feasibility
- Need process relevant high quality experimental data for techno-economic analysis (TEA)

Fast Pyrolysis & Ex-Situ Upgrading

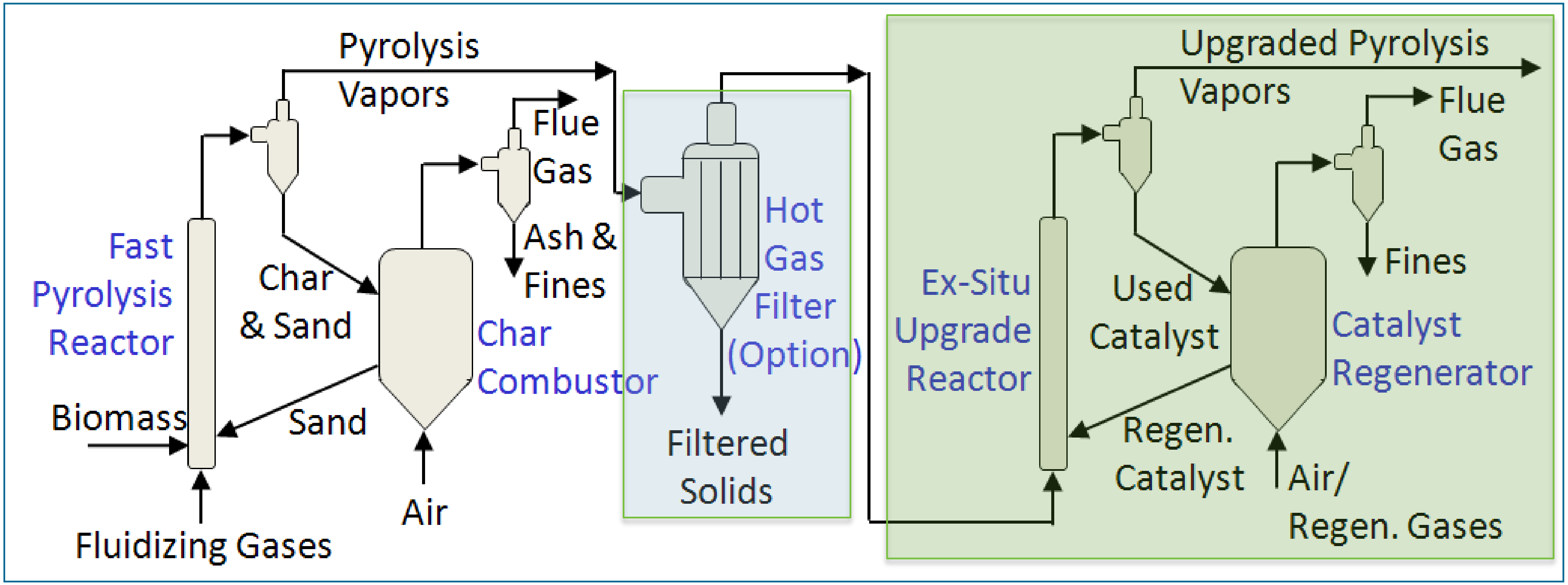


***Diagram represents one possible process configuration. E.g. upgrading reactor can be a fixed bed system instead of circulating.**

- Like in-situ: Yields decrease with improved product quality; need data
- Upgrading reactor: Circulating or fixed bed, based on catalyst functionality
- Circulating bed: Regeneration of catalysts like ZSM-5 via coke burn off
- Opportunity to produce desired molecules via catalyst functionality
- Benefits need to offset expected higher capital cost vs. in-situ upgrading
- Optional hot gas filter in between fast pyrolysis & upgrading reactors

Condensation & Filtration

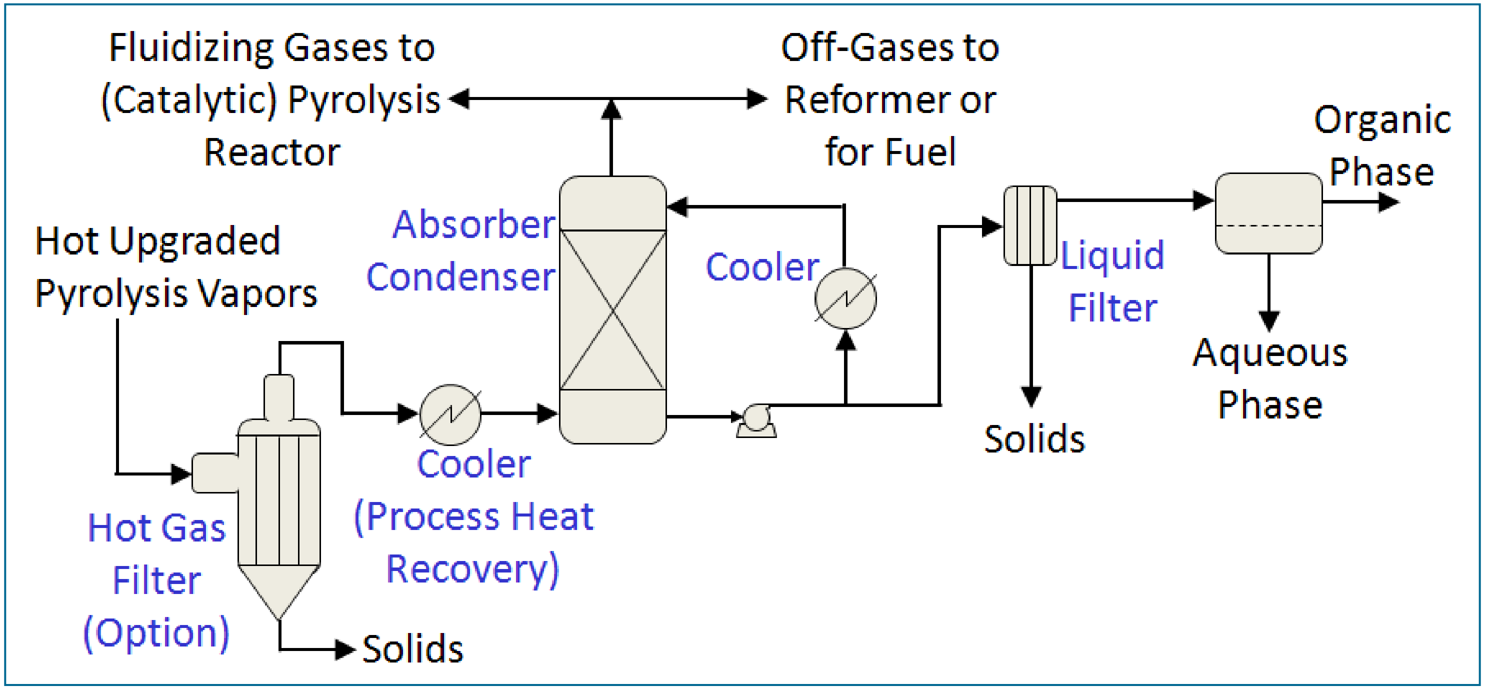
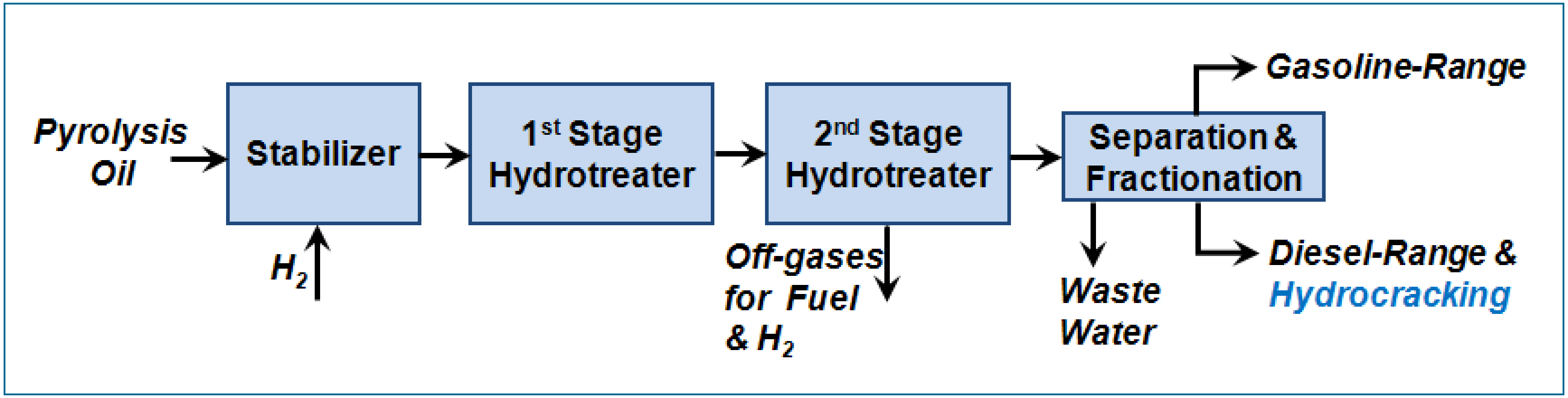


***Diagram represents one possible process configuration**

- Option of hot gas filter needs to be studied in detail for:
  - Benefits on product quality, added capital cost, & product losses
- Significant product quality improvement over fast pyrolysis can allow process heat recovery, separation & fractionation of organic phase
- Potential for refinery integration made feasible by a stable organic intermediate, for insertion at suitable point in a petroleum refinery

Hydroprocessing of Pyrolysis Oils



Simplified block diagram (one possible process configuration for fast pyrolysis oil hydroprocessing)

- Expected upgrading in fixed bed at 255-410°C and ~2000 psi
- Reduced steps and less hydrogen consumption expected vs. fast pyrolysis hydroprocessing steps shown above
- Preliminary target <1 wt% O in product (with <1 wt% C in wastewater), although ultimately dictated by economics of getting to finished fuel
- May be able to hydrotreat in a single step depending on oil quality
- Heavy oil fraction may not be significant, eliminating hydrocracking step
- Need long-term catalyst tests, fuel quality tests, & speciation of olefins, aromatics and oxygenates to understand & optimize hydrogen usage

Hydrogen Generation

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- Via steam reformer, water gas shift reactor and pressure swing adsorption (PSA) unit
- Use off-gases (non-condensables) from pyrolysis, vapor upgrading and hydrotreating sections
- Supplement with natural gas to cover any H_2 deficit
- Potential use of part of the aqueous phase (wastewater) for steam reforming (need experimental verification)
- Need experimental information on the effect of off gas quality on reforming catalyst performance
- Need to consider options of fixed bed and fluidized bed reformers

Utilities: Steam, Electricity, WWT

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- Excess process heat used for steam and power generation
- Efforts will be made to reduce water consumption
  - Major losses through use of cooling water & evaporation
- Wastewater treatment (WWT):
  - Likely contain phenolics, aldehydes and acids
  - Need better understanding trace compounds and their impacts
  - Need data and experiments to prove effective and economical treatment, e.g. by microbial action
    - Try to recover some of the carbon from this stream
    - Consider wastewater use in thermochemical processes that need steam

- Aspen Plus and Chemcad based techno-economic models were developed based on literature information
  - Identified key technology gaps that need to be addressed (mentioned in previous slides) for $3/gallon minimum fuel selling price
  - Detailed design case to be developed in FY14
    - Use new and existing experimental data available at that time to fill some of the current data gaps & assumptions
- Sustainability and life-cycle analysis
  - Understand the impact of design assumptions and process requirements on the sustainability metrics of the process
  - This is very important if supplemental natural gas is used for hydrogen generation in the process

Critical Success Factors

- Provide objective assessments to allow good decision making
- Close interaction with research and use of relevant experimental data
- Provide sensitivity analysis when data is not available
- Use representative capital costs e.g. from similar technology; ask vendors or industrial partners
- Peer review of analysis products
- Make results available in the public domain

Relevance and Future Work

Directly support program goal for cost-competitive liquid transportation fuels via improvements to the pyrolysis pathway. Techno-economic assessment outputs are expected to be incorporated in the MYPP to show the direction of the research.

- Near-term: Provide information about the key impediments for lowering costs to help guide research activities
- FY14: Provide a more detailed report showing possible cost-competitive pathways, based on what is deemed achievable through research
- Future: Assessments of the impact of the research towards achieving cost and sustainability goals, and provide State of Technology updates

Summary

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Key research needs for cost-competitiveness:

- Catalyst & reactor development objectives
  - Reduce carbon losses to gas & solid phases; deoxygenate & stabilize intermediate, reduce downstream hydrodeoxygenation
  - Viable catalyst maintenance, regeneration & stability
  - Understand fundamental kinetics & apply to reactor design
- Experimentally quantify losses & cost benefits of hot gas filter
- Optimize hydroprocessing for specific intermediates
- Understand intermediates and product properties for efficient refinery integration
- Optimize overall process yields based on catalyst functionalities
- Improve & validate hydrogen generation capability from off-gases & waste streams; understand wastewater treatment need

Acknowldegments

- BETO: Melissa Klembara, Liz Moore, Alicia Lindauer, Zia Haq, Kristen Johnson
- NREL: Mary Biddy, Mark Davis, Adam Bratis, Thermochemical Conversion and Biorefinery Analysis teams
- PNNL: Alan Zacher, Aye Meyer, Doug Elliott, Mariefel Olarte

- Responses to reviewer comments:
  - New project (no previous review)

Publications and Presentations

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Biddy, M.; Dutta, A.; Jones, S.; Meyer, A. (2013). Ex-Situ Catalytic Fast Pyrolysis Technology Pathway. 9 pp.; NREL Report No. TP-5100-58050; PNNL-22317. http://www.nrel.gov/docs/fy13osti/58050.pdf http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22317.pdf

Biddy, M.; Dutta, A.; Jones, S.; Meyer, A. (2013). In-Situ Catalytic Fast Pyrolysis Technology Pathway. 9 pp.; NREL Report No. TP-5100-58056; PNNL-22320. http://www.nrel.gov/docs/fy13osti/58056.pdf http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22320.pdf