2014 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting

Hydrogen Generation for Refineries

DOE Phase II SBIR

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TDA Research Inc.

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Project: PD104

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Project Overview

- Timeline
  - Project start date: 8/14/09
  - Project end date: 8/14/14
  - Percent complete: 90
  - P.I. : Dr. Girish Srinivas
- Budget
  - DOE share: $850,000
  - Cost Share: ~$450,000 (ongoing management time for commercialization efforts)
  - Funding received in FY13: $0
  - Total funding planned for FY14: $0
  - Spent as of 3/31/14
    - $656,145 (Ph II)
    - $100,000 (Ph I)
    - $756,145 (total)
- Barriers
  - Demonstration of continuous operation with circulating fluidized bed reactor system
  - Engineering scale up
  - Pilot scale demonstration
- Partners
  - Matheson Tri-Gas

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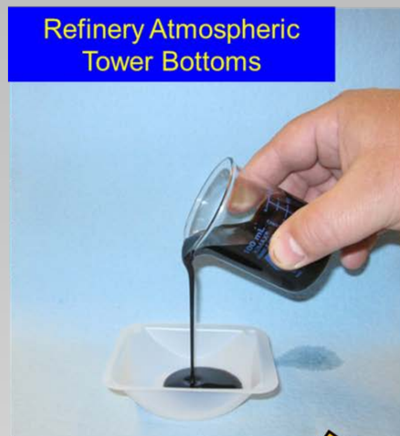
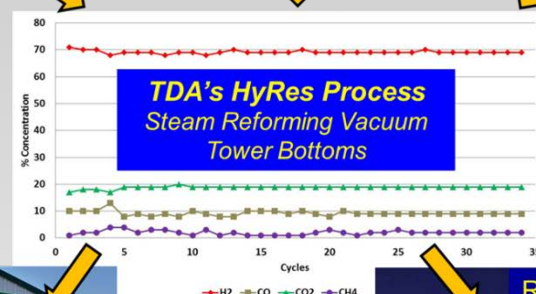
Hydrogen from Heavy, Renewable and Waste Oils – TDA *HyRes* Process





Steam/carbon = 5
70% H_2
20% CO_2
10% CO
~2% CH_4

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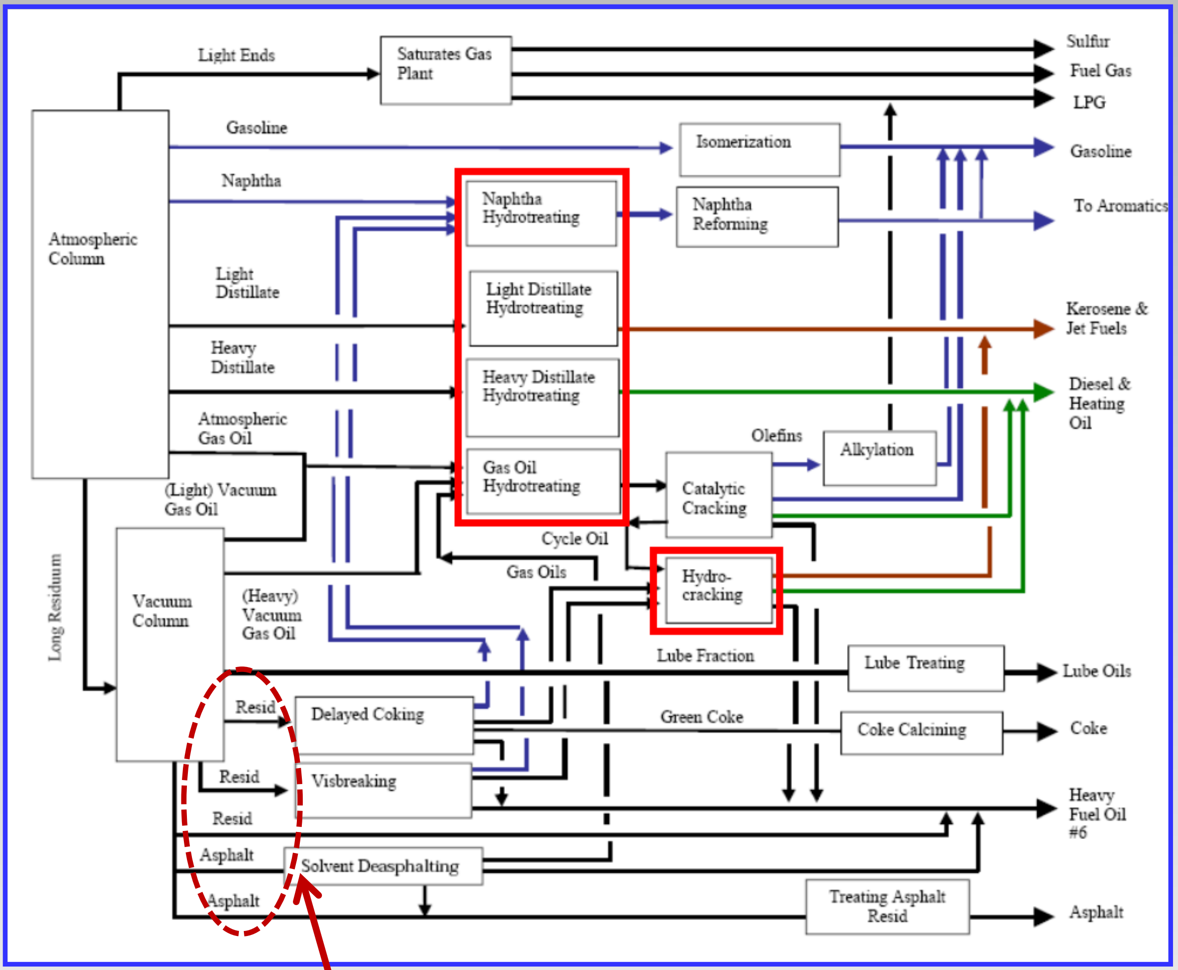
Relevance: Processing Heavy Crudes



- Refineries are processing increasingly sour, heavy crudes
- Catalytic reforming of paraffins to aromatics and hydrogen cannot supply enough H_2 for hydrotreating
- Typical 100,000 bbl/day hydrocracking refinery will be short 23 *million* ft^3/day of H_2

- TDA *HyRes* process can generate additional H_2 from residuum

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H_2 Required for Heavy Crudes

Residuum type	°API	Sulfur (wt%)	Carbon residue, Conradson (wt%)	Nitrogen (wt%)	Hydrogen (scf/bbl)
Venezuela, atmospheric	15.3–17.2	2.1–2.2	9.9–10.4	—	425–730
Venezuela, vacuum	4.5–7.5	2.9–3.2	20.5–21.4	—	825–950
Boscan (whole crude)	10.4	5.6	—	0.52	1100
Tia Juana, vacuum	7.8	2.5	21.4	0.52	490–770
Bachaquero, vacuum	5.8	3.7	23.1	0.56	1080–1260
West Texas, atmospheric	17.7–17.9	2.2–2.5	8.4	—	520–670
West Texas, vacuum	10.0–13.8	2.3–3.2	12.2–14.8	—	675–1200
Khafji, atmospheric	15.1–15.7	4.0–4.1	11.0–12.2	—	725–800
Khafji, vacuum	5.0	5.4	21.0	—	1000–1100
Arabian light, vacuum	8.5	3.8	—	—	435–1180
Kuwait, atmospheric	15.7–17.2	3.7–4.0	8.6–9.5	0.20–0.23	470–815
Kuwait, vacuum	5.5–8.0	5.1–5.5	16.0	—	290–1200

- Processing heavy crudes requires large quantities of hydrogen
- The lower the API gravity, the heavier the crude
- Heavy crudes contains high sulfur and high molecular weight hydrocarbons

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Example: H_2 Shortage

(Basis: 100,000 bbl/day crude feed)

Process Unit	Throughput 1000 Barrels per Day (MBPD)	Hydrogen Usage Million Standard Cubic Feet per Day (MMSCFD)
Atmospheric Crude Distillation	100	0
Vacuum Distillation	40	0
Light Ends; Gasoline Isomerization	10	0
Naphtha Hydrotreater (Atmospheric and Delayed Coker naphtha)	20	2 (consumed)
Catalytic Reforming	22	22 (supplied)
Light Distillate to Hydrotreating for Kerosene/Jet Fuel)	10	2 (consumed)
Heavy Distillate & Cycle Oil to Hydrotreating for Diesel/Heating Oil	10	3 (consumed)
Atmospheric Gas Oil to Gas Oil Hydrotreating	10	5 (consumed)
Light Vacuum Gas Oil to Gas Oil Hydrotreating	12	6 (consumed)
Heavy Vacuum Gas Oil to Gas Oil Hydrotreating	13	7 (consumed)
Delayed Coker Gas Oil to Gas Oil Hydrotreating	7	4 (consumed)
Cycle Oil to Hydrocracking	8	16 (consumed)
Catalytic Cracking	31	0
Resid to Delayed Coking	15	0
Resid to Resid Hydroprocessing	0	0
Additional Hydrogen Supplied	H_2 shortage	23 (supplied)

Source: AIChE petroleum refining CD

- A 100,000 bbl/day refinery that has hydrocracking is typically *short* about 23 million standard ft^3/day of H_2
- TDA process can be used to generate the extra hydrogen from bottom of the barrel vacuum residuum

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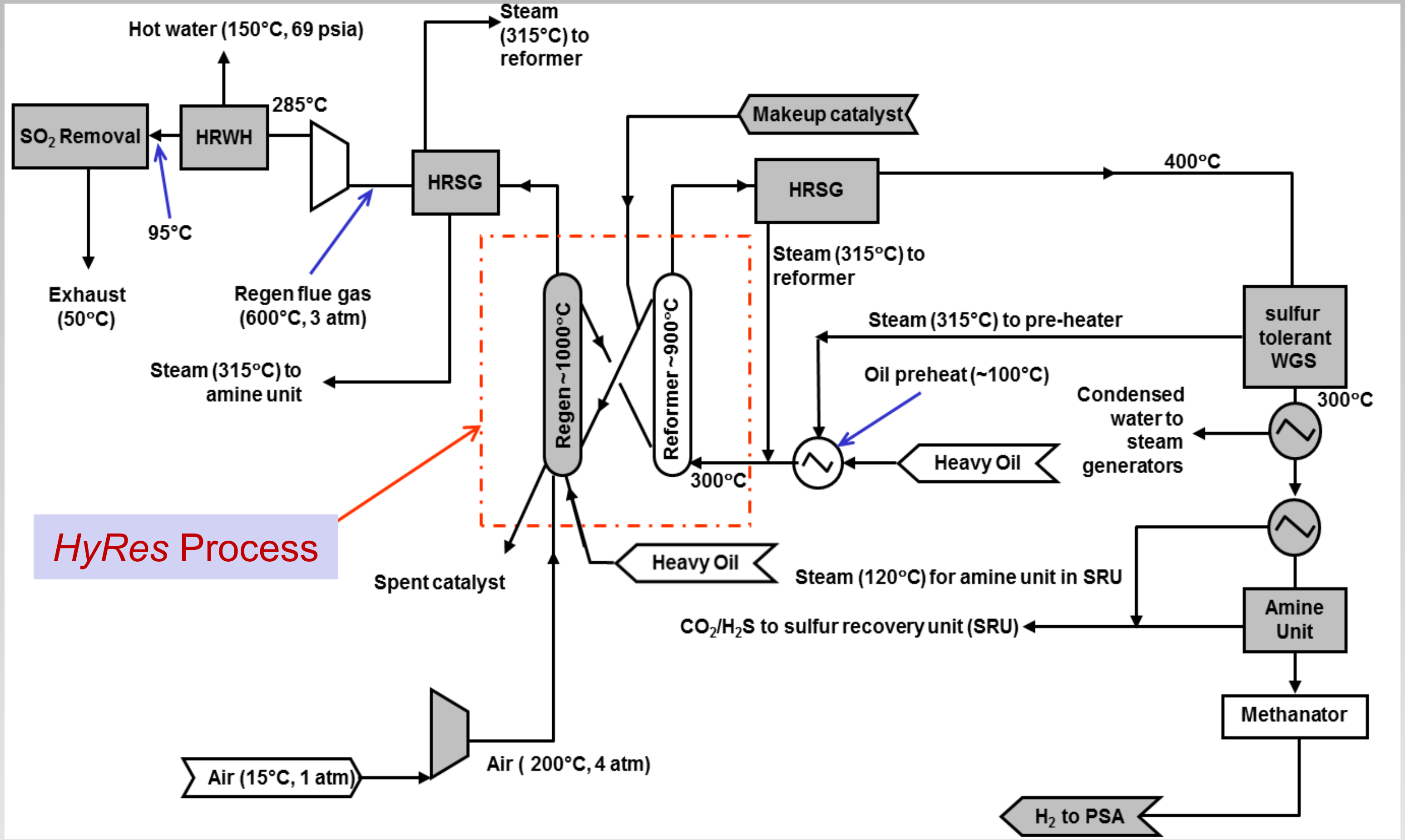
Hydrogen Prices

	Typical volume (MMSCFD)	Typical 1998 Price LOW ($/1000 SCF)	Typical 1998 Price HIGH ($/1000 SCF)	2013 Price LOW ($/1000 SCF) 3% inflation	2013 Price HIGH ($/1000 SCF) 3% inflation
Pipeline	2 to 50	$1.25	$2.25	$1.95	$3.51
Large on-site SMR	10 to 100	$1.50	$2.75	$2.34	$4.28
Small on-site SMR	0.5 to 10	$3.00	$6.00	$4.67	$9.35
Delivered Liq H2	0.01 to 1	$6.00	$18.00	$9.35	$28.04
Delivered gas H2	0.001 to 0.1	$12.00	$15.00	$18.70	$23.37

Target market

- TDA's process for residuum steam reforming to generate hydrogen a.k.a. *HyRes*
    - Cost of hydrogen approximately $4/1000 SCF
    - Lower capital cost than small steam methane reforming plant
    - Suitable for smaller refineries (~50,000 bbl/day)
    - Less expensive alternative for expanding H_2 capacity

Approach: Generating H_2 from Resid

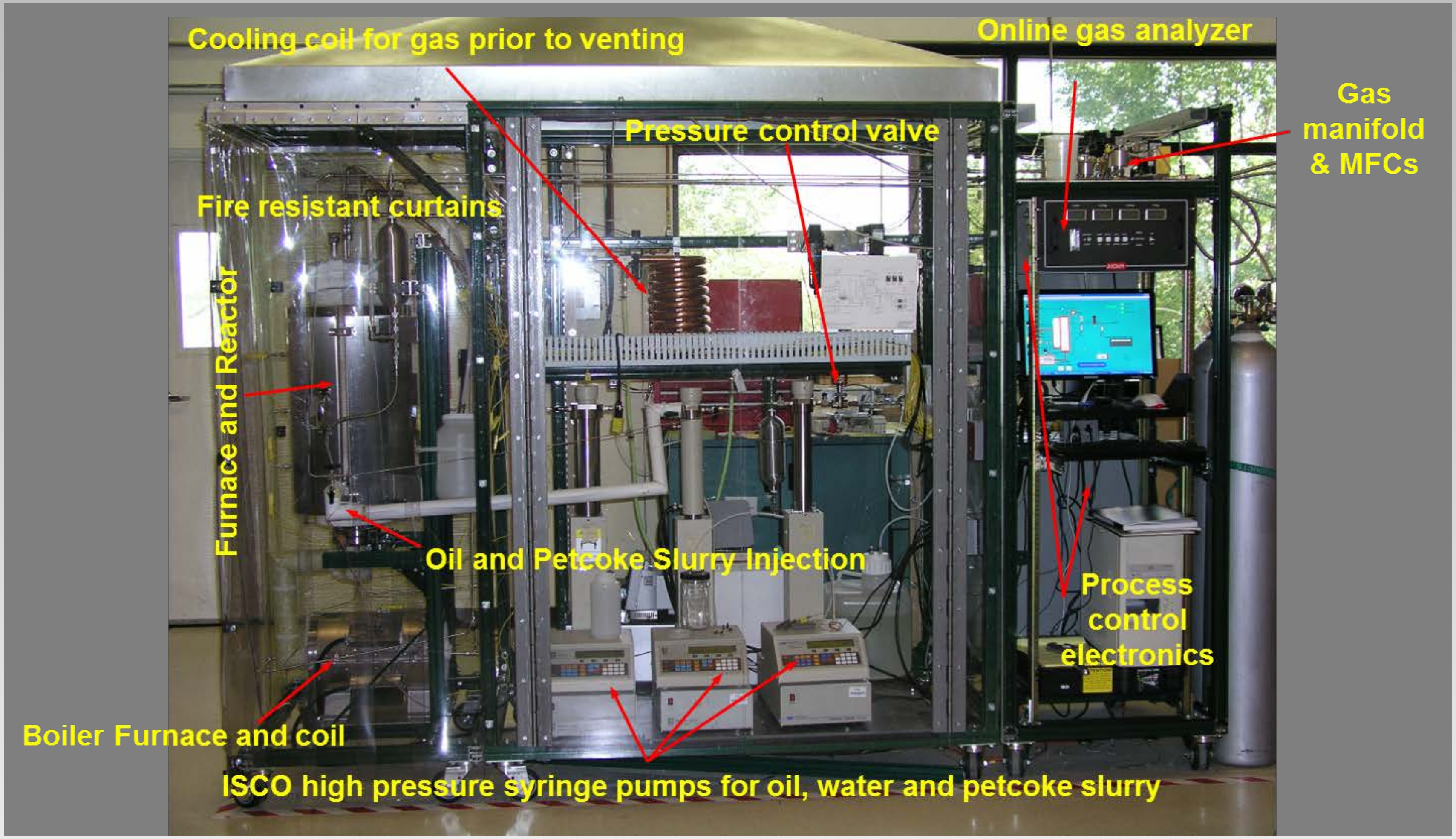


- Diagram shows a complete, _*stand alone*_ hydrogen plant
- Unit operations already in the refinery can be used

Catalyst

- Catalyst is cycled between reforming and regeneration with air
- Same charge of catalyst used been tested in the laboratory over the course of 2.5 years with NO deactivation
- Feeds processed include:
  - Atmospheric residuum (aka: atmospheric tower bottoms (ATB), long residuum)
  - Vacuum residuum (aka: vacuum tower bottoms (VTB), vacuum resid)
  - Dilbit (tar sand bitumen diluted with 30% condensate)
  - Biomass fast pyrolysis oil (whole raw oil)
  - Norpar 12 (C_{11}/C_{12} paraffinic solvent – used as naphtha simulant)

Laboratory Scale Test Apparatus



Accomplishments

- Steam reforming of atmospheric tower bottoms (ATB)
  - ATB is the stream from atmospheric distillation of crude oil that boils at T > 650^{o}F
  - ATB is normally sent to vacuum distillation (or sometimes the fluid catalytic cracker)
  - No catalyst deactivation
- Steam reforming of vacuum tower bottoms (VTB)
  - VTB is the stream from vacuum distillation of ATB that would boil at T > 1050^{o}F at atmospheric pressure
    - 1050°F is an extrapolated boiling point because in reality VTB would pyrolyzes before boiling at atmospheric pressure)
  - No catalyst deactivation
- *Same catalyst sample used in all the tests for more than 2.5 years*

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Characteristics of ATB

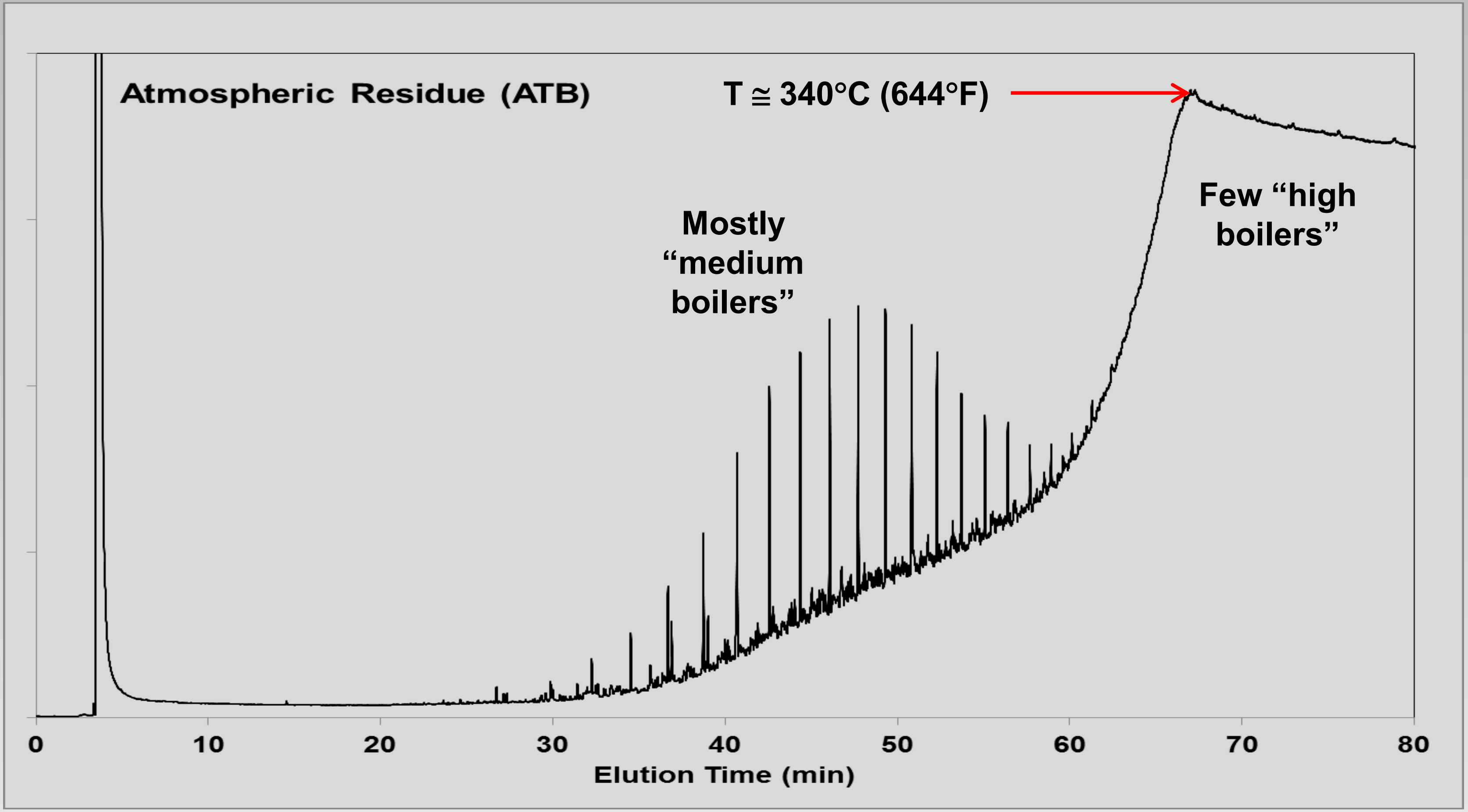
H:C ≅ 1.68

Huffmann elemental analysis				1.68	H/C
		Basis: 100 grams Oil			
		#1	#2	Average	moles
Carbon	wt%	86.58	86.69	86.64	7.22
Hydrogen	wt%	12.04	12.25	12.15	12.15
Nitrogen	wt%	0.11	0.13	0.12	0.01
Oxygen	wt%	0.58	0.52	0.55	0.03
Sulfur	wt%	0.80	0.81	0.81	0.03

- Elemental analysis primarily done to determine sulfur content of the feed
- Chemistry of ATB, VTB etc. is more important than H:C content and is reflected in API gravity and boiling point, however…
- Only the H:C ratio affects *HyRes* (and only slightly)

Room Temperature Viscosity

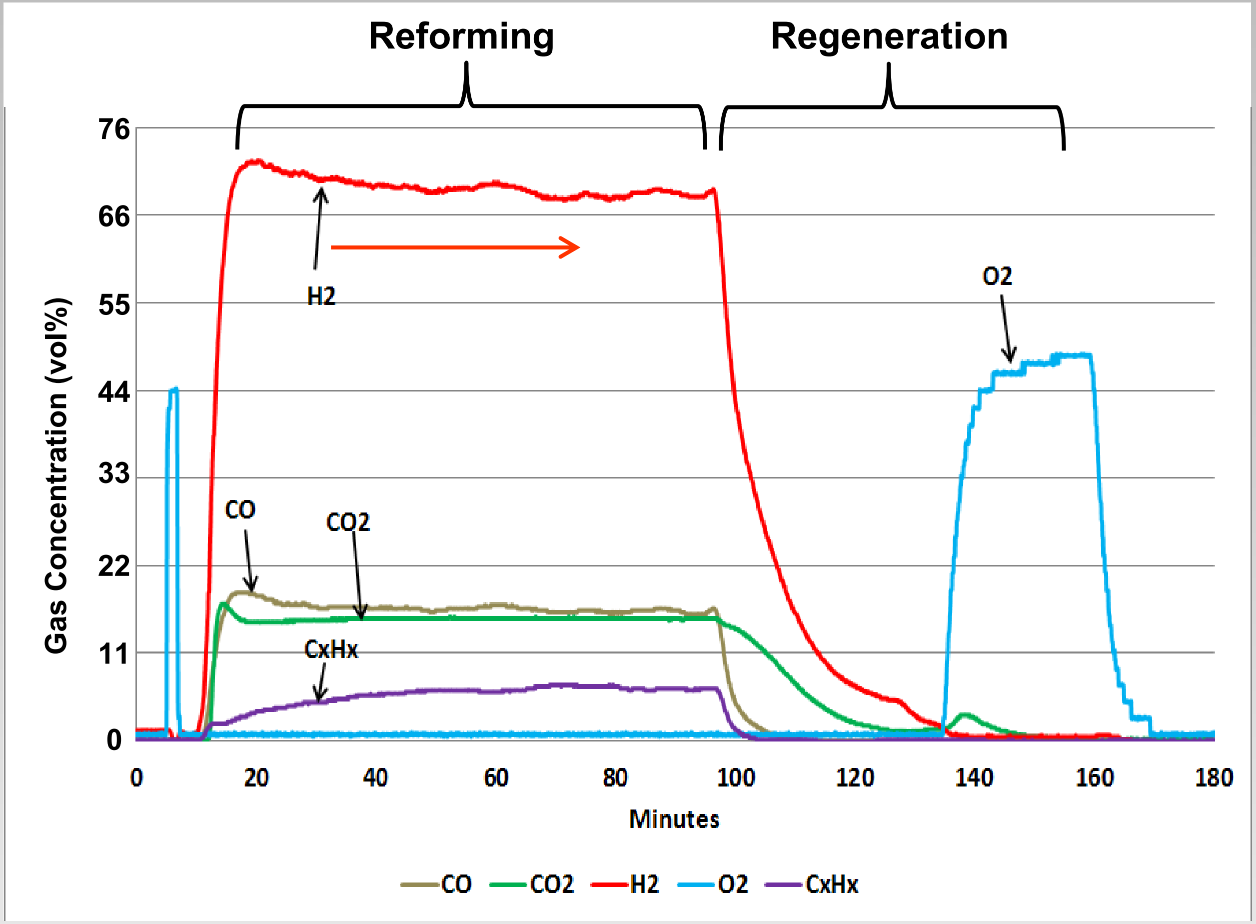
GC Analysis of ATB



- A few high boilers (very highest boilers cannot elute from GC column)
- ATB is liquid at room temperature

Single Cycle Shown for ATB

Steam/Carbon = 3



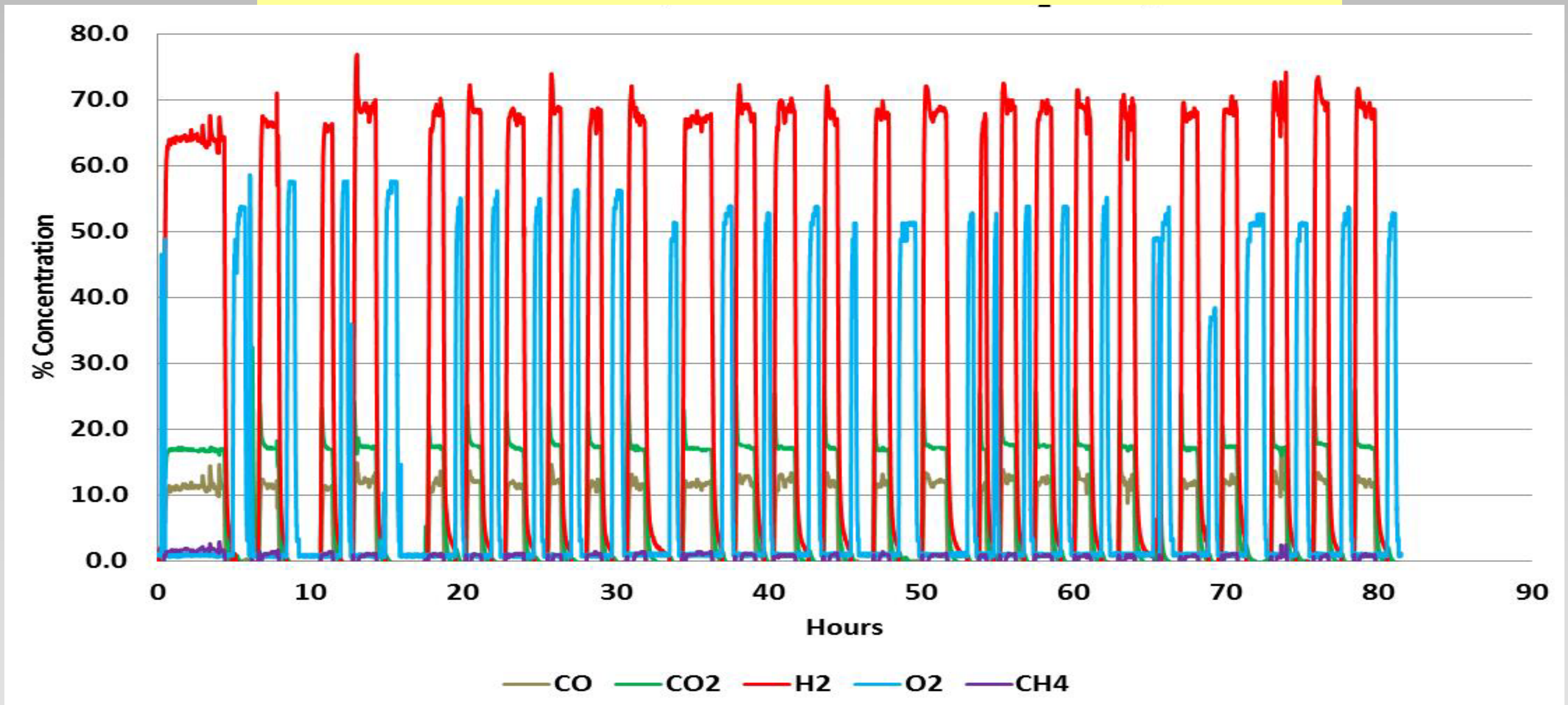
- ATB reforming
- Steam/carbon = 3
- Syngas generated during reforming
  - 70% H_2
  - 20% CO
- Syngas composition agrees with thermodynamic equilibrium predictions (dry basis)
- Purge with N_2*
- Regenerate with air (stop when O_2 levels off)
- Purge with N_2*
- Start another reforming cycle

*N_2 purges used for fire prevention because experiments are done in a single reactor vessel

Multiple Reforming Cycles: ATB

Steam/Carbon = 5

Constant H_2 production (red) during reforming step indicates no catalyst deactivation

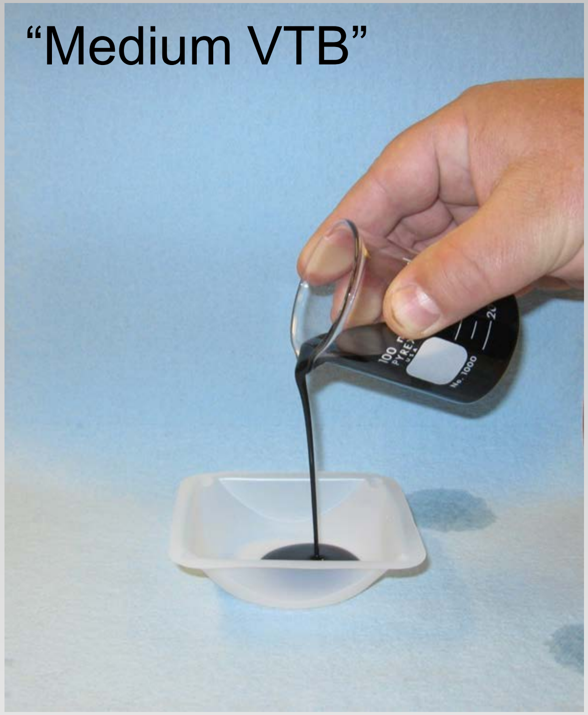


- ATB reforming at T = 865°C (1589°F) & P = 50 psig
- Hydrogen ~70 vol%
- No catalyst deactivation in 83 hours (26 cycles)

Vacuum Tower Bottoms (VTB)

- Two sources of VTB were tested
  - Liquid at 50°C "medium"
  - Not liquid until T = 150°C "extra heavy"

Viscosity at 50°C
(solid at room temp)



H:C ≅ 1.71

Huffmann elemental analysis				1.71	C/H ratio
		Basis: 100 grams Oil			
		#1	#2	Average	Moles
Carbon	wt%	86.99	87.18	87.09	7.26
Hydrogen	wt%	12.37	12.46	12.42	12.42
Nitrogen	wt%	0.21	0.20	0.21	0.01
Oxygen	wt%	0.30	0.26	0.28	0.02
Sulfur	wt%	0.27	0.27	0.27	0.01

- Elemental analysis primarily done to determine sulfur content

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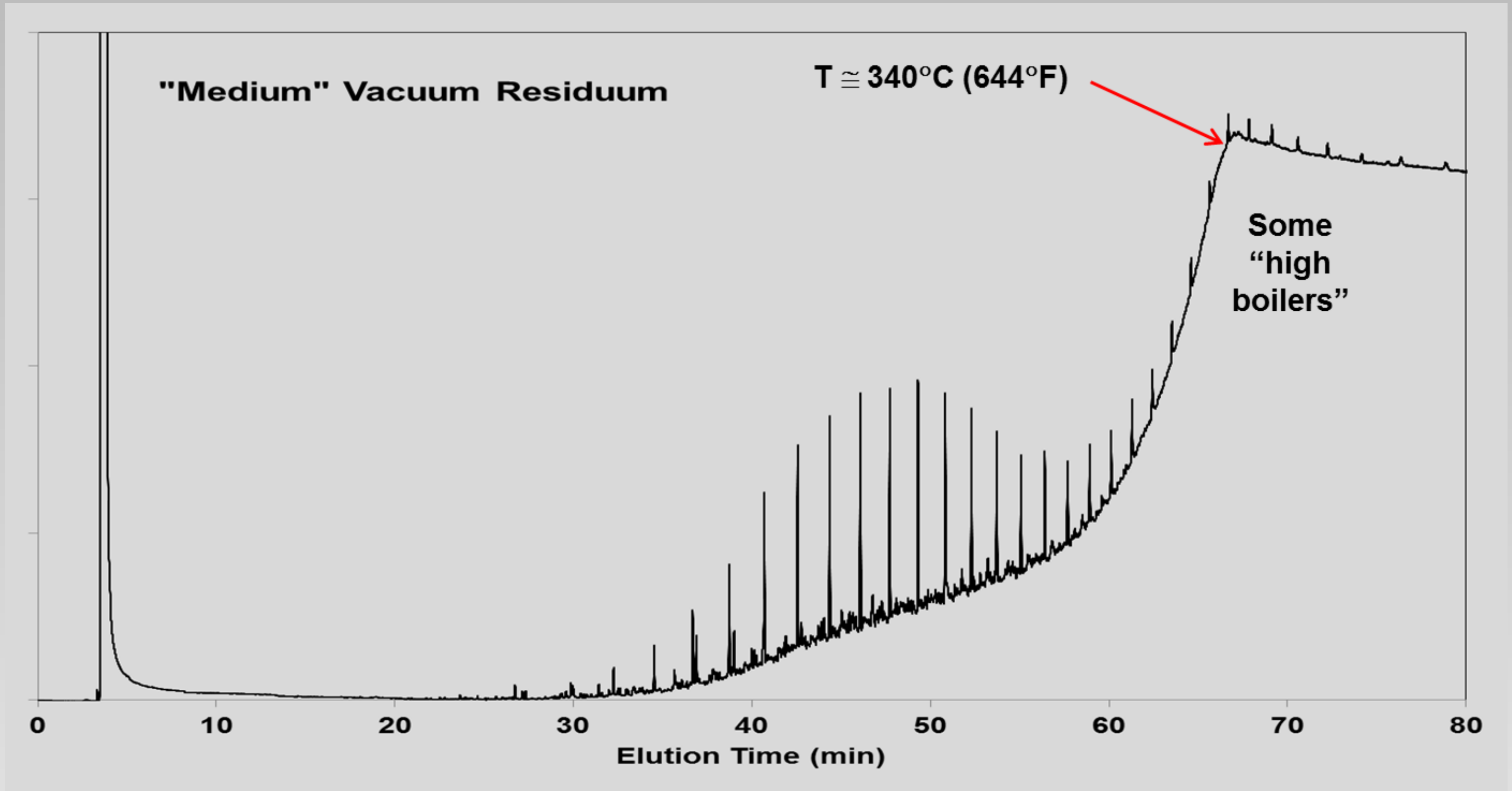
GC Analysis of “Medium VTB”



- Some “high boilers”
- Solid at room temperature
- Heat to 50°F to feed to lab-scale reactor as a liquid

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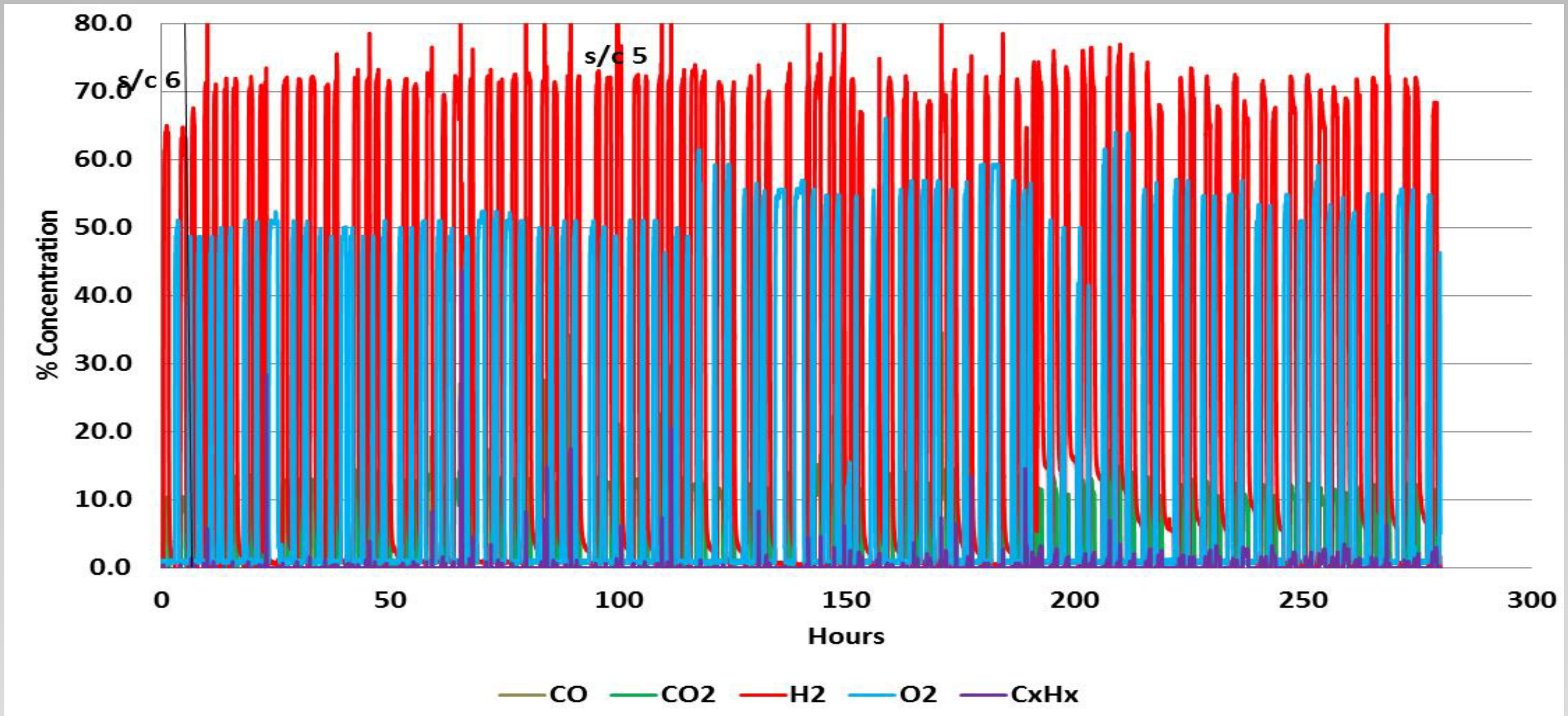
Reforming Cycles: "Medium VTB"

Steam/Carbon = 5



- "Medium VTB" reforming at T = 865°C (1589°F) & P = 50 psig
- Steam/carbon = 5
- Hydrogen ~70 vol%
- H_2 production rate (red) is *constant during each reforming step indicating there is no catalyst deactivation* in 280 hours (96 cycles)

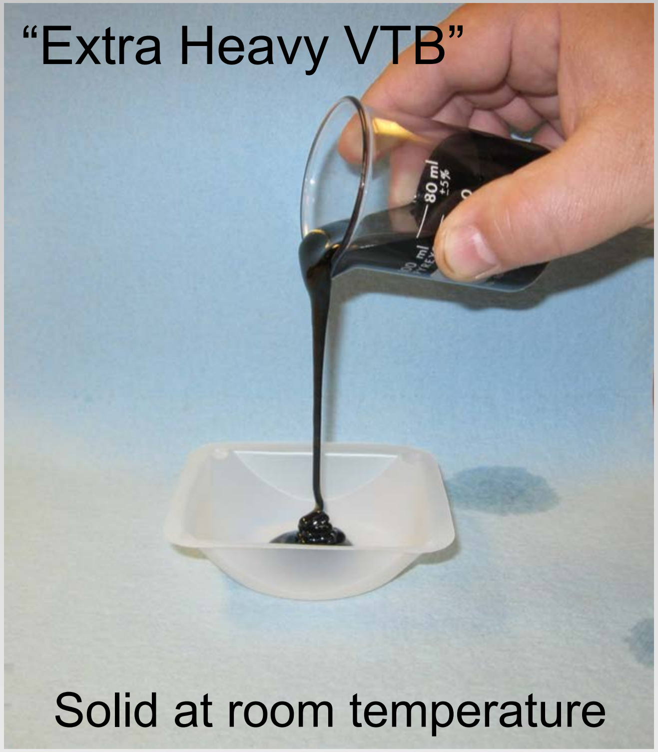
"Extra Heavy" Vacuum Residuum (VTB)

H:C ≅ 1.53

Huffman Elemental Analysis		1.53	H/C
	#1	#2	moles
Carbon (wt%)	85.99	86.09	7.17
Hydrogen (wt%)	10.89	10.98	10.94
Nitrogen (wt%)	0.42	0.43	0.03
Oxygen (wt%)	0.49	0.52	0.03
Sulfur (wt%)	2.02	2.02	0.06

- Slightly lower H:C than ATB
- Elemental analysis primarily done to determine sulfur content
- 2.5X as much sulfur as ATB
- Had to cut with 20 wt% xylene because we cannot operate our pump at 150°C which would be needed to reduce viscosity enough to feed whole oil to test reactor

20% xylene added to make fluid; heated to 50°C to feed to reactor



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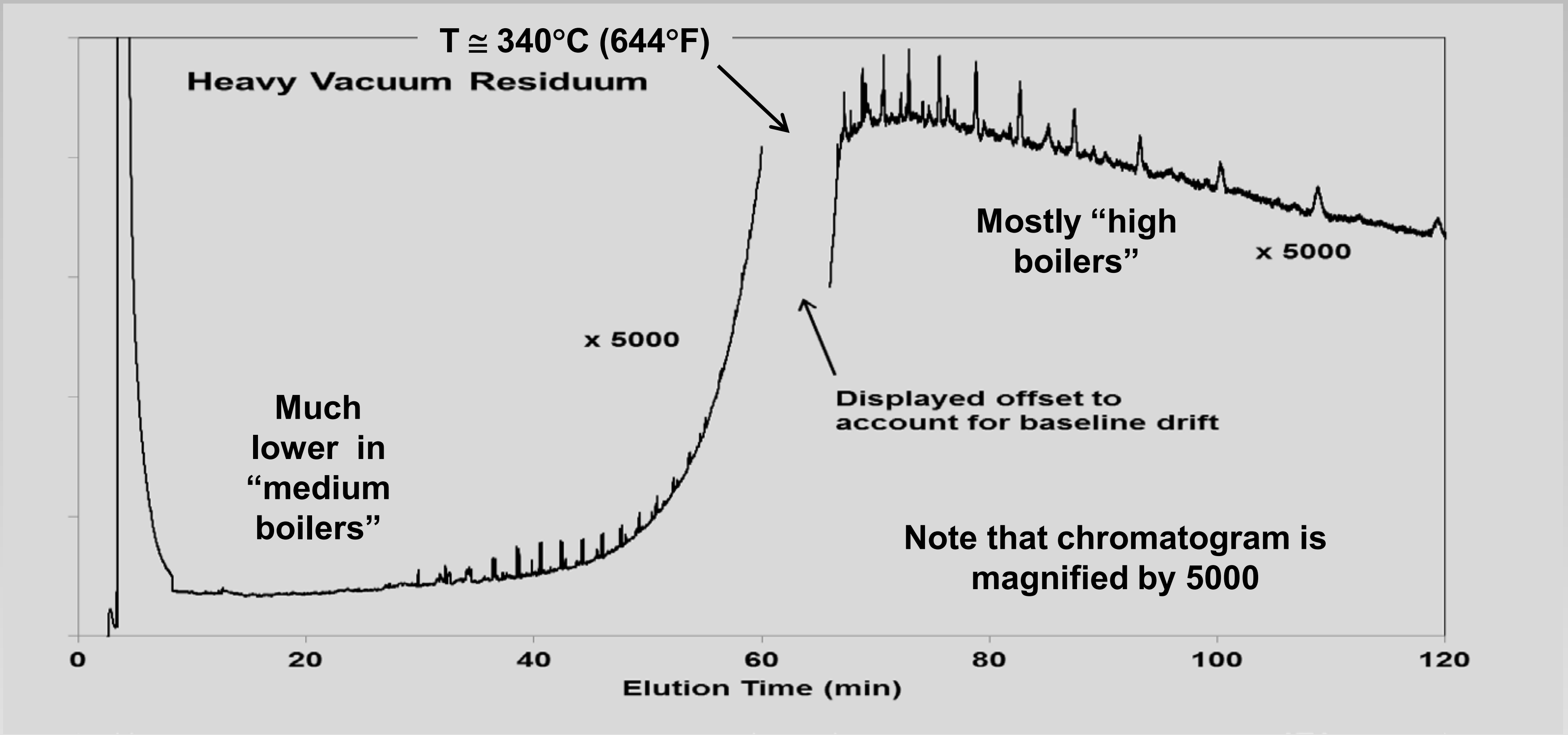
GC Analysis of “Extra Heavy VTB”



- Largely “high boilers” (however, most of sample cannot elute from column)
- Solid at room temperature
- Had to cut with 20% xylene to be able to feed to the reactor (cannot maintain 150°C in the heat high pressure feed pump)

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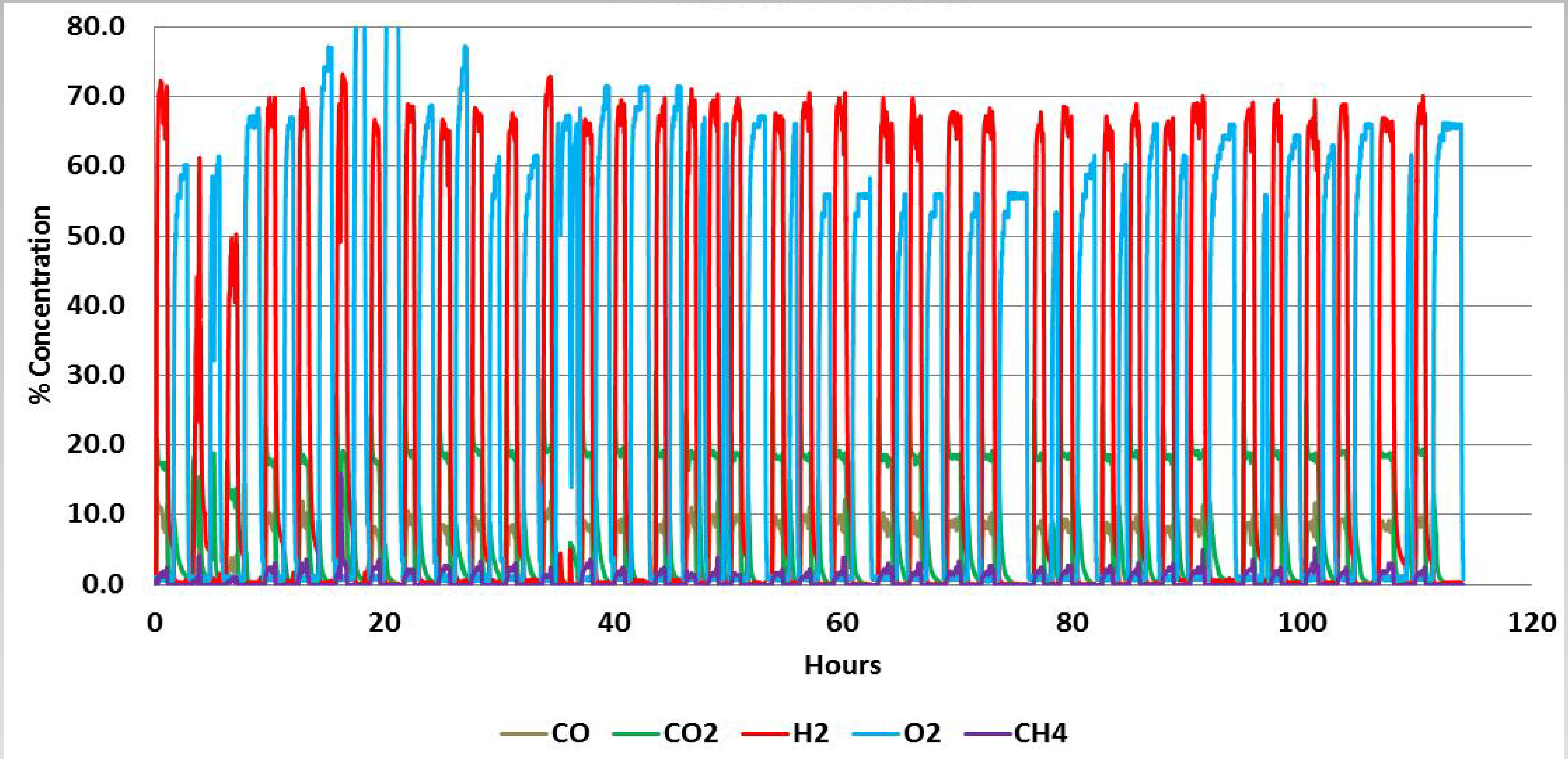
Reforming Cycles: "Extra Heavy VTB"

Steam/Carbon = 5



- Hydrogen ~70 vol%
- H_2 production rate (red) is constant during each reforming step indicating there is no catalyst deactivation in 115 hours (37 cycles)

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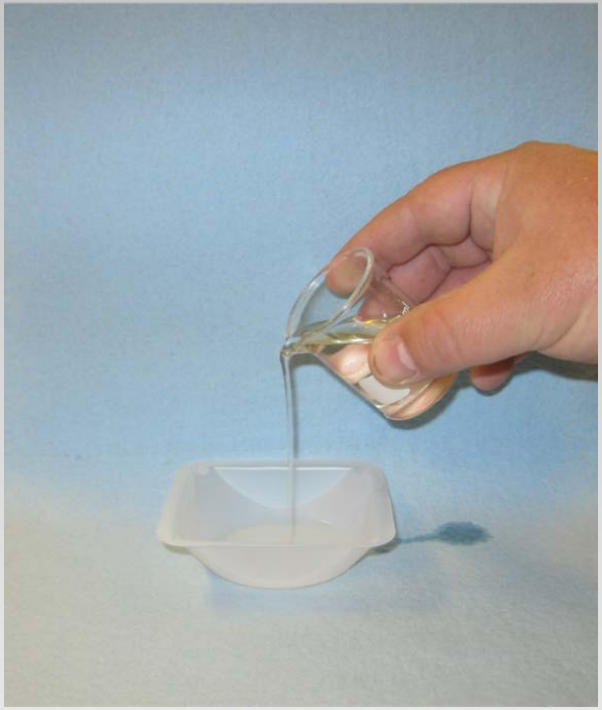
Feedstock Flexibility: Norpar 12

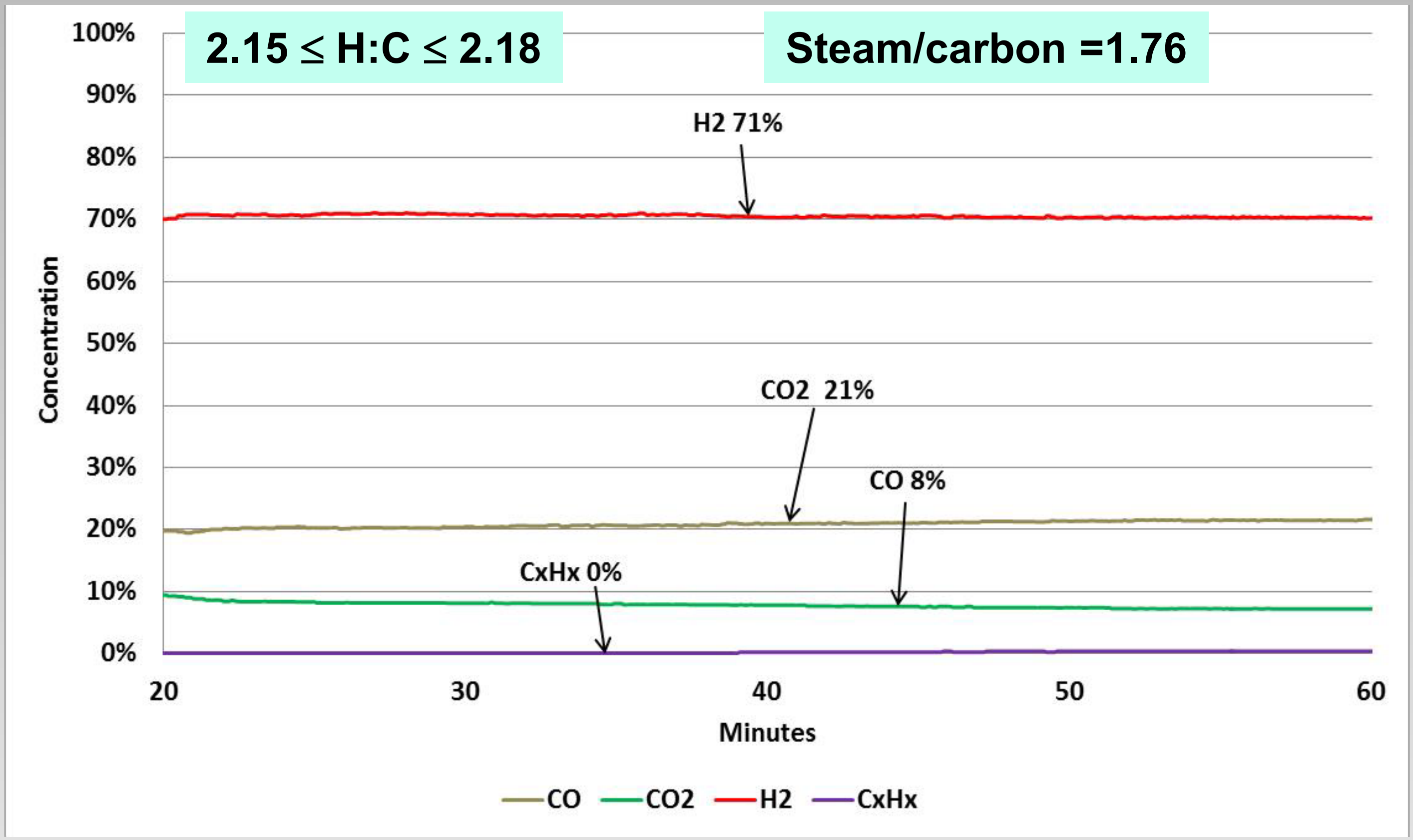
- Norpar 12
  - ExxonMobil product
  - ~1:1 C_{11} and C_{12} alkanes (paraffins)
  - Demonstrates using TDA's *HyRes* process to generate hydrogen from middle distillates
  - Very easy feedstock for hydrogen generation using *HyRes*

Colorless, low viscosity liquid at RT



H_2 Generation from Norpar 12

(simulates steam naphtha reforming)



- Very easy feedstock to process
- 71% H_2 agrees with thermodynamic equilibrium prediction (dry basis)
- Operates at very low steam to carbon ratios (S/C < 2)
- Lower CAPEX alternative to conventional fixed bed steam naphtha reforming (e.g. in Europe)

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Hydrogen Generation from Bitumen

- DILBIT (bitumen diluted with 30% condensate)
  - Liquid at room temperature
  - Tested in TDA's *HyRes* process
  - Performance essentially identical to that obtained with refinery residuum ATB and VTB (i.e. 70 vol% H_2 in raw syngas and no catalyst deactivation)
- Sales oil (diluted with 15% condensate)
  - Currently testing, expect good performance
- Emulsion
  - Cannot test directly with apparatus in current configuration (two phase mixture of tar in water)
  - Might not be possible to test raw bitumen (after water removal) in the lab because of feed heating limitations

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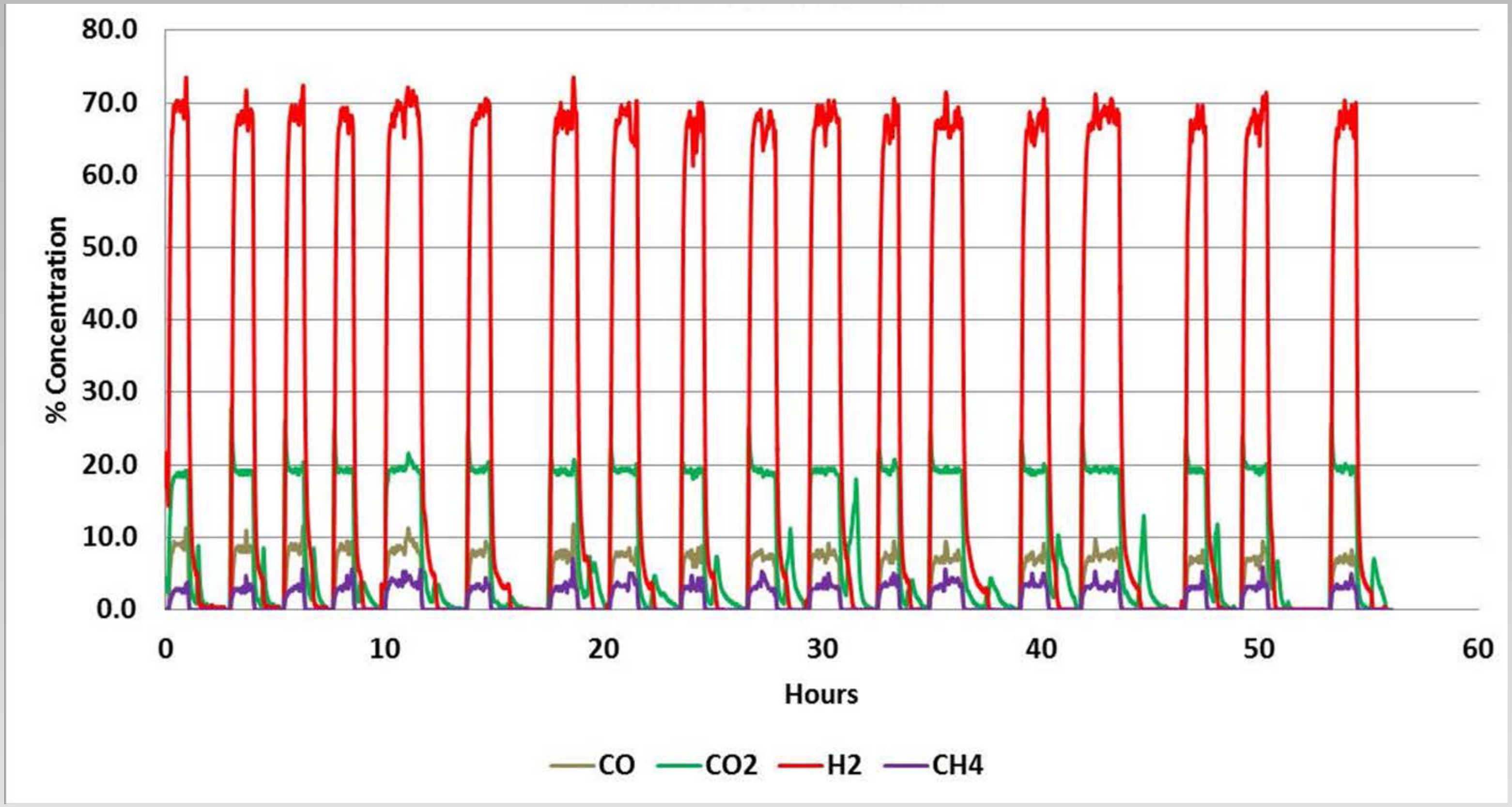
DILBIT Test Results



- Approx. 70 vol% H_2 in syngas
- No catalyst deactivation
- Results essentially <u>identical</u> with those obtained when testing the refinery feedstocks (ATB, medium and heavy VTB

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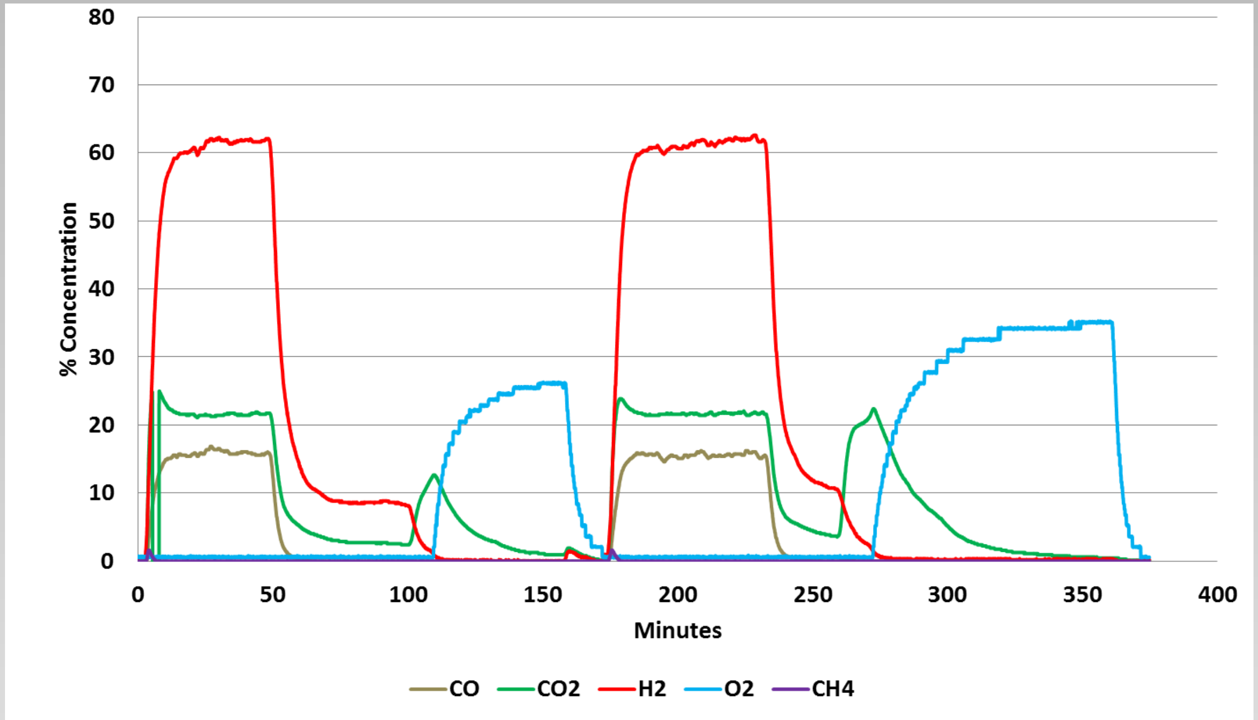
Biomass Fast Pyrolysis Oil



- Two cycles shown to see details
- Slightly lower H_2 in syngas than obtained with hydrocarbon feeds because bio-oil contains oxygen, which is rejected as water
- Steam to carbon = 2 (low S/C reduces energy required to raise steam)
- No catalyst deactivation in subsequent cycling
- Whole raw oil can used without any prior processing (except filtering)

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Team Members and Future Work

- Biomass pyrolysis oil testing
- Continued oil sands bitumen testing
- Waste oil testing
- Other feedstocks of interest to DOE
- Preliminary design of continuous system, process simulation, economics
- Teaming with a major industrial gas supplier as a partner
- TDA has a patent application on file covering the process

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Summary

- <u>Hydrogen for Refineries</u>
  - *HyRes* can be used to generate hydrogen from middle distillates (viable alternative for naphtha steam reforming)
  - *HyRes* can be used to generate hydrogen from refinery residuum feedstocks (e.g. ATB and VTB) at $4/1000 CF
  - Catalyst is regenerated between reforming cycles by burning off coke and sulfur in air before they can deactivate the catalyst
  - No catalyst deactivation (well over 500 hours of laboratory testing with assorted heavy refinery feedstocks)
  - Gives refiners an alternative to coking or asphalt production from bottom of the barrel fractions
  - Can generate H_2 from bitumen for syncrude production
  - No oxygen separation plant is needed and no nitrogen ends up in the syngas because steam reforming and catalyst regeneration are done in separate vessels

Summary - Continued

- Renewable Hydrogen
  - *HyRes* can be used to generate renewable H_2 from raw, whole biomass fast pyrolysis oil
  - Can operate at steam/carbon ratios of 1 - 2
  - *HyRes* system is *much* simpler than a gasifier
  - *HyRes* process is *much less expensive* than a gasifier
  - *HyRes* better suited to small distributed plants compared to a gasifier