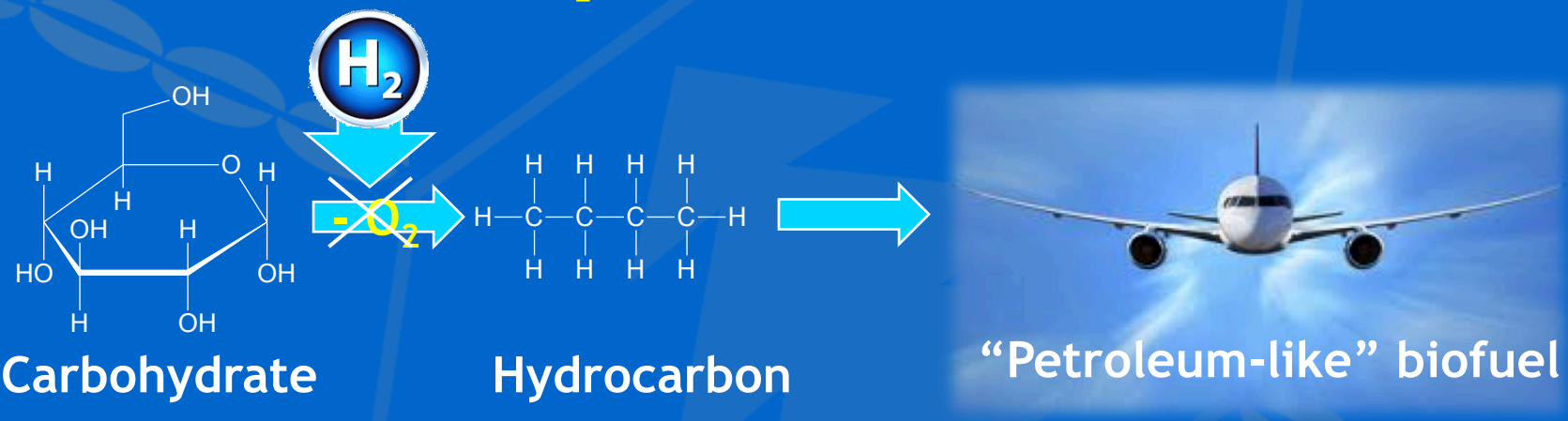
The potential and challenges of "drop in" biofuels



Sergios Karatzos, Jim McMillan and Jack Saddler

International Energy Agency Bioenergy Task 39 (liquid biofuels)

Forest Products Biotechnology/Bioenergy (FPB/B)

Commissioned Task 39 ‘drop in’ biofuel report

- OVERVIEW
  - Definition
  - Role of Hydrogen in drop in biofuels
  - Role of Hydrogen in petroleum industry
- TECHNOLOGIES

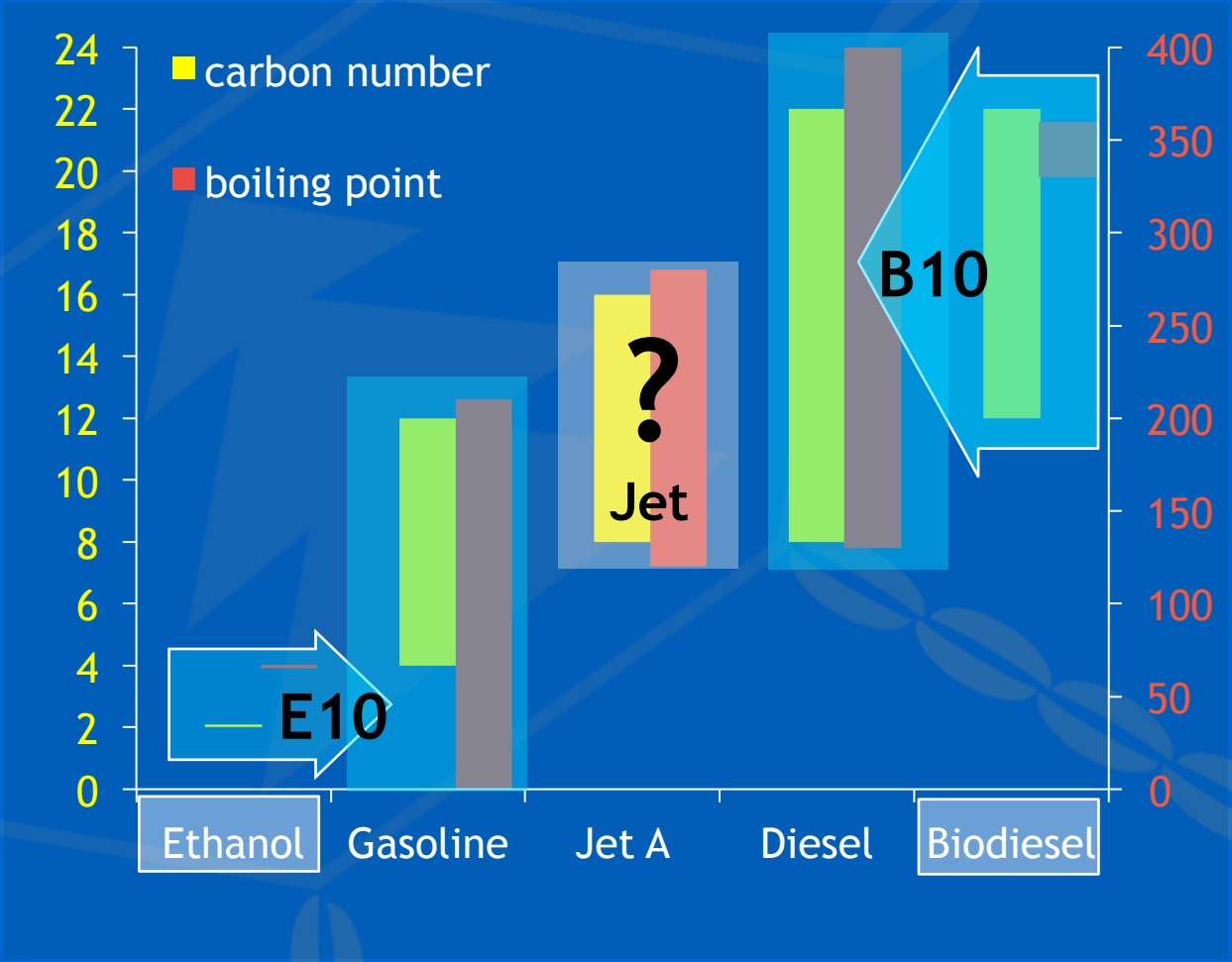
Definition of a "drop-in" biofuel

- Bioethanol: Biogenic ethyl alcohol
- Biodiesel: Fatty acid methyl esters (FAME)
- Drop-in biofuels are liquid hydrocarbons that are **functionally** equivalent and as **oxygen-free** as petroleum-derived transportation blendstocks (fuels)
- Examples:
  - Hydrotreated Vegetable Oils (HVO)
  - Hydrotreated Pyrolysis Oils (HPO)
  - Fischer Tropsch Liquids (FT liquids)

Properties of transportation fuels

Drop-in biofuels need to have similar properties to petroleum fuels:

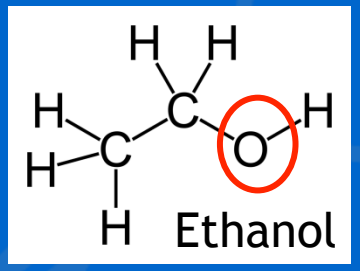
- Fit the carbon number range
- Low to No oxygen

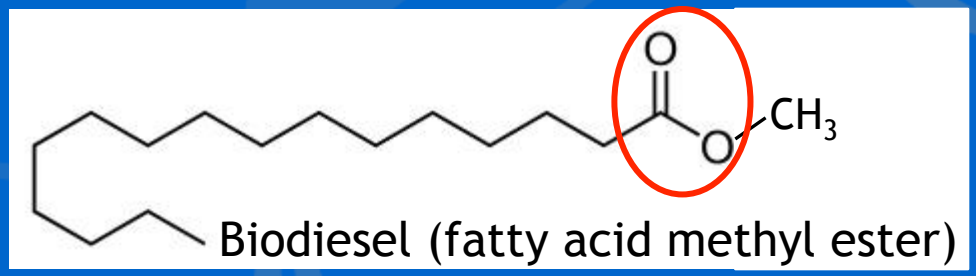


Unlike conventional biofuels, "drop-in" biofuels should be indistinguishable from petroleum fuels for end uses!

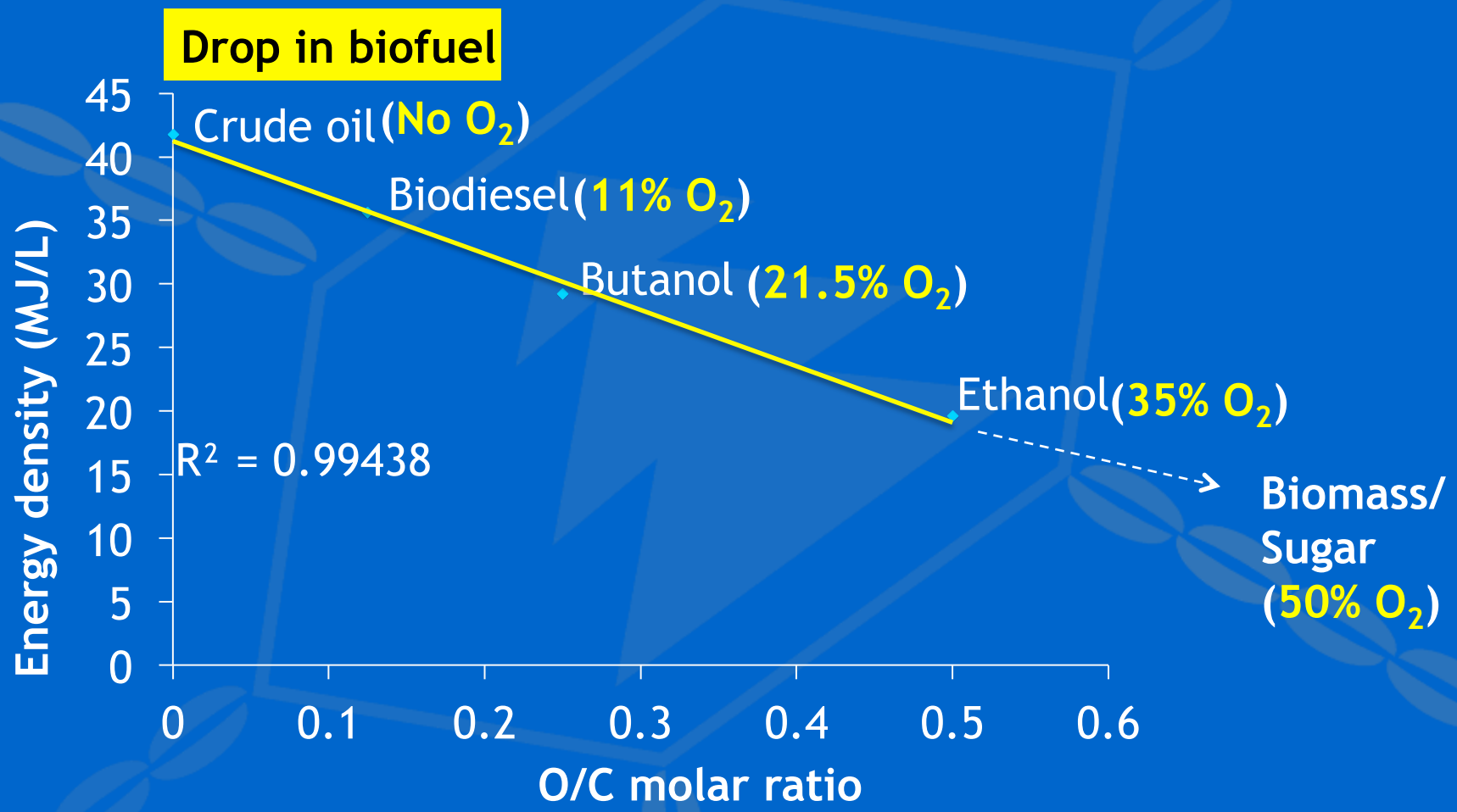
Oxygen Challenge

- Oxygen is present in biomass in the form of hydroxyls, esters, and ethers
- Can oxidize fuel components, reactors and pipeline metallurgy to cause corrosion
- Oxygen content reduces energy density



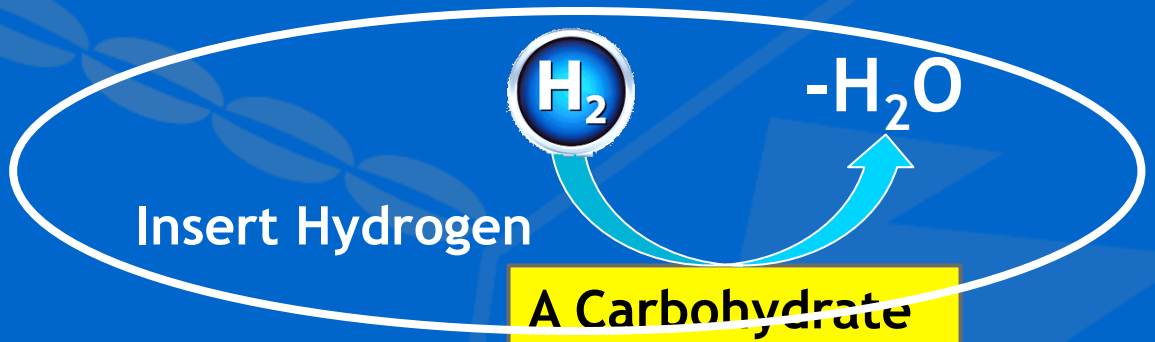


Oxygen content vs. energy density

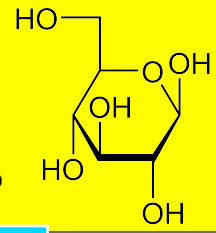


Increasing Oxygen content reduces fuel energy density

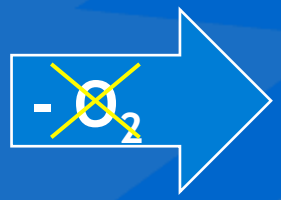
Deoxygenating biomass dilemma …add H_2 or lose yield?



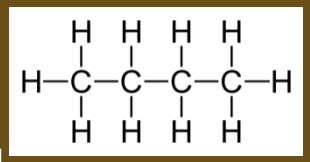
A Carbohydrate
e.g. Glucose



$C_6H_{12}O_6$



A Hydrocarbon
e.g. Butane



C_4H_{10}

High H/C ≈ 2

Oxidize Carbon

"sacrificing" feedstock

$-CO_2$

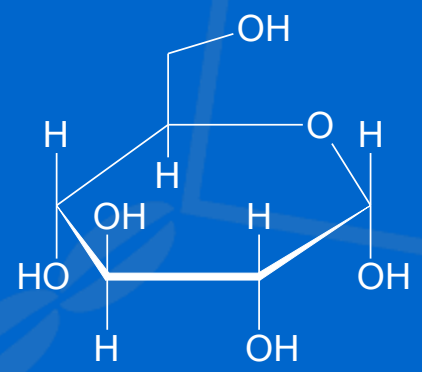
Objective is to deoxygenate and enrich H_2 content of biomass

Effective hydrogen to carbon ratio (H_{eff}/C)

- A high Effective Hydrogen to Carbon ratio is desired for drop-in biofuels

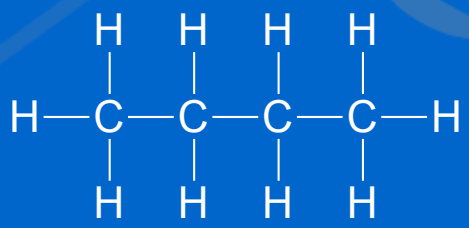
- H_{eff}/C $= n(H) - 2n(O)/n(C)$

$H_{eff}/C = 0$



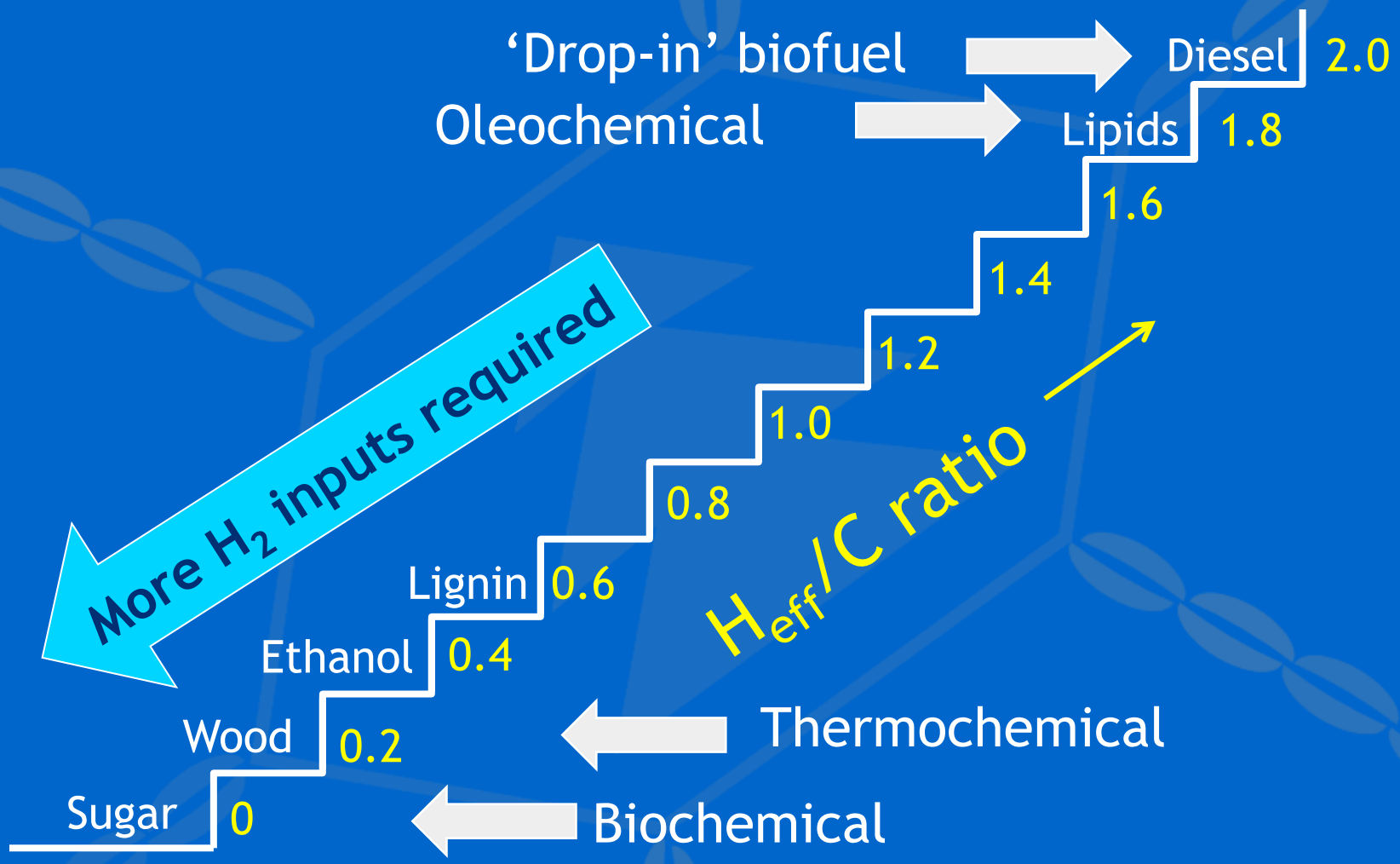
Carbohydrate

$H_{eff}/C \approx 2$



Hydrocarbon
(e.g. Butane, Diesel)

The Effective H/C ratio staircase…



High O_2 or low H/C feedstocks require more processing and H_2 inputs

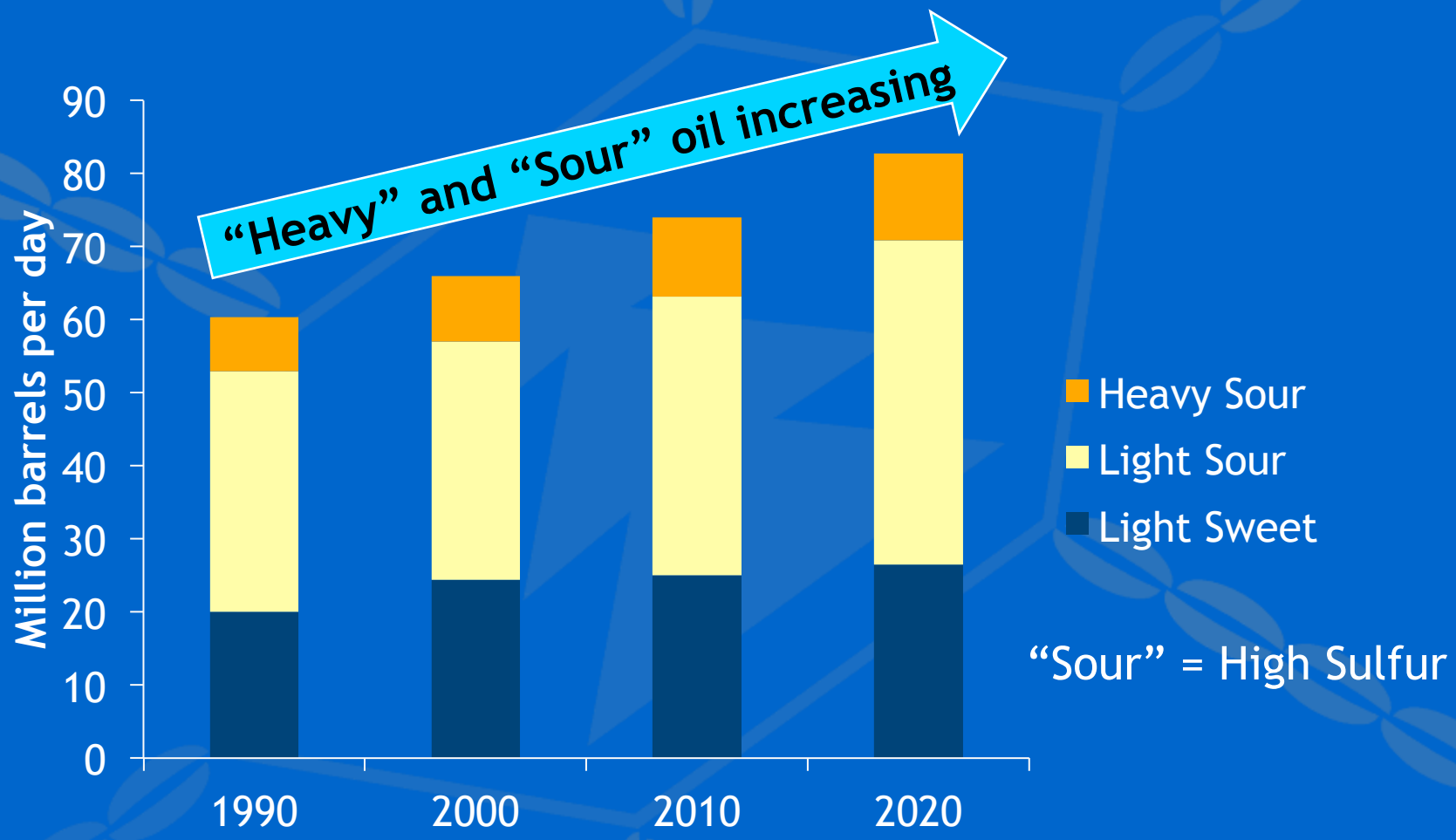
The Hydrogen-Oxygen dilemma

- "Drop-in biofuels" is a loose term referring to liquid biofuels containing low or no oxygen content
- Deoxygenation requires hydrogen inputs or "oxidizing/burning" of feedstock carbon
- High H_{eff}/C ratio feedstocks such as lipids are well suited for drop-in biofuel production

What will determine the success of "drop in biofuels"?

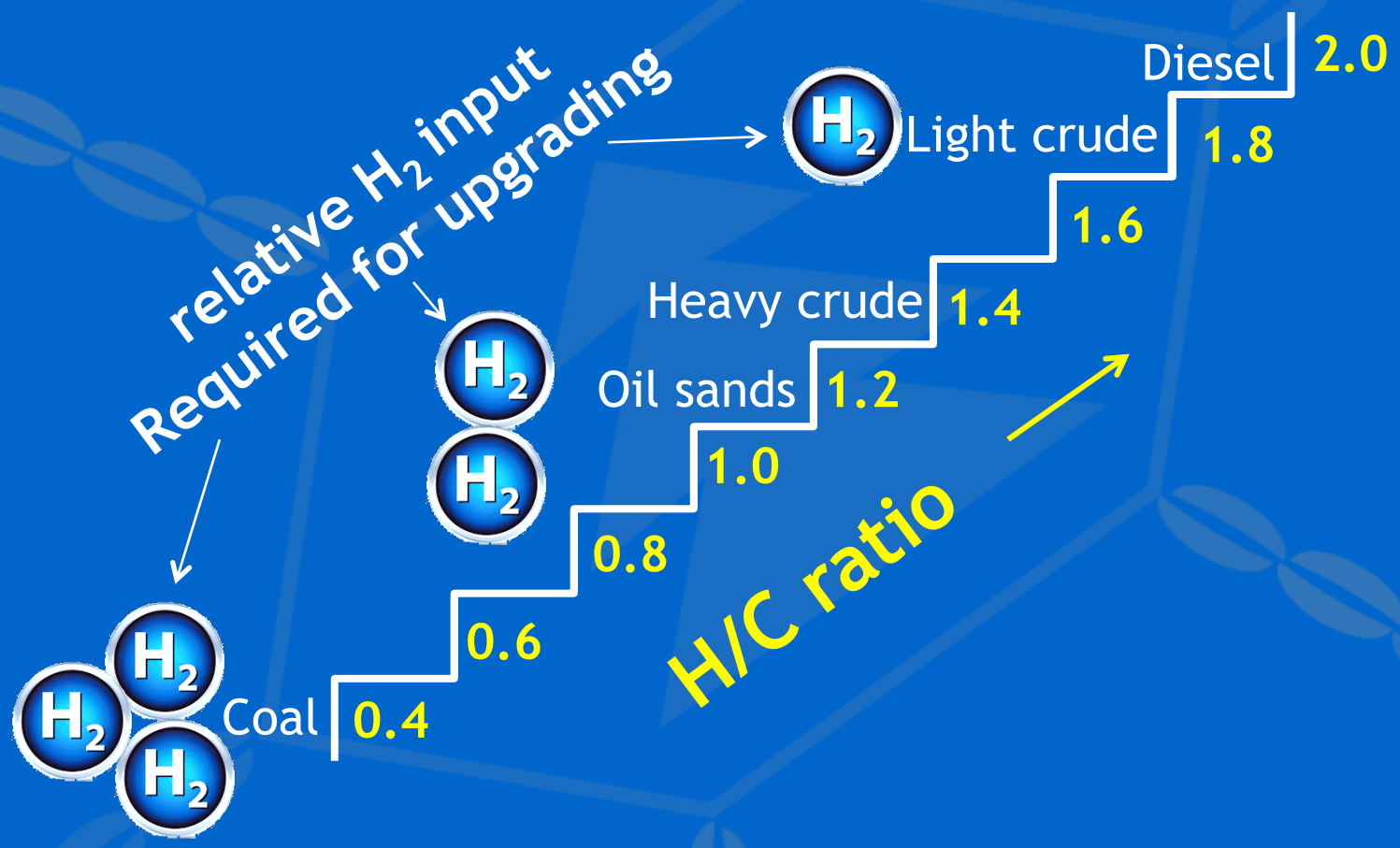
- Drop-in biofuel technologies complexity/ selectivity and hydrogen demand
- Commercialization challenges such as capital, yield and refinery insertion
- Crude oil is becoming increasingly hydrogen deficient ('heavier' and 'sourer')

Crude oil quality declining…



Purvin & Gertz forecast for world crude oil quality (Source: data from EIA)

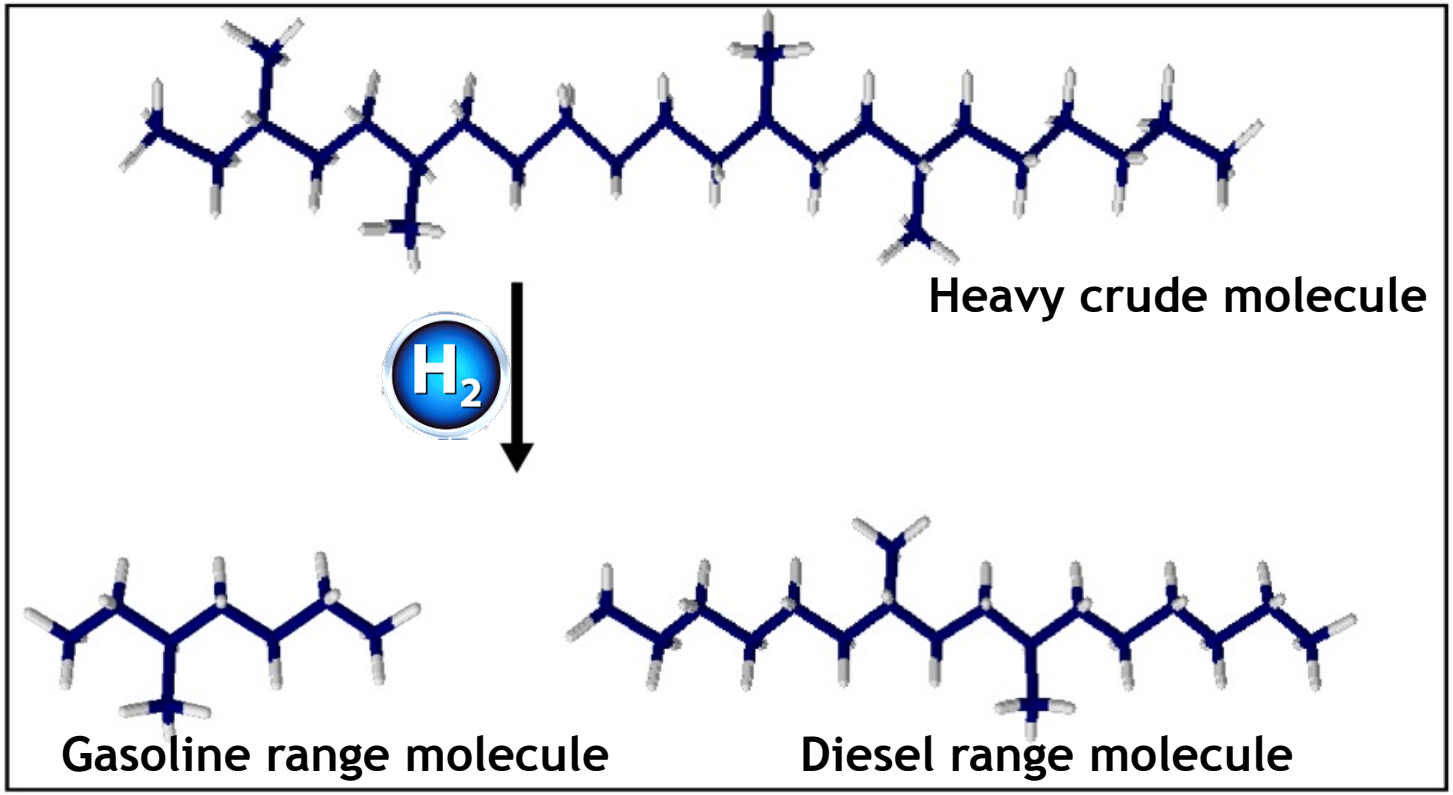
The H/C ratio staircase for petroleum…



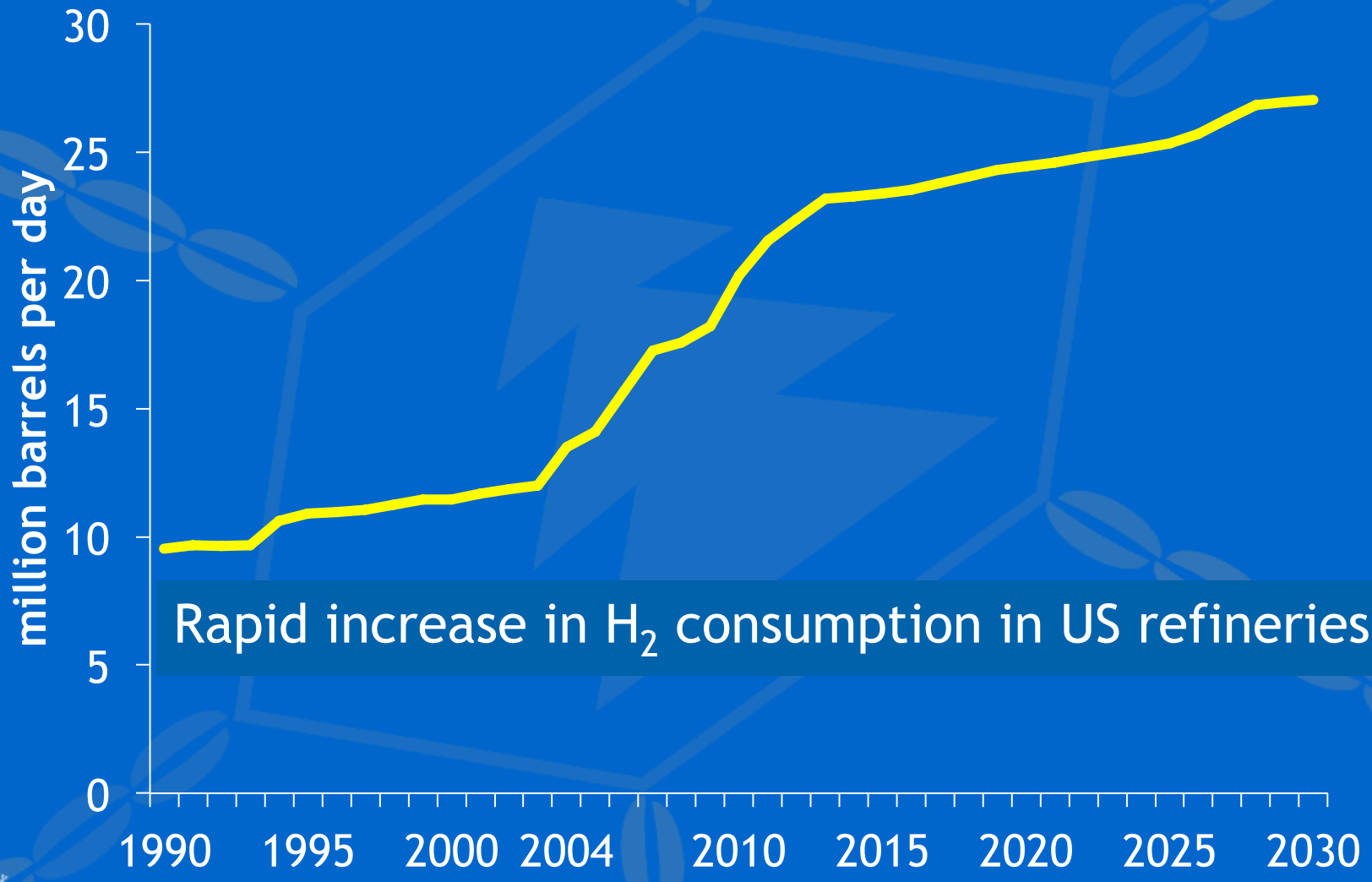
Lower quality fossil feedstocks = lower H/C ratio = higher H_2 inputs

Hydrotreating and Hydrocracking

- Hydrotreating (Removes sulfur impurities as H_2S)
- Hydrocracking (breaks heavy oil to lighter molecules)



US Hydrotreating capacity 1990-2030



Rapid increase in H_2 consumption in US refineries

Source EIA, Annual Energy Outlook 2006

Natural gas: Where H_2 comes from

- 90 % of commercial H_2 comes from <u>steam reforming natural gas</u>

ENERGY INTENSIVE PROCESS!!

Role of H_2 in upgrading petroleum and drop-in biofuels

Petroleum

- Increasing Sulfur content
- Increasing heavy oil needs cracking

Drop-in Biofuels

- No Sulfur
- High Oxygen content of feedstock needs hydrogenation

Both require Hydrogen for upgrading to finished fuels

Hydrogen will likely come from Natural Gas

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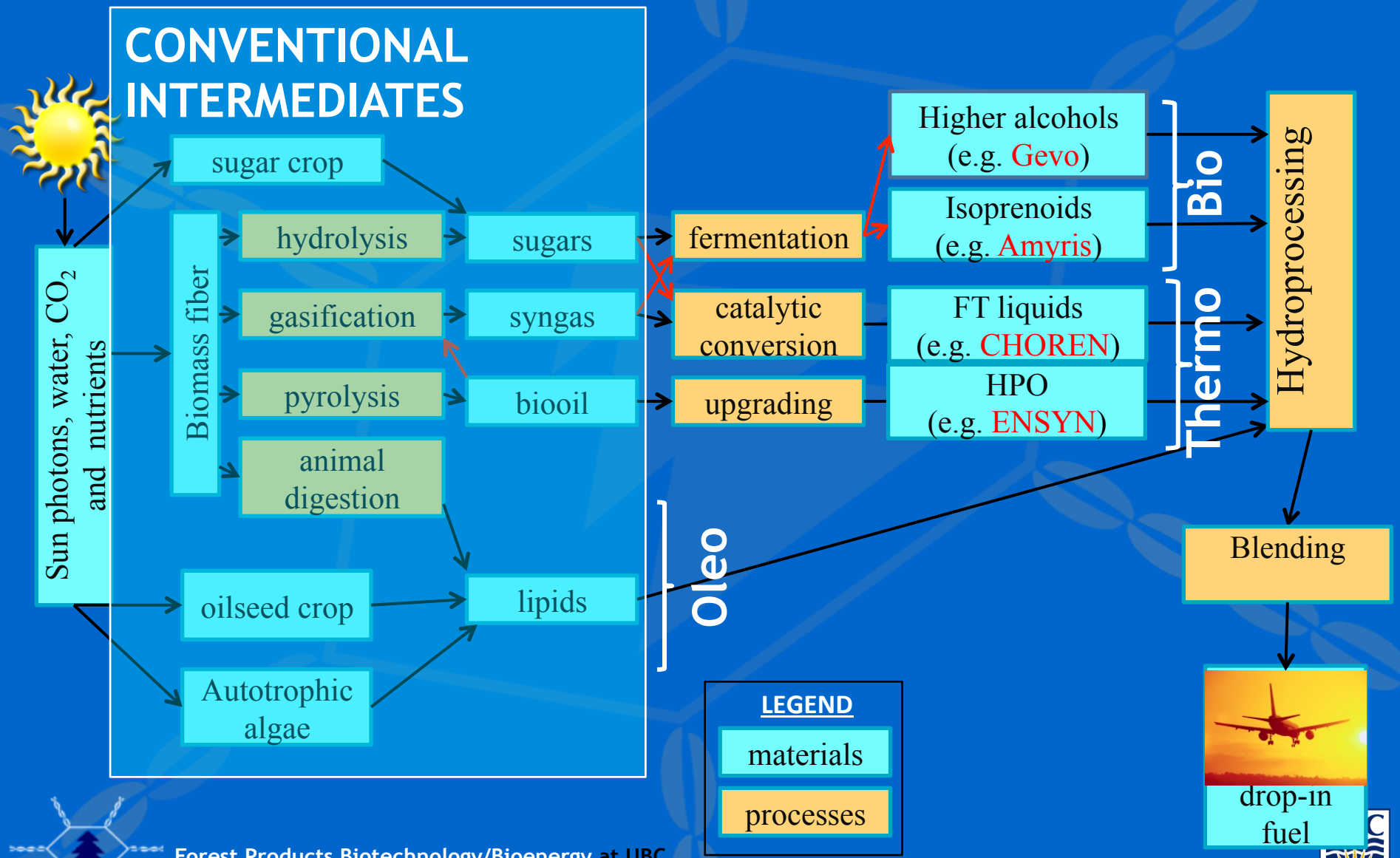
The commercialization potential of Drop in Biofuel platforms and their H_2 dependence

- Oleochemical (HVO, algae)
- Thermochemical (Pyrolysis - HPO, Gasification FT-liquids)
- Biochemical (Advanced Fermentation)
- Hybrid platforms (e.g. Virent, Zeachem, Lanzatech)

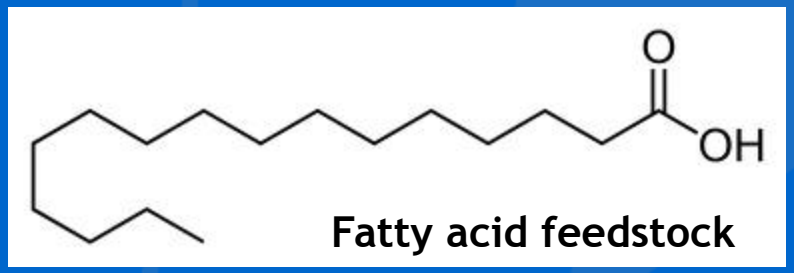
Technology pathways to "drop-in"

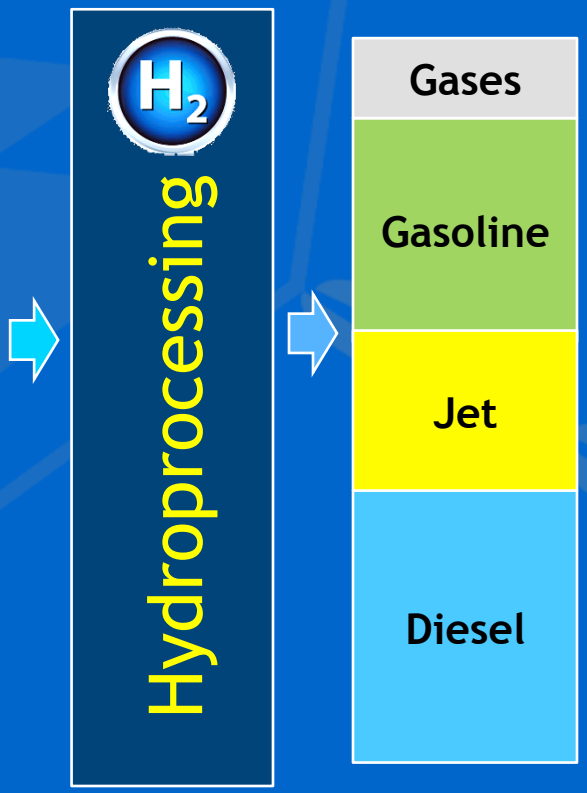


Oleochemical Platform
Hydrotreated Vegetable Oils or HEFAs

Major advantages

- "Simple" technology, low risk (processes already commercial)
  - Bio SPK ASTM certification
- High Hydrogen to carbon ratio (low Oxygen) of Feedstock
  - Palm oil
  - Tallow (rendered animal fat)





Challenges

- Costly feedstock (approx. $500-1000/t)
- Sustainability?

Commercial drop-in biofuel companies

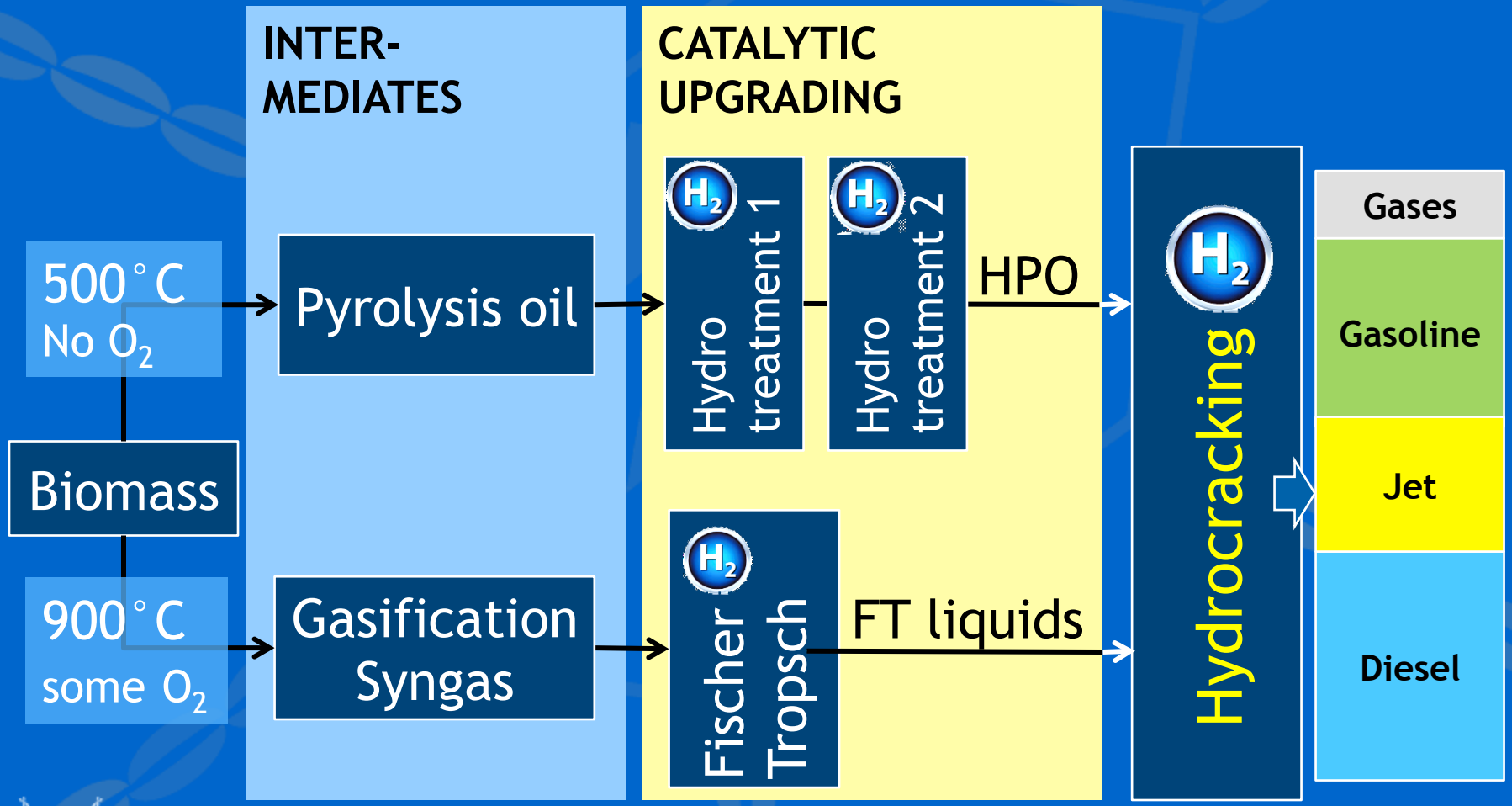
Neste Oil facility, Rotterdam

- All based on oleochemical
  - Neste Oil: 2,400,000,000 L diesel from palm oil
  - Dynamic Fuels: 280,000,000 L diesel fr animal fat

Many examples of commercial biofuel flights

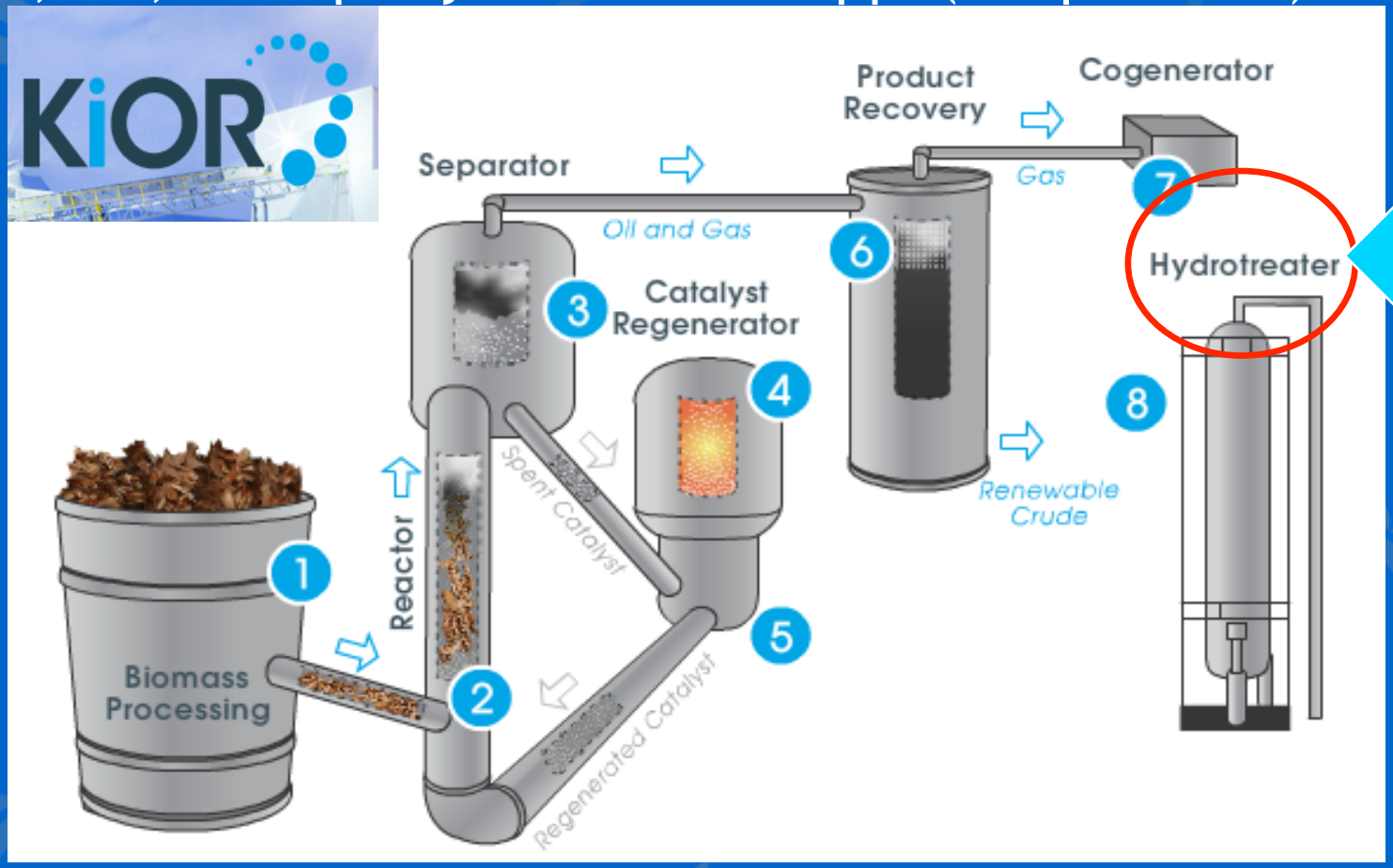
- Virtually all based on oleochemical
  - US Navy: Sept 2011 Solazyme algae oil and palm oil
  - Continental Airlines: Nov 2011 Solazyme algae oil
  - Alaska Airlines: Jan 2012 tallow and algae
  - Lufthansa: July 2011 Jatropha, Camelina
  - Finnair: July 2011 Used Cooking Oils
  - Many more

Thermochemical drop-in biofuel platforms



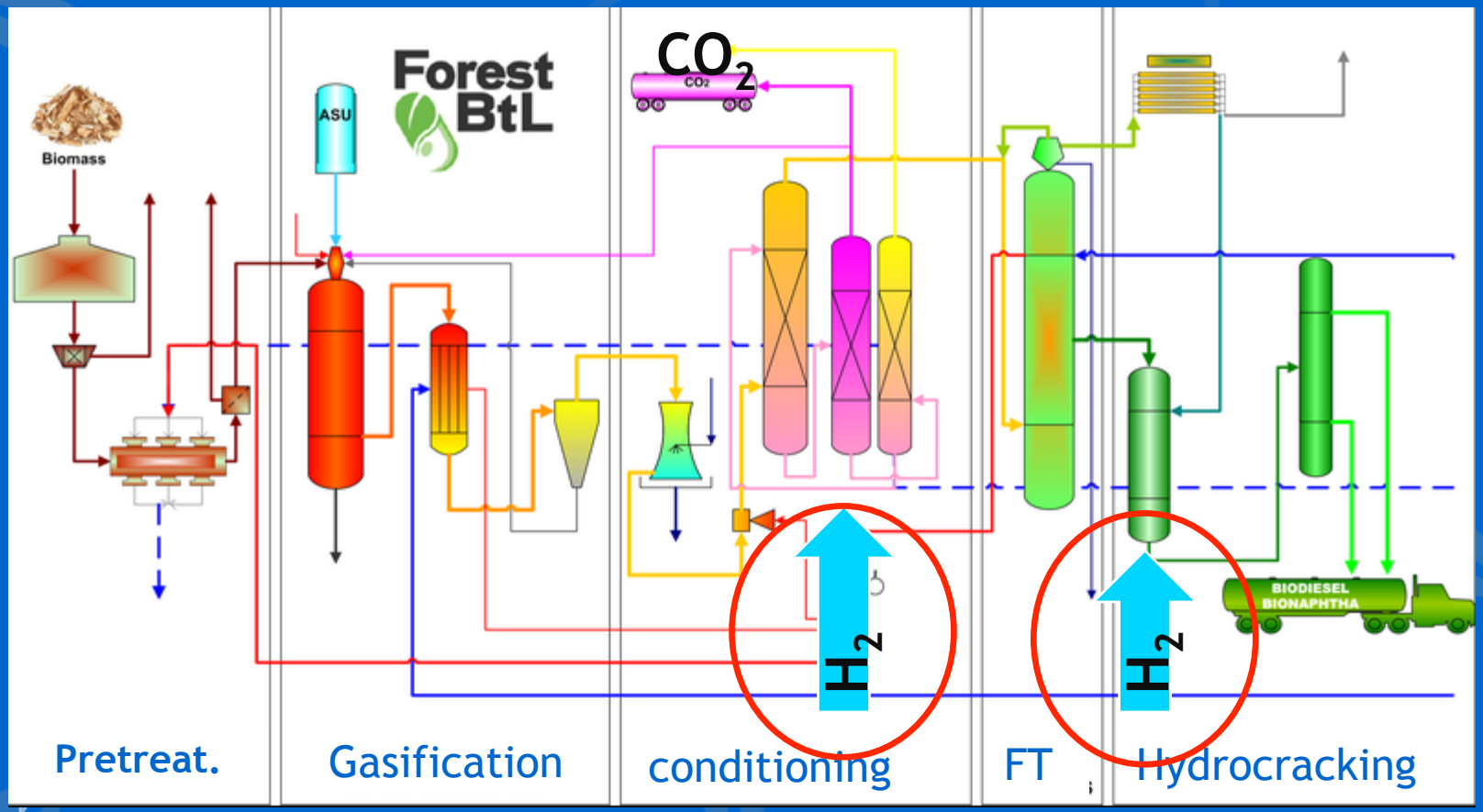
Example of pyrolysis drop in facility: KiOR

- 50,000,000 L per year in Mississippi (in operation)



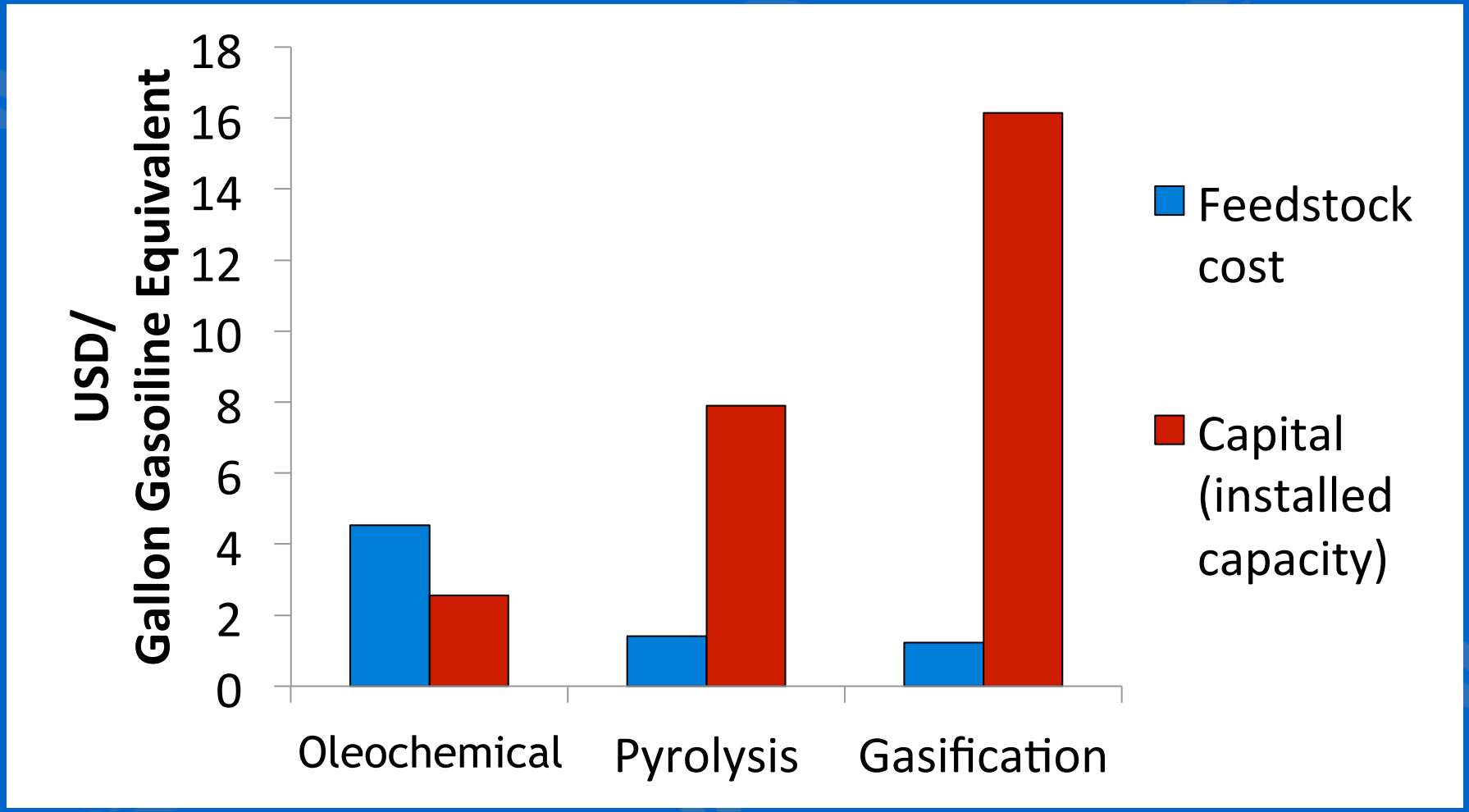
Forest BtL Oy and Choren's Carbo-V

- 130,000,000 L per year of Gasification FT liquids by 2016 (Finland)



Sundrop biofuels 190 MLPY

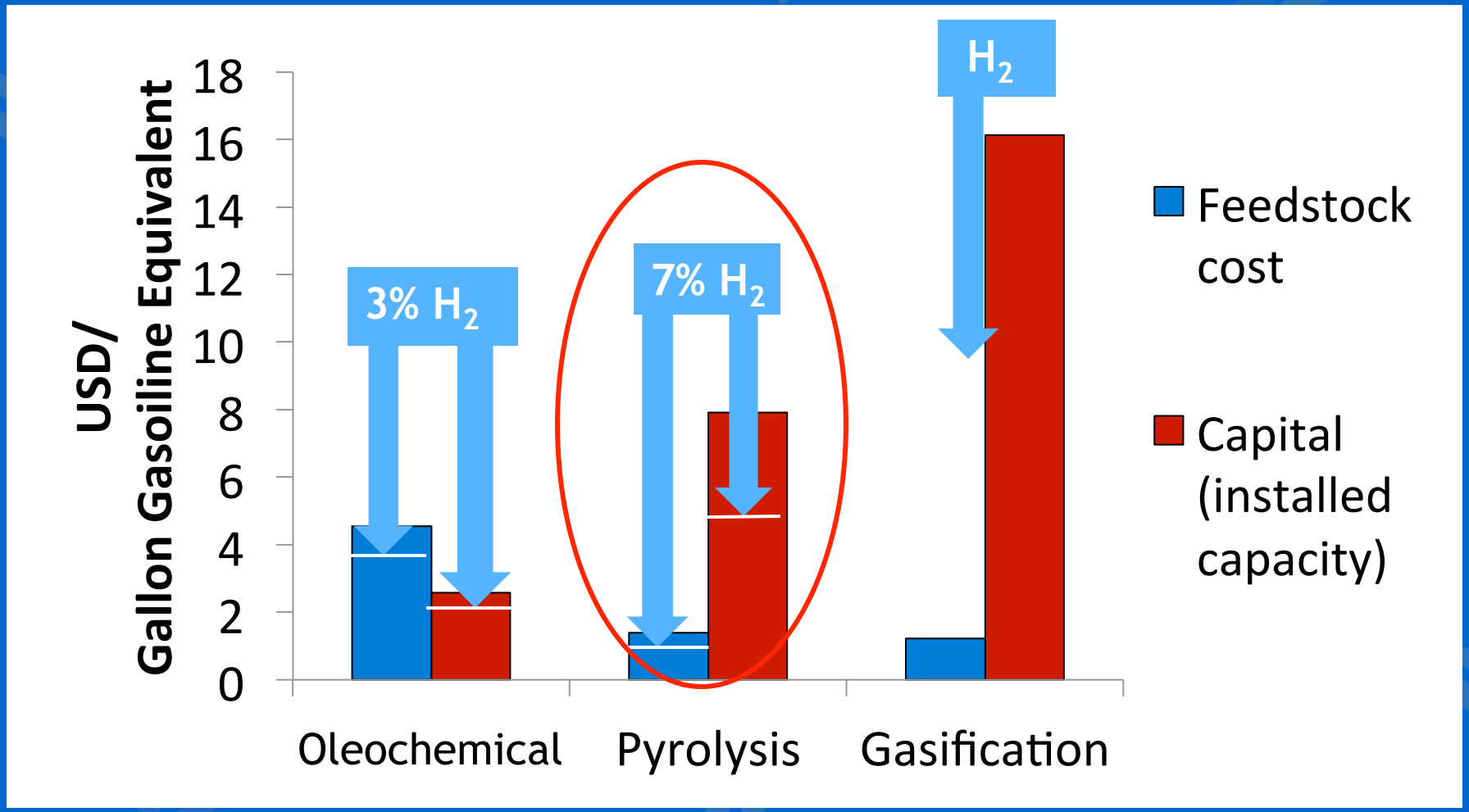
Feedstock and Capital cost of drop-in Biofuels



Feedstock intensive vs Capital intensive platforms

Source: Kazi et al. 2010, Pearlson et al. 2011, Jones et al. 2009

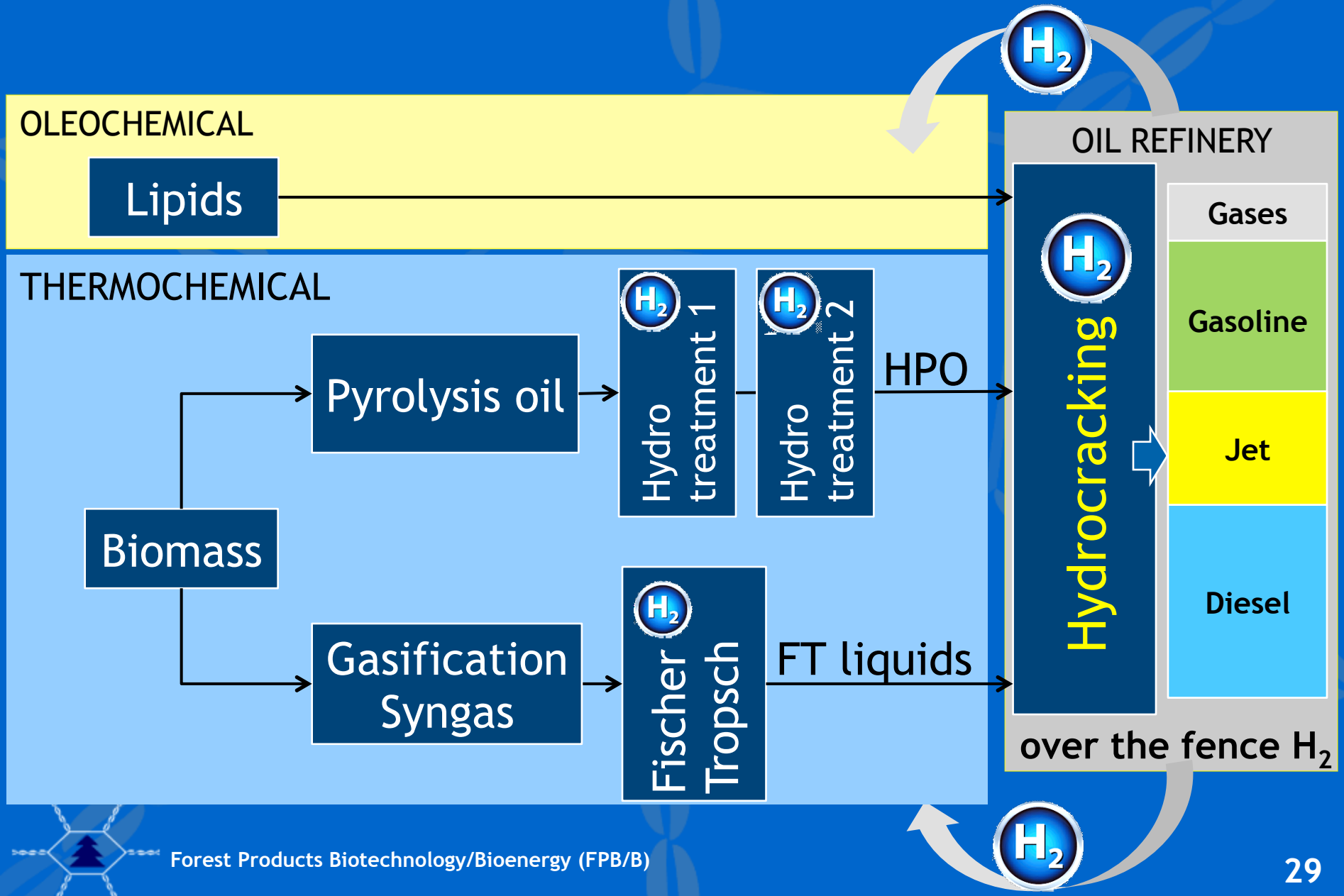
"Over the fence" Hydrogen inputs can reduce capital and feedstock costs



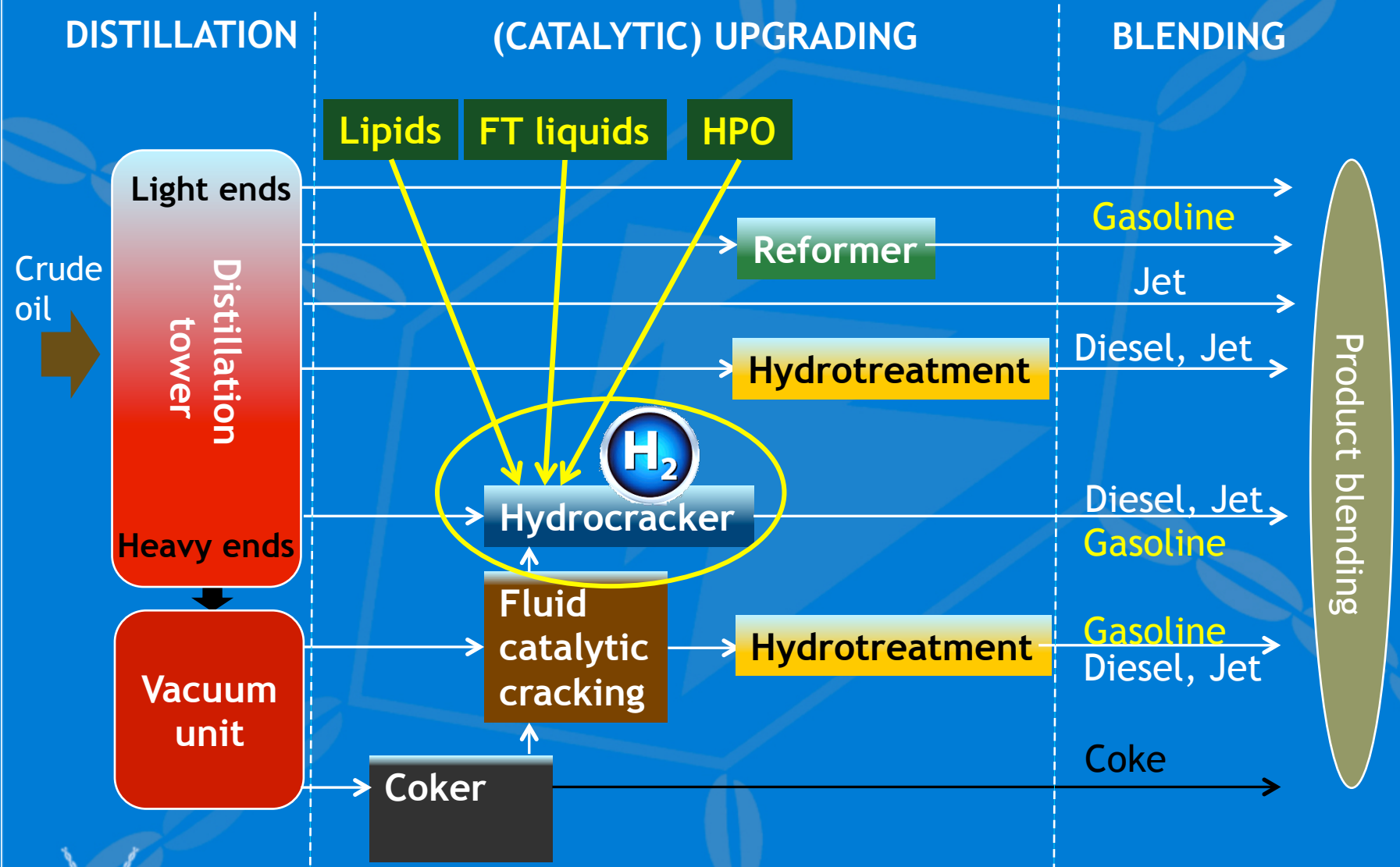
Pyrolysis is highly dependent on access to cheap Hydrogen

Source: Kazi et al. 2010, Pearlson et al. 2011, Jones et al. 2009

Drop in biofuels leveraging on Oil refineries



Drop in biofuels leveraging on Oil refineries



Challenges of hydroprocessing biofeed:
The Haldor Topsoe experience

HALDOR TOPSØE
CATALYSING YOUR BUSINESS

- Higher Hydrogen consumption
  - requirements more than doubled when just 5% of feed was replaced with biofeed!
- Presence of oxygenated gases such as CO and H_2O
- Heterogeneity of feedstock (Catalyst design challenges)

Source: Haldor Topsoe, 2009

Major scale up challenges for each platform

- Pyrolysis
  - Hydrogen
  - Hydrotreating catalyst
- Gasification
  - Capital / scale
  - Feedstock /yields
- HVO oleochemical
  - Feedstock
- Refinery insertion challenges

Sources: Jones et al. 2009; Swanson et al. 2010; Pearlson et al. 2011

Biochemical: Sugar fermentation to drop-in

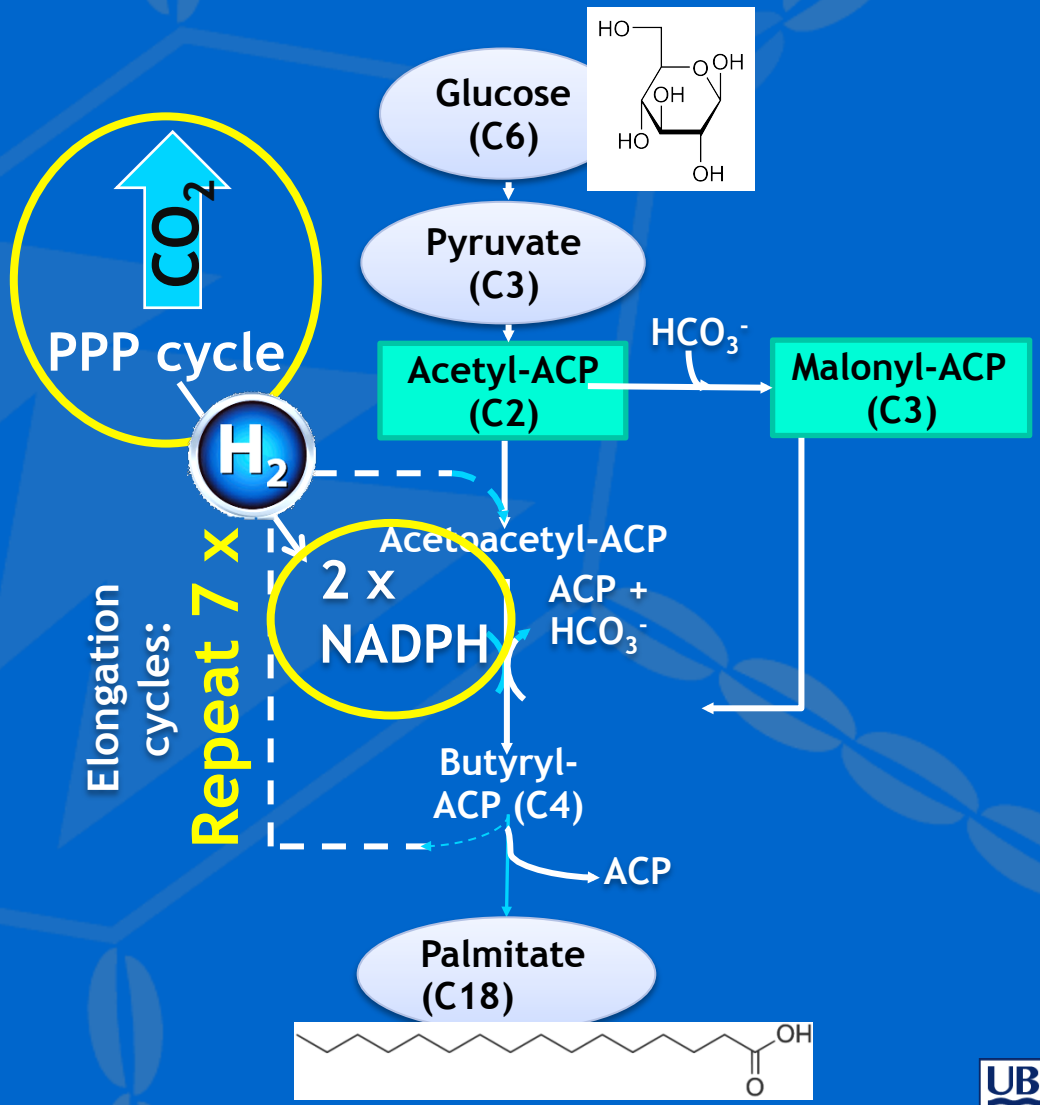
SUGAR	→	FERMENTATION	→	Target molecule
		Modified algae, bacteria or yeast		Long alcohols Aliphatic chains

- Major advantages
  - Pure and "functionalized" product streams suitable for value added markets
- Major challenges
  - Volumetric productivity about 10x lower than ethanol
  - Recovery challenges: e.g. recovery from fermentation broth and intracellular expression
  - Sugar feedstock highly oxidized (H/C = 0)

Fermentation pathways for deoxygenating Carbohydrates

Compared to ethanologenic yeast:

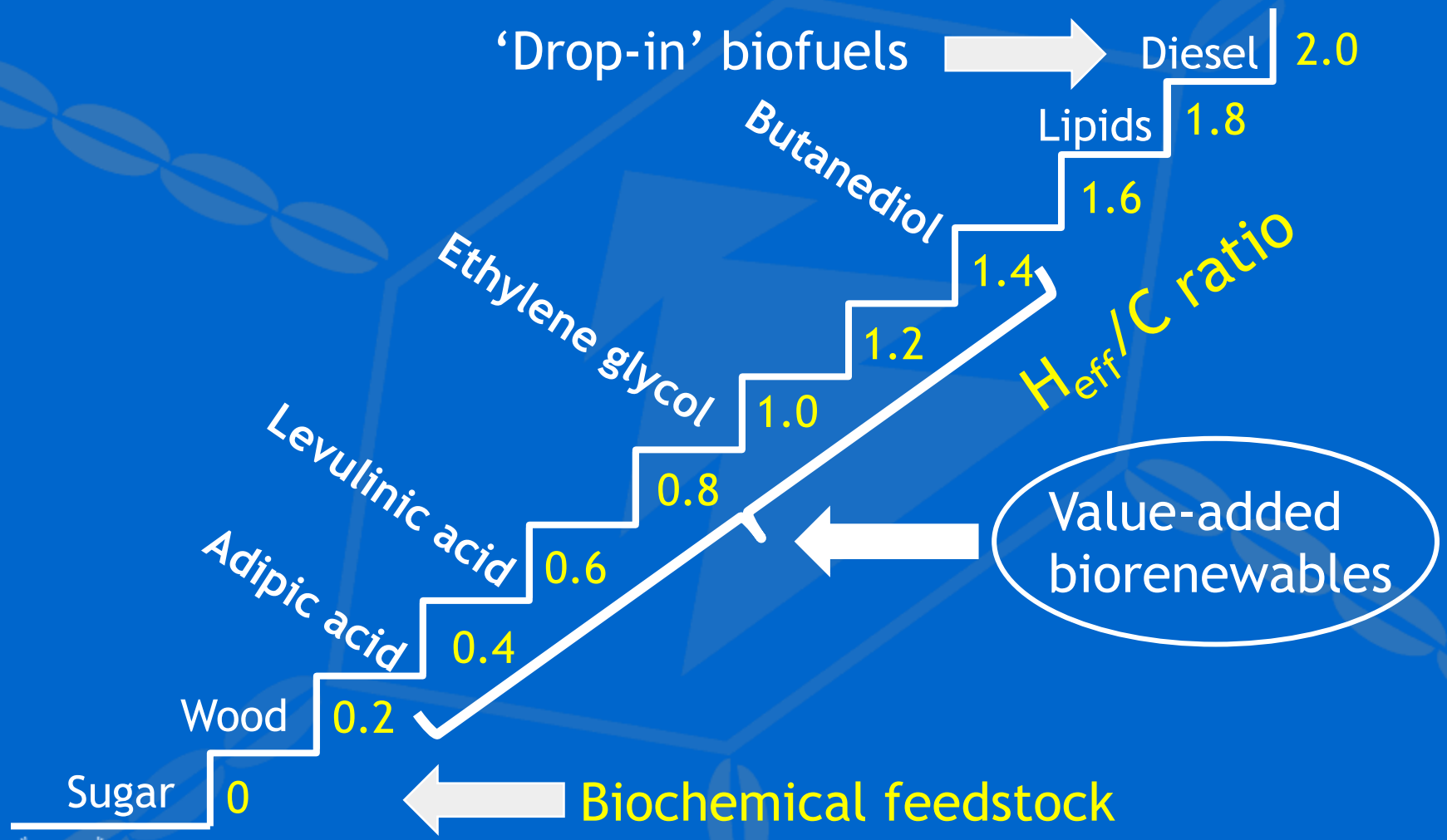
- Energy intensive
- High requirement for reducing power (derived from NADPH or Hydrogen)



Lanzatech CO_2 + H_2 example

Climbing fewer steps on the H_{eff} /C staircase

…



Value added chemicals have lower H_{eff} /C ratios than fuels

Summary

- Oleochemical: commercial now and less H_2-dependent with considerable potential for growth (feedstock challenges?)

- Thermochemical well suited for long term drop-in biofuels
  - H_2 and catalyst challenges (Pyrolysis), Scale challenges (Gasification)
  - Leveraging on oil refineries: more challenging than expected

- Biochemical "drop-in" products more valuable in rapidly growing chemicals markets

- Accessing cheap/renewable Hydrogen will be a key challenge for both drop-in biofuels and crude oil of decreasing quality

ACKNOWLEDGEMENTS

International Energy Agency Bioenergy Task 39 colleagues

Task 39
IEA Bioenergy

www.Task39.org

Future competition for Hydrogen inputs…

- Heavy oil processing

e.g.

Venezuela and Alberta

- Ammonia industry
- <u>Drop-in biofuels?</u>