Dr. Satya Chauhan, Battelle
Email: chauhan@battelle.org • 614.424.4812
August 8 - 12, 2016

SCALE-UP OF BATTELLE'S DIRECT COAL-TO-LIQUIDS (CTL) PROCESS FOR JET FUEL USING BIOMASS-DERIVED SOLVENTS

33rd International Pittsburgh Coal Conference, Cape Town, South Africa

Battelle
The Business of Innovation

Outline

- Background on jet fuel from non-petroleum sources
- Indirect vs. direct liquefaction of coal-to-liquids (CTL) technologies for jet fuel
- Battelle's novel approach to improve direct CTL for jet fuel using biomass-derived solvents
- Scale-up of Battelle's new direct CTL process

Need for Alternative Feedstocks for Jet Fuels

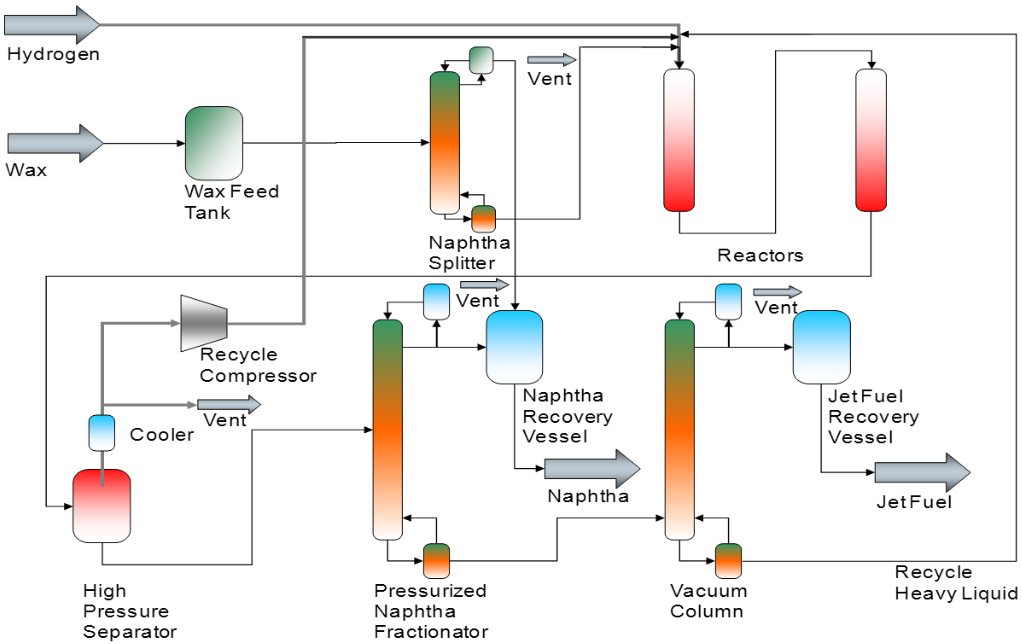
- Increasing demand and limited supply of petroleum crude
  - 500 million barrels per year U.S. demand for jet fuel
- Secure supply of jet fuel is a priority of the United States
  - Large U.S. coal reserves available and easily accessible
  - Coal can be easily stored and stocks can be drawn on in emergencies
- Greenhouse gas (GHG) emission reduction requirements are driving consideration of biomass as a feedstock
  - Due to the dispersed nature and limited renewal rate of biomass, options are being considered for hybrid processes using coal plus biomass

Advanced Technologies for Alternative Jet Fuels

- Fischer-Tropsch (FT) technology
  - Gasification of coal, biomass, or natural gas, followed by FT synthesis and upgrading
  - FT Synthetic Paraffinic Kerosene (FT-SPK) and FT Synthetic Paraffinic Kerosene with Aromatics (FT-SKA) approved by FAA
  - Example Process: Battelle-developed microchannel FT, being commercialized by Velocys
- Lipids-based fuels
  - Deoxygenation and upgrading of edible and non-edible oils (lipids); Hydroprocessed Esters and Fatty Acids (HEFA) approved by FAA; paraffinic
  - Example Process: Catalytic Hydrothermolysis (CH) of lipids to introduce aromatics; under development by ARA (ReadiJet)
- Carbohydrate-based fuels
  - Conversion to sugars followed by fermentation and then conversion to jet fuels; Direct Sugar to Hydrocarbons (DSHC) and Alcohol to Jet (ATJ) approved by FAA

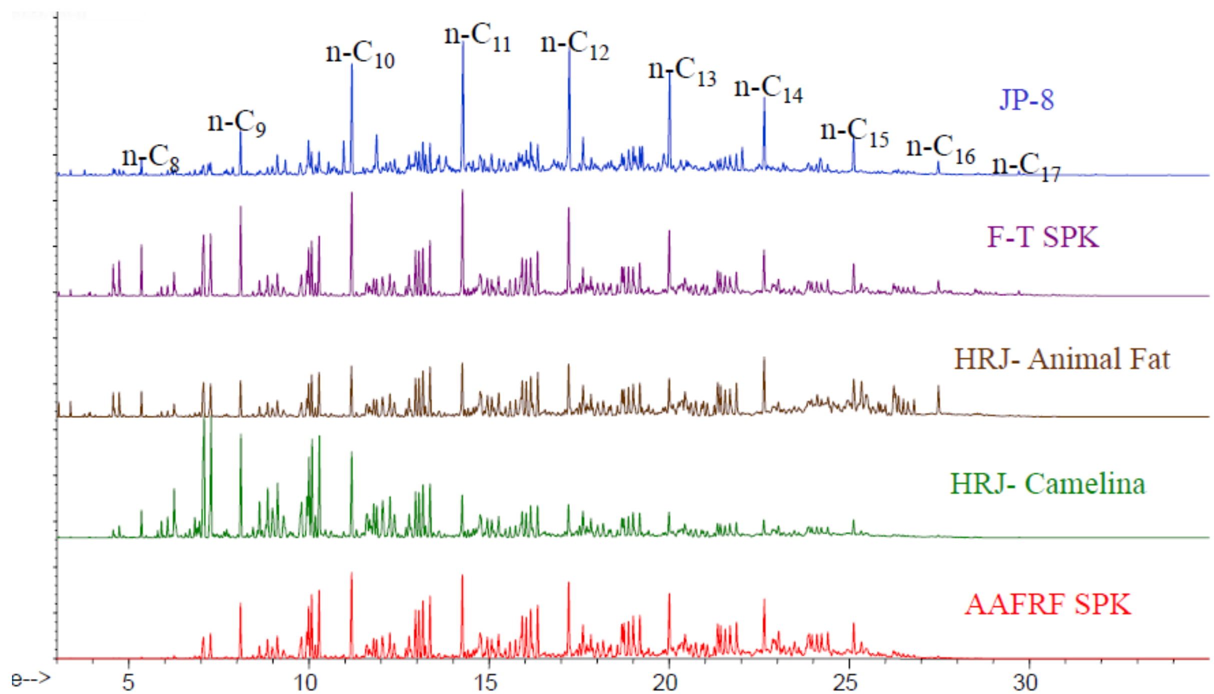
Alternative Jet Fuels Testing

- Battelle has been working with the U.S. Air Force and UDRI for the last 10 years to generate small quantities of alternative jet fuels for characterization
- Battelle has designed, built, and operated a 1 barrel/day facility called Assured Aerospace Fuels Research Facility (AAFRF); tested on FT and bio-based intermediates



Battelle
The Business *of* Innovation

AAFRF SPK Produced from FT Wax



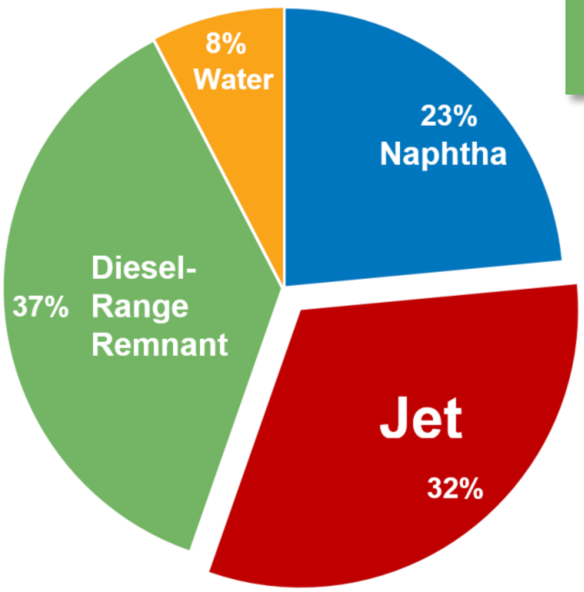
AAFRF SPK properties are nearly identical to other jet fuels

Battelle
The Business of Innovation

Some Shortcomings of Alternative Jet Fuels Technology

- Most products are paraffinic in composition, but a minimum of 8% aromatics are currently required for Jet-A fuels
  - The jet fuel fraction is C_8 to C_{16} paraffins; blended with alternative sources of aromatics
- Most technologies produce only about 30% in jet fuel range; rest is diesel remnants or naptha

ReadiJet
(CH Process)



Battelle
The Business of Innovation

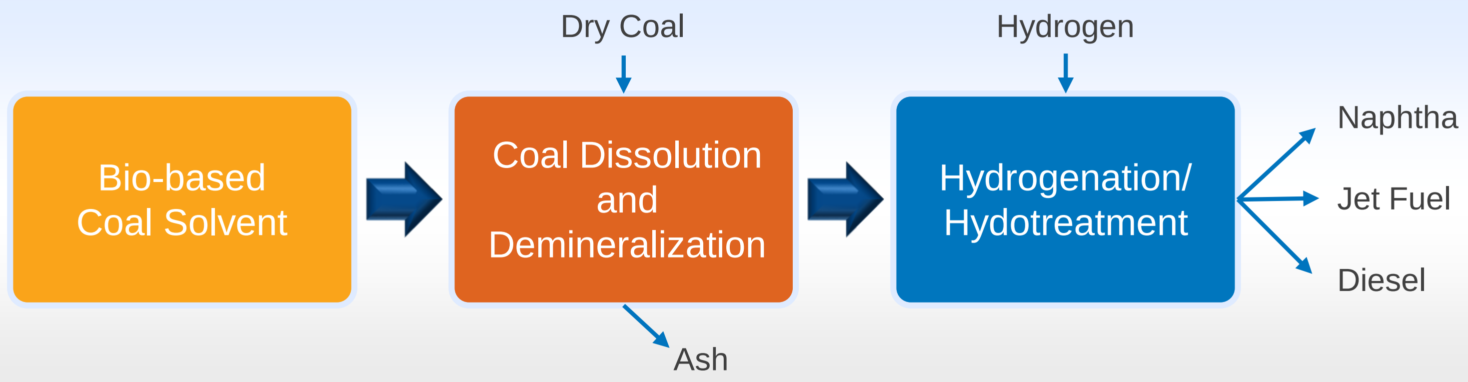
Direct Coal-to Liquids (CTL) for Jet Fuel

- Direct CTL Technology Options
  - Conventional, three-phase hydroliquefaction
  - Two-stage liquefaction using hydrogen-donor solvents
  - Coal-tar distillate/petroleum cycle-oil co-processing (PennState)
- Common concerns of direct CTL
  - While more thermally efficient than indirect CTL, current direct CTL is still inefficient, costly, and generates excessive amounts of GHG emissions
  - Provides far more aromatics than the minimum 8% desired in jet fuel
  - Complicated design and operation to maintain the proper solvent properties and balance
  - Requires molecular hydrogen (H_2); uses it inefficiently
  - Process is economical at larger (>5,000 tons/day of coal) scale

A New Technology for Direct Coal Liquefaction

- Battelle concept for using biomass-derived solvents for coal liquefaction
  - Provides much more hydrogen transfer than ~0.3% required to dissolve coal (*Chauhan, et.al., “Short Residence Time Coal Liquefaction, ACS Symposium Series, No. 139; 1980*)
- Radically different from previously researched technologies
  - Solvent Refined Coal II process using coal-derived solvents
  - Exxon Donor Solvent process using tetralin as hydrogen donor solvent
  - PennState effort using cyclic petroleum-derived fractions as solvent
- Once-through use of the hydrogen-donor, biomass-derived solvent eliminates need to regenerate and recycle solvent
- Need for molecular H_2 for coal liquefaction completely eliminated; reduces pressure and eliminates need for on-site H_2 generation

New CTL Technology



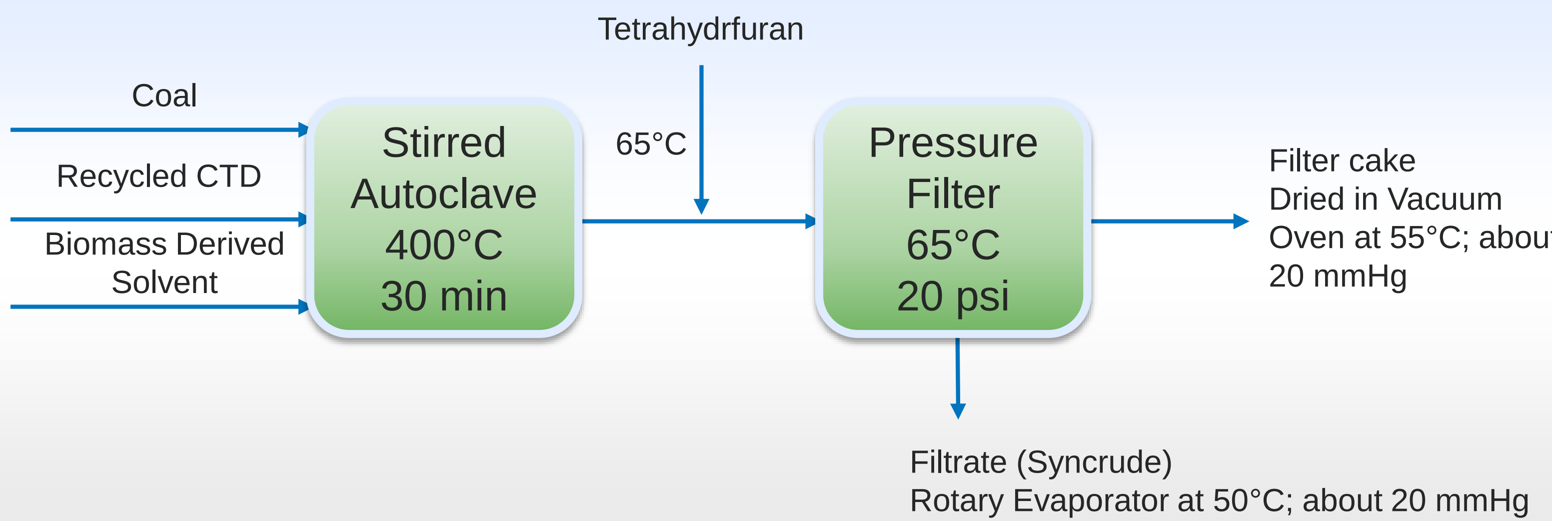
- Straightforward integration of proven subsystems with novel liquefaction chemistry
- Significant reduction in the capital and operating costs due to mild operating conditions (500 vs. 2500 psi)
- Elimination of CCS at coal liquefaction site and minimization of CCS at the coal-derived-syncrude-refining site due to reduced H_2 demand
- Meet jet fuel specifications with minimal blending with petroleum-based components

Battelle
The Business of Innovation

Bench-Scale Testing

- Three coals
  - West Virginia (WV) Coal; High Volatile A, Bituminous
  - Ohio (OH) Coal; High Volatile A, Bituminous
  - Wyoming (WY) Coal; Sub-bituminous
- Biomass-Derived Solvents (BS)
  - 40 proprietary solvents tested and compared with tetralin
  - Some in native form; others pre-treated to improve performance
- Liquefaction Testing
  - 0.5L autoclave
  - Microreactor (at PennState)
- Catalytic Upgrading
  - Two-stage catalytic upgrading
  - Multiple microreactors (~20 g catalyst)
  - GC-MS, GCXGC, and ultimate analysis

Typical Batch Liquefaction Processing Conditions



- Run in 0.5L Batch System; Coal Tar Distillate (CTD) as recycle solvent
- Percent liquefied coal calculated based on dried solid; some additionally confirmed by ash analysis
- Syncrude quality checked by measuring viscosity at 50°C

Batch Autoclave Coal Liquefaction Screening Results on WV Coal

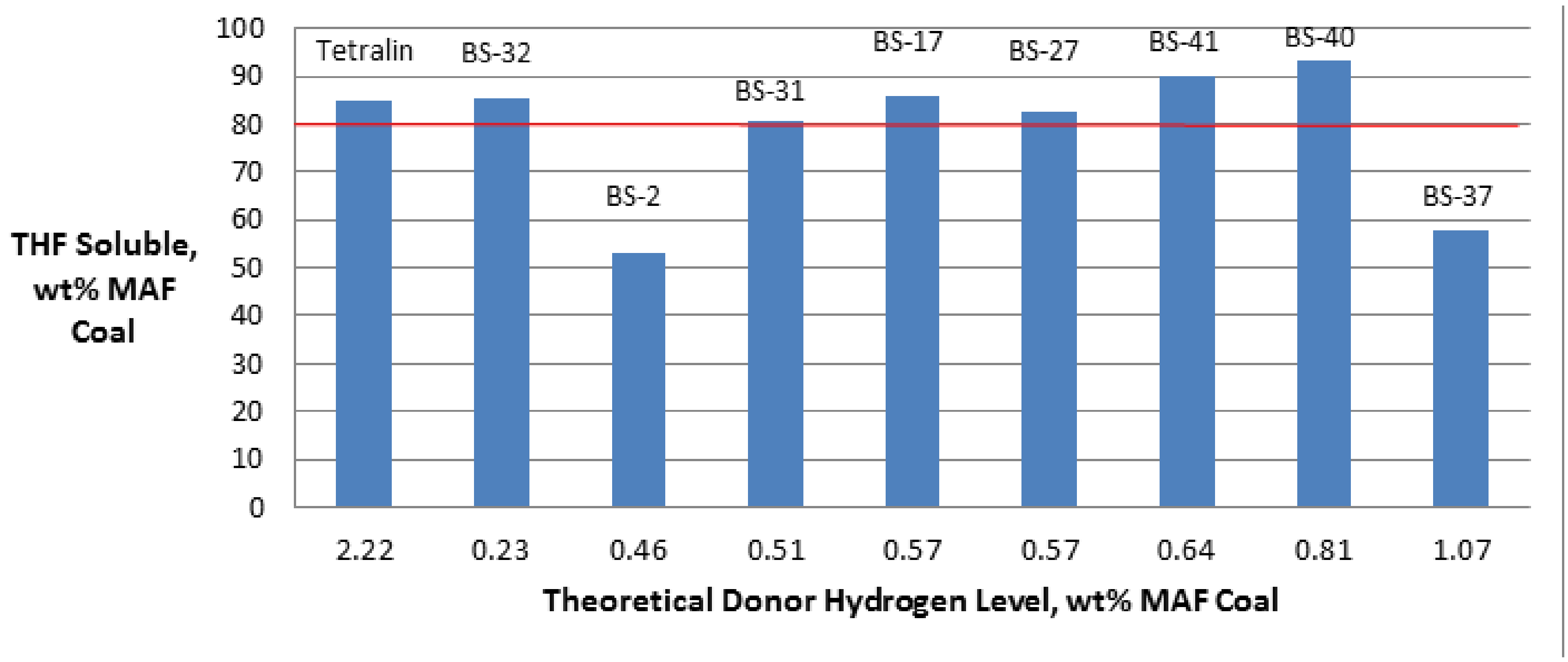
Solvent	Solvent/Coal wt%	Coal Solubilized % MAF Coal
Tetralin	60.2	86.6
Bio-solvent #2 (BS-2)	60.1	53.1
BS-3	60.1	86.7 ✓
BS-9	60.1	85.5 ✓
BS-10	60.0	69.8
BS-14	60.1	56.9
BS-15	60.0	87.9 ✓

✓ *Exceeded 80% solubility target; typical H/C ranged from 0.86 in coal to 1.08 in syncrude*

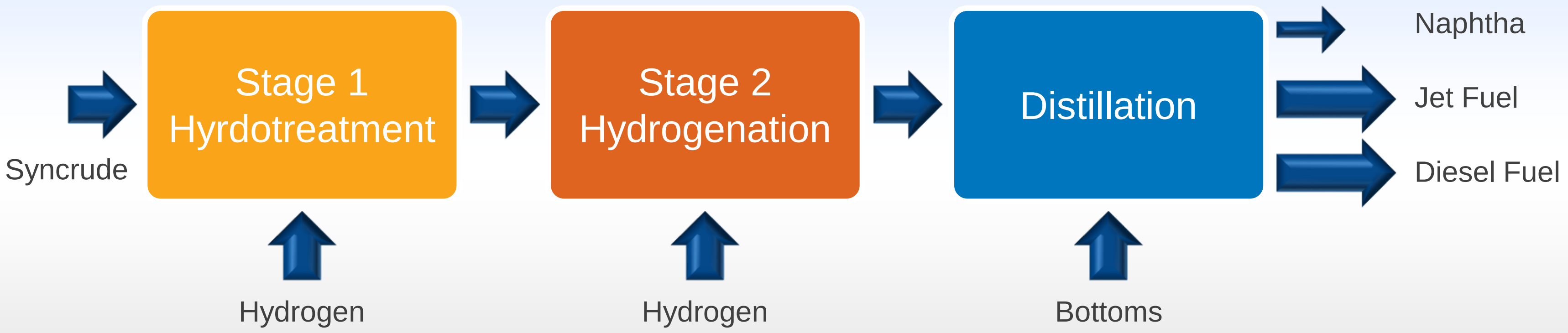
Batch Autoclave Coal Liquefaction Screening Results for Ohio Coal

Biomass-Derived Solvent	Solvent/Coal wt%	Coal Solubilized %MAF Coal THF Soluble	Syncrude Viscosity @ 50°C cp
Tetralin	60.0	84.9	325
BS-12	60.3	88.3	96.6
BS-15	60.4	86.2	9.2
BS-15A	24.0	85.1	20.0
BS-19	60.0	84.5	190
BS-19A	23.9	82.0	50.0
BS-19B	18.0	82.2	31.7
BS-23	60.3	85.2	1632
BS-25	60.2	83.6	1330
BS-27B	24.1	88.2	403
BS-32	11.9	85.5	658
BS-40D	24.0	92.1	639

Solubility Verses Hydrogen Available for Transfer



Bench-Scale Two-Stage Hydrotreatment/Hydrogenation

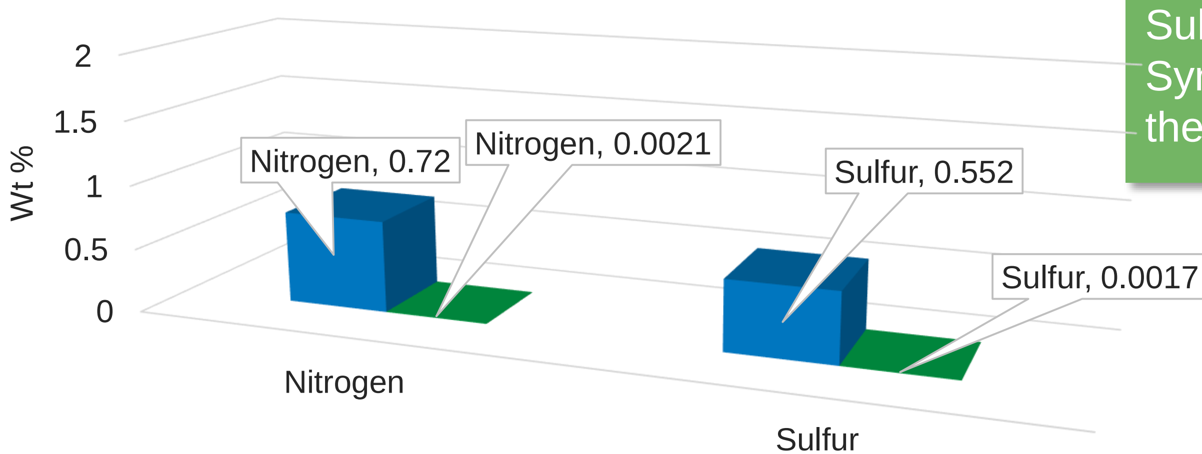


- Stage 1: Heteroatom removal
- Stage 2: Hydrogenation/hydrocracking
- Distillation: Separation into distillate fractions; not performed at bench-scale

Stage 1 Hydrotreatment

- Objective: Reduce N, S, and O content (LHSV = 0.15 hr^{-1})
  - Achieved 99.7 and 99.9% HDN and HDS after Stage 1
  - Residual oxygen reduced to below analysis limit

Sulfur in hydrotreated Syncrude is far below the Jet A 0.3% S limit



	Nitrogen	Sulfur
Before	0.72	0.552
After	0.0021	0.0017

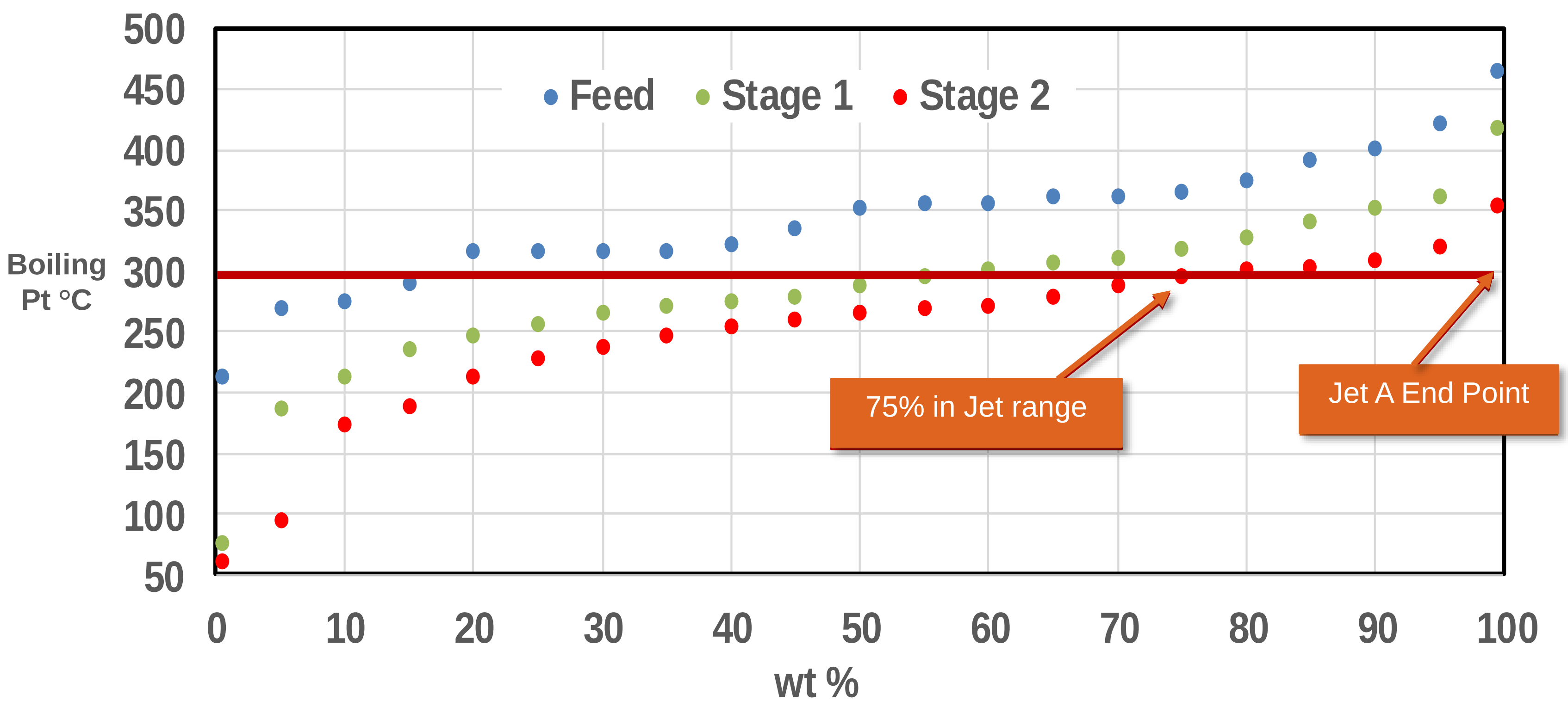
Before After

Battelle
The Business of Innovation

Syncrude Feed and Bench-Scale Upgrading Products

Syncrude	Stage 1a	Stage 1b	Stage 2
1.13 g/mL	380°C, 1250psi	380°C, 1250psi	240°C, 1250 psi
	0.97 g/mL	0.93 g/mL	0.93 g/mL

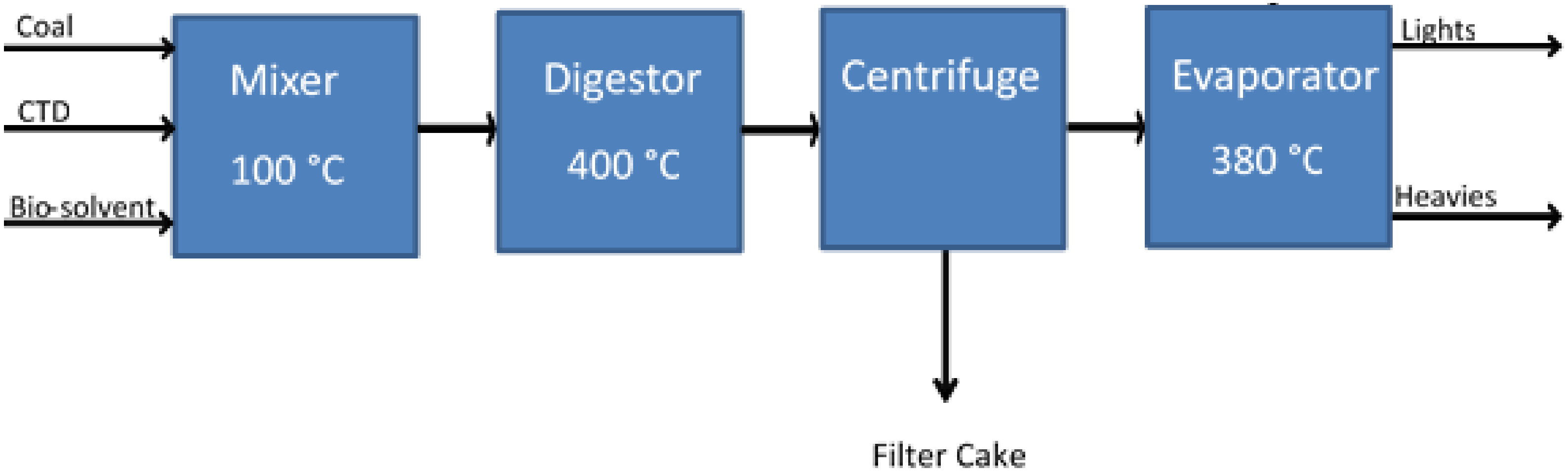
Simulated Distillation of Feed and Bench-Scale Upgrading Products



Liquefaction Scaled Up

- Process scaled up at Quantex 1 ton/day facility (6 tests)
- 400-410°C; 500 psig pressure; 30-minute treatment time
- Product slurry centrifuged; centrate split in a single-stage evaporator at ~380°C

Quantex Continuous Coal Liquefaction System



Pilot-Plant Liquefaction Results

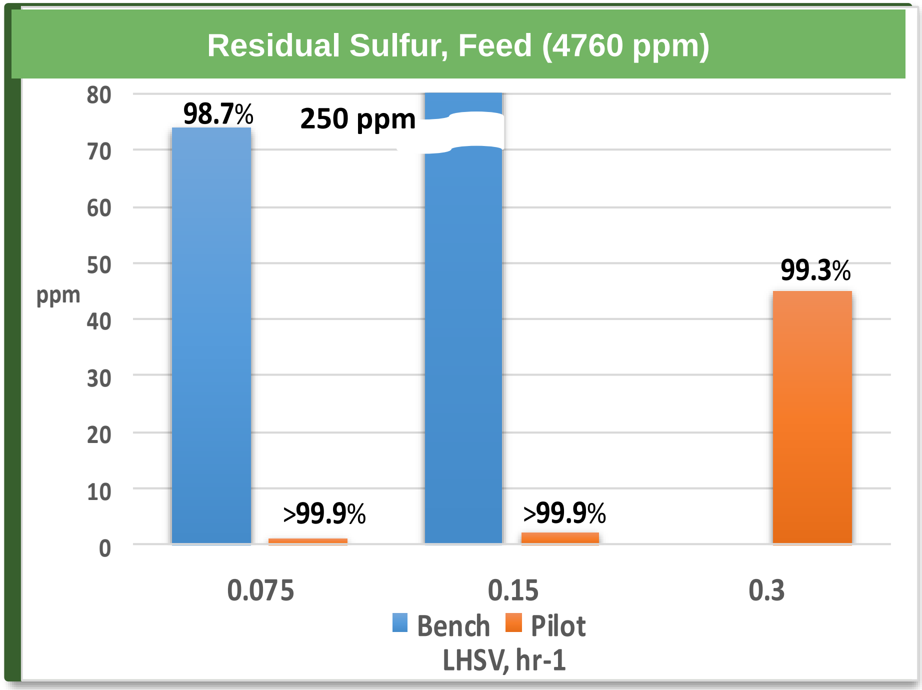
- THF-soluble yield of 75-85 wt.% of MAF coal; somewhat lower than bench test yield values
- The product slurry was easy to centrifuge, yielding over 40 wt% solid in centrifuge cake
- The centrate had a viscosity of ~60 cp at 50°C, compared to ~100-260 cp in corresponding bench test
  - This is considerably lower than the 325 cp viscosity for bench test with twice as much tetralin
  - The ash content was reduced to <0.07 wt.%
- Two batches of syncrude were distilled to 500°C cut for scale-up of upgrading process
  - ~80 wt.% was <500°C boiling point

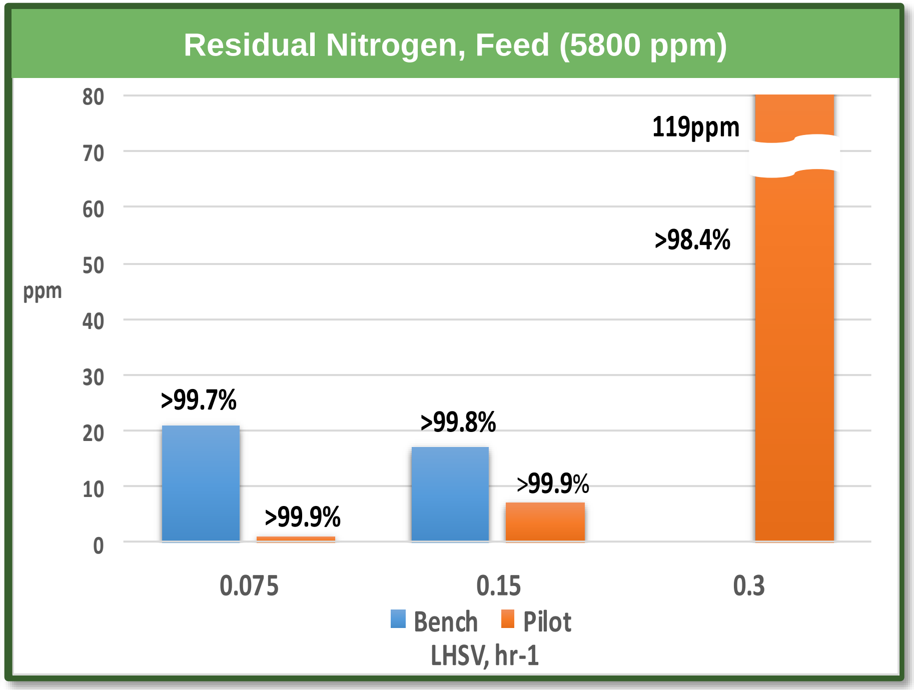
Scale-Up of Hydrotreating/Hydrogenation of Syncrude

- Scaled-up at Intertek's 20 L/day facility
- Two 150 hr. continuous runs using 2-stage catalytic upgrading

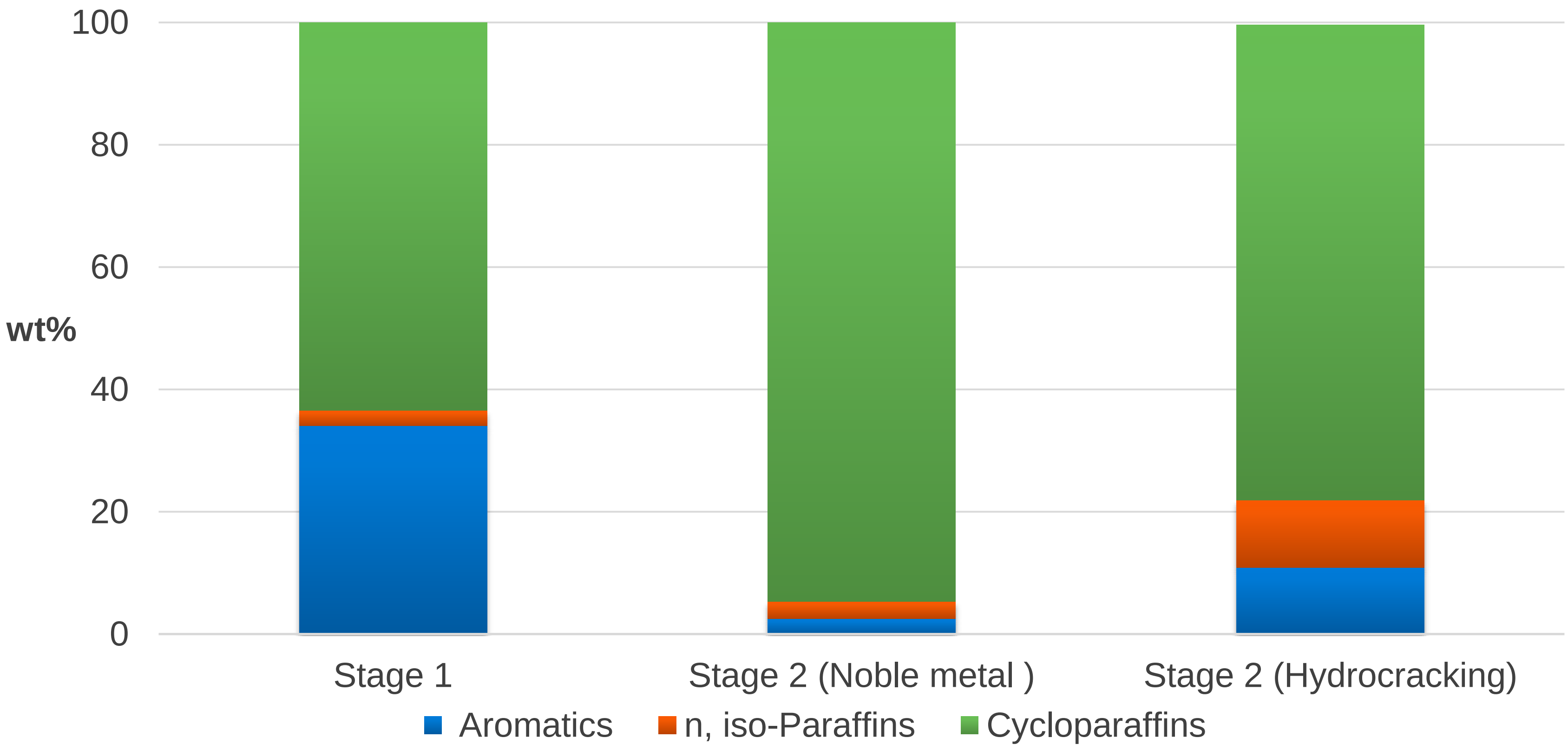
Intertek's 20 L/day Continuous Syncrude Hydrotreatment System

Residual "S" and "N" at Different LHSV in Lab & Pilot Scale Reactors





Stage1 & 2 Composition by GCxGC-MS

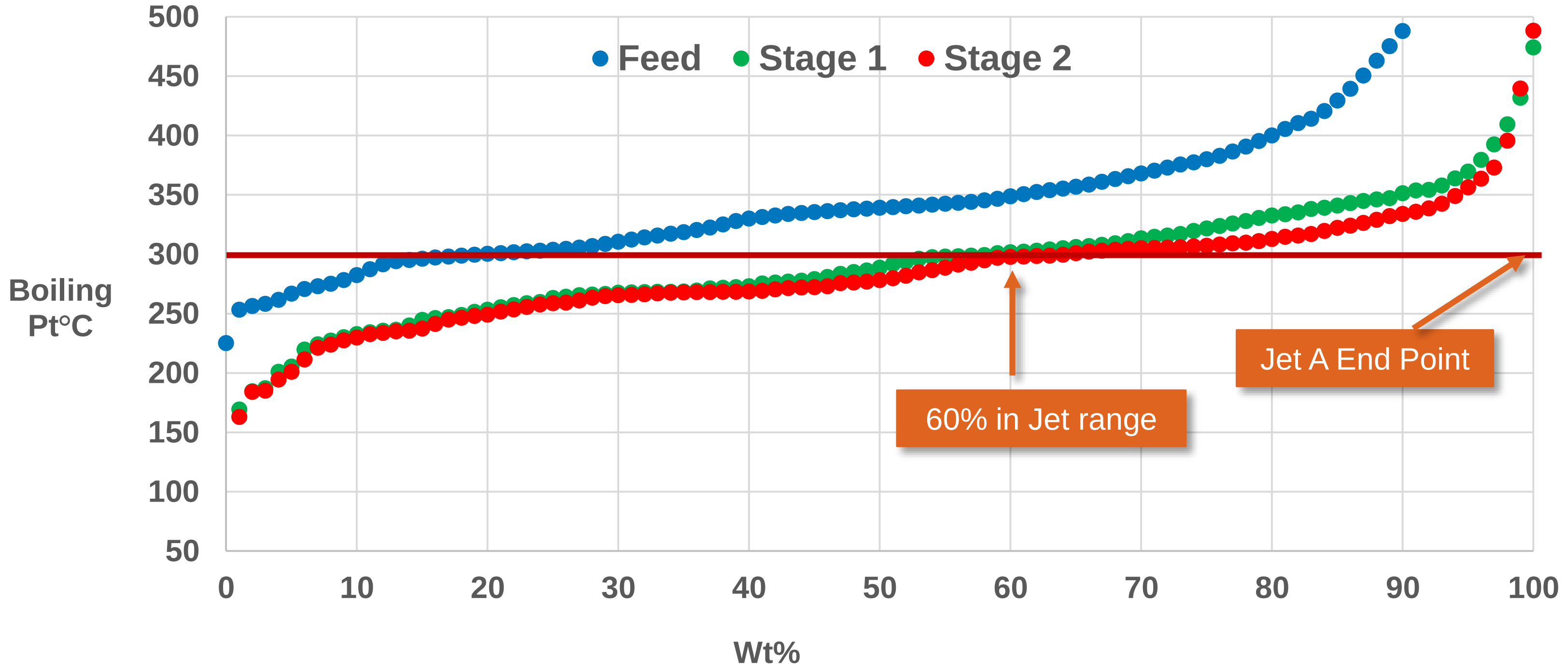


Syncrude Feed and Pilot-Scale Upgrading Products

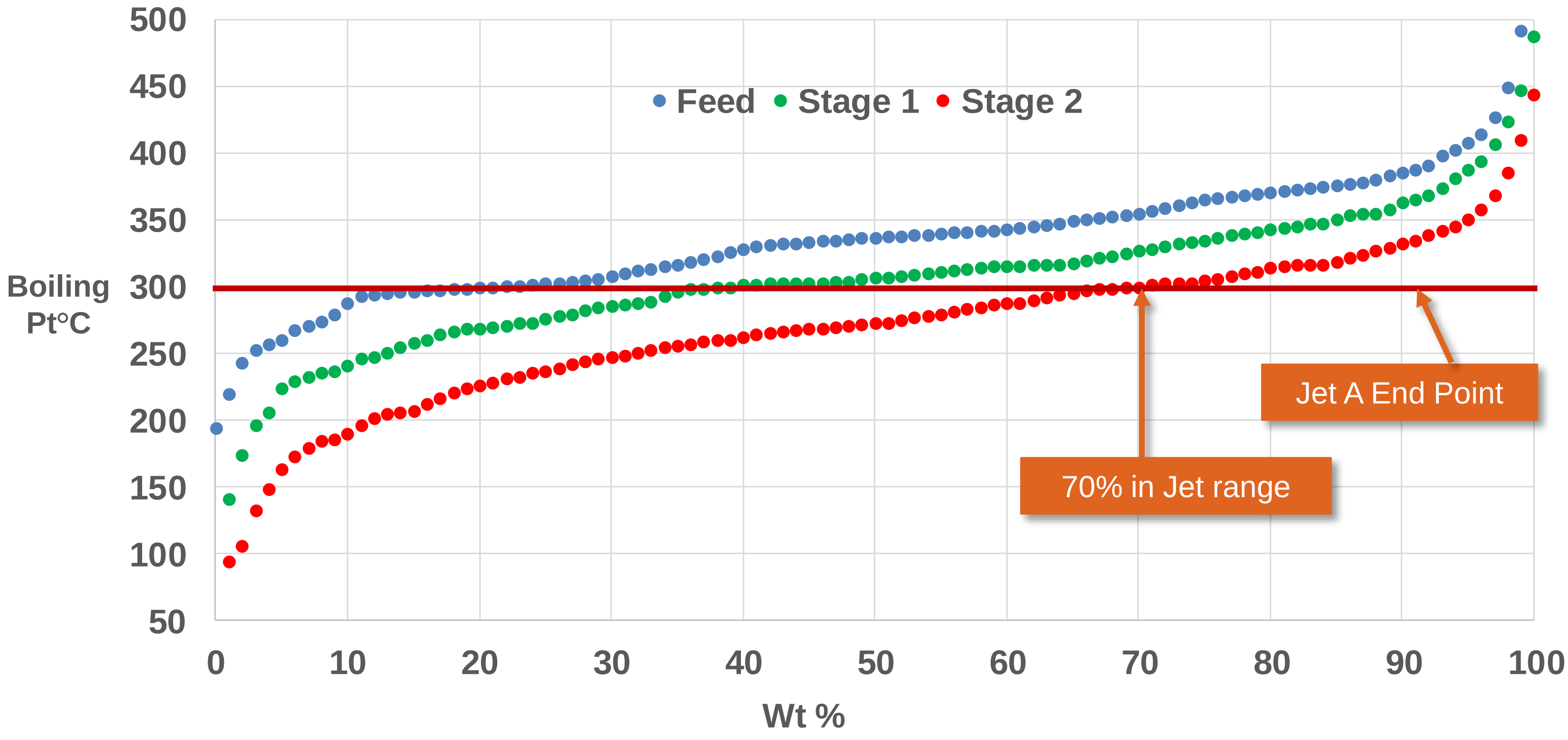
Syncrude	Stage 1	Stage 2	Jet fuel	Diesel	Fraction
1.13 g/mL	380°C, 1250psi 0.97 g/mL	240°C, 1250psi 0.93 g/mL	0.89 g/mL	0.91 g/mL	>300°C 0.91 g/mL

Battelle
The Business of Innovation

Simulated Distillation of Feed and Pilot-Scale Upgrading Products (Run 1)



Simulated Distillation of Feed and Pilot-Scale Upgrading Products (Run 2)



Battelle
The Business of Innovation

Biomass-Derived CTL Process Benefits

- Blend of biomass-derived solvents to
  - Provide effective hydrogen transfer
  - Solubilize products of bond cleavage in coal
  - Improve slurry transport
  - Provide high H/C precursors for jet fuel and diesel fuel
- Lower Capital and Operating Costs
  - Mild operating conditions for liquefaction
  - Order of magnitude smaller liquefaction plants (<1000 tons/day)
  - No H_2 required for coal liquefaction, eliminating need for on-site generation
  - Approximately 30% increase in H/C ratio during liquefaction without using H_2
  - Reduced complexity due to once-through solvent use and no catalyst required for liquefaction
  - Carbon Capture & Storage (CCS) avoided at liquefaction plant and much reduced at syncrude upgrading site due to reduced H_2 required

Conclusions

- The Battelle CTL process employing once-through use of biomass-derived coal solvent is a unique approach
  - Elimination of H_2 and regeneration of solvent for liquefaction greatly simplifies the process
  - Use of biomass-derived solvents provides a synergistic effect during liquefaction, which also reduces the GHG footprint
- Various bituminous and subbituminous coals were successfully converted to syncrude using one of many identified biomass-derived solvents without the use of H_2 or catalyst
- A 2-stage, catalytic hydrotreatment/hydrogenation can convert 60-70% of the CTL syncrude to jet fuel and ~100% to diesel fuel
  - More than 99.9% of nitrogen and sulfur is removed, and oxygen is reduced below detection limit
- Both coal liquefaction and syncrude hydrotreating/hydrogenation sub-systems have been successfully scaled from Technology Readiness Level (TRL) 2-3 to TRL 5 (1 ton/day coal liquefaction and 20 L/day upgrading)

Acknowledgements

- Funding Agencies: U.S. DOE/NETL (Jason Lewis, Technical Lead) and State of Ohio (OCDO/ODSA; Gregory Payne, Technical Lead)
- Battelle: Daniel B. Garbark; Rachid Taha; Grady Marcum
- UDRI: John J. Graham; Matt DeWitt
- PennState: Caroline B. Clifford; Ron Wincek
- Quantex: Elliott B. Kennel; Gilbert Chalifoux
- ARA: Ed Coppola; Sanjay Nana
- Intertek: John Brophy; Chad Chrostowski

U.S. DOE/NETL

For More Information Contact:
Dr. Satya P. Chauhan, 614-424-4812, Chauhan@Battelle.org

Battelle

The Business of Innovation

800.201.2011 | solutions@battelle.org | www.battelle.org