Biofuels and Biorefineries

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Why Biofuels?

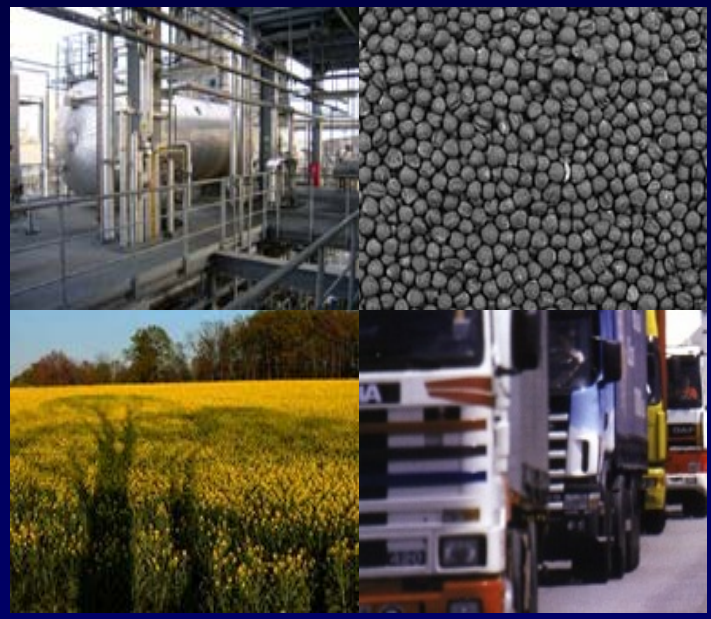
The production and use of biofuels …

- Follows environmental EU commitment
  - Green Paper, Kyoto Protocol
  - 2003/30/EC, v.3423/2005
- Contributes to reduction of atmospheric pollution
  - CO, SO_x, HC, PM
- Causes decrease of greenhouse gas emissions

Why Biofuels?

The production and use of biofuels …

- Reduces dependence of oil imports
- Can boost national economy
  - Consolidate and amplify agricultural economy by energy crops cultivation
  - Create new employment opportunities
  - Reinforce other industries
    - » Sugar industry, Paper industry etc



What is Biomass?

- Biodegradable part of products as well as wastes of agricultural, forestry, industrial and municipal origin
  - Energy crops
    - » Sunflower, rapeseed, cotton, corn, barley, soy, sweet- sorghum, sugar-beet etc
  - Lignocellulosic material
    - » Wood, paper industry waste, forestry waste etc
  - Animal fats
  - Agricultural and municipal waste
  - Recycled vegetable oil
  - …

EU Biofuels Market

Biodiesel

- Market size (2004)
  - 1.52 billion euros
  - 1,902,500 tons consumed
- Growth rates
  - 8% yearly
- Market competition
  - » 82 companies
  - » Top 3 covering 60% market share
- Market potential (2011)
  - 8.5 billion euros

Bioethanol

- Market size (2004)
  - 367 million euros
  - 611,000 tons consumed
- Growth rates
  - 72% yearly
- Market competition
  - » 17 companies
  - » Top 3 covering 72% market share
- Market potential (2011)
  - 4.5 billion euros

Bioethanol

- Produced by Biomass
  - Hydrolysis and fermentation (prevalent method)
    - » Sugarcane, sugar-beet, sweet sorghum, molasses, corn, wheat, potato, rice stem, paper industry wastes, municipal waste, cellulosic waste etc
    - » Yields 2100-5600 lit per hectare
  - Gasification
- It is estimated that for 100 Joules energy consumed for bioethanol production, 135 Joules energy is provided by using ethanol as fuel
- Employed already in large scale as transportation fuel
  - Brazil: Cars use pure ethanol or E10 mix (gashol)
  - USA: E10 covers more than 1/8 of the total gasoline market
    - » All cars manufactured after 1970 are E10 compatible
  - E85 is the ideal ethanol-gasoline mix
    - » Used by FFVs (Flexible Fuel Vehicles)
    - » Many cars manufactured after 1999 are also compatible with E85

Bioethanol Properties

- Used as gasoline additive for improving gasoline's octane number and its environmental properties
  - Similar combustion properties with conventional gasoline
  - Reduction of atmospheric pollutants
    - » CO, NO_x, HC, PM
  - Higher octane number
    - » Already used as gasoline additive in North and South America
  - Lower inflection point
    - » Increase engine performance
  - Ethanol-gasoline mixtures require high purity ethanol
    - » 99.5-99.9%

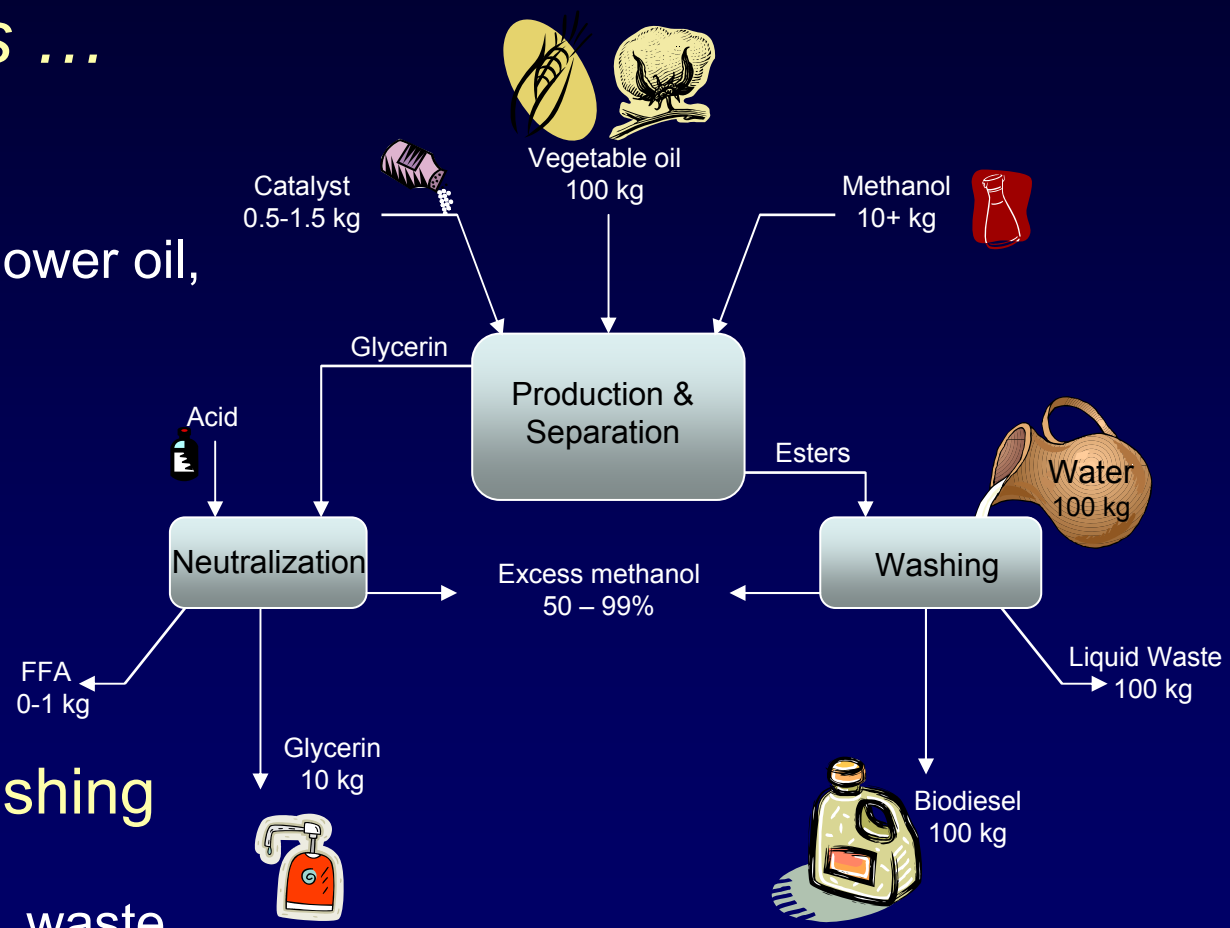
Biodiesel

- Production processes
  - Transesterification of vegetable oils or vegetable wastes (FAME biodiesel)
    - » Rape-seed oil, sunflower oil, cotton oil, tallow, used vegetable oils, etc
  - Conversion of Fischer-Tropsch wax
- Environmentally friendly properties
  - Reduced content of SO_x, CO, aromatics
- Safe for transportation and storage
  - Unstable at low temperatures
- Positive thermal properties regarding combustion in diesel engine
  - Higher cetane number and lubricity
  - Small reduction of engine performance
- Used as mixture with conventional diesel
  - B5 to B20

Biodiesel Production FAME

Quality parameters …

- Feedstock quality
  - Vegetable oil type (rapeseed oil, sunflower oil, corn oil, etc)
  - Methanol purity
- Transesterification reaction yield
  - Temperature, oil/methanol ratio, catalyst
- Separation and washing yield
  - Glycerin, methanol, waste



Biodiesel - Diesel

- + Minimal SO_x, CO_x, and PM emissions
  - » Near zero sulfur content
  - » High cetane number
- + Lower toxicity and higher biodegradability
  - » Low aromatics content
- + Safe for transportation and storage
  - » Higher ignition point
- + Positive effect on engine
  - » Increased lubricity
- — Lower yield of fuel
  - » Decreased viscosity
- — Lower oxidation stability
- — Unstable behavior in very low temperatures
  - » Higher pour point, higher cloud point

Biodiesel Quality Control

Biodiesel

- Specifications EN14214:2003
  - Transportation Diesel specification (EN590)
    - » Burning, transportation, storage
    - » Oil analysis
    - » Oxidation, purity
  - Miscellaneous analysis
    - » Content of methanol, catalyst etc

Biodiesel/Diesel Mix

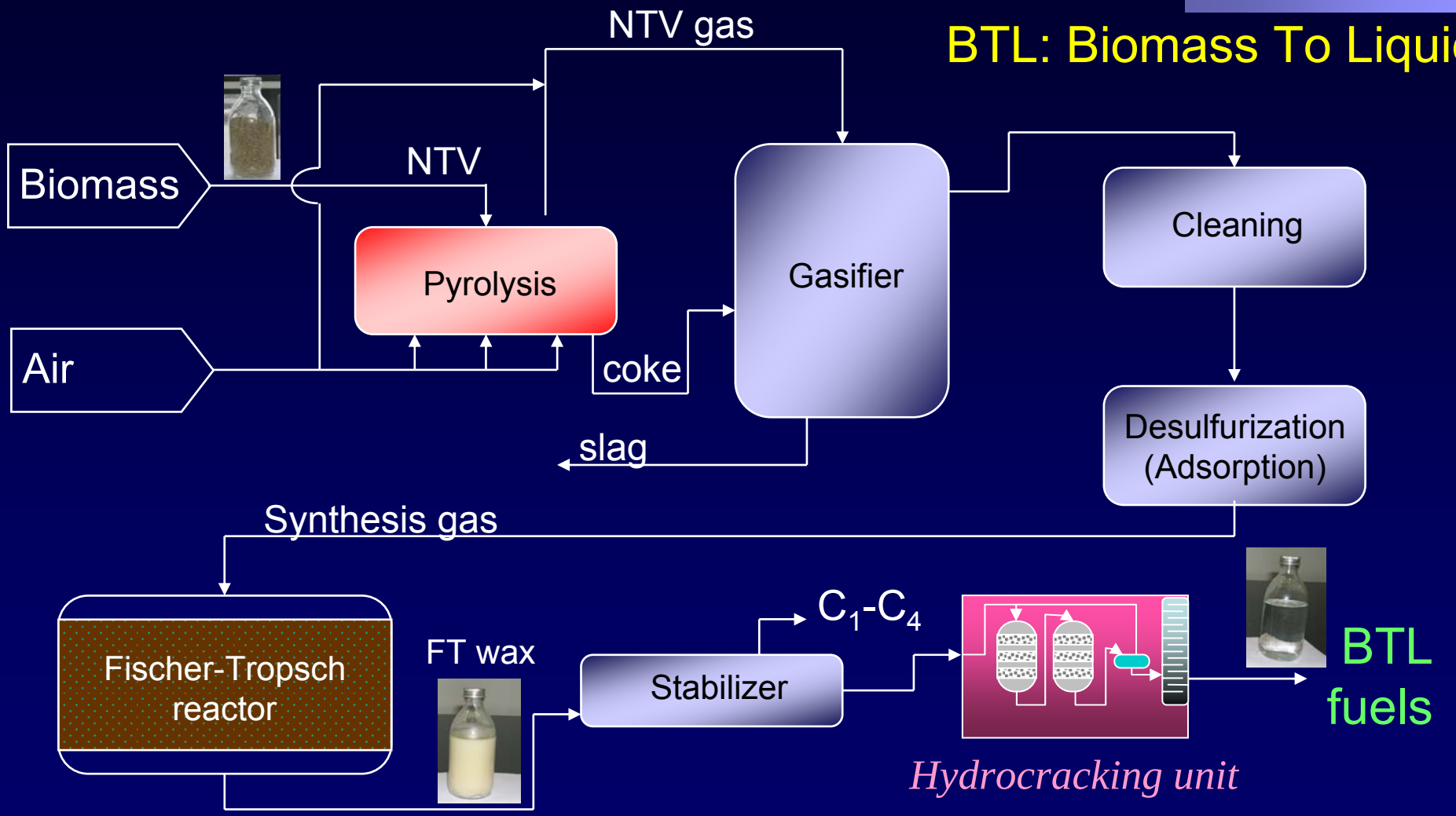
- Specification EN590:2004
  - Maximum permitted mixing percentage is 5% biodiesel
- Biodiesel B5 (Mix of 5:95 biodiesel:diesel)
  - Shows similar behavior within engine and while transported
  - Reduces SO_X, CO, PM emissions
  - Improves lubricity

Biofuels Production @ LEFH

- BTL (Biomass To Liquid)
  - Biomass gasification and synthesis gas production
    - » Lignocellulosic material, wood chips, waste, etc
  - Fischer-Tropsch reaction of synthesis gas to FT-wax production
  - Hydrocracking or catalytic cracking for FT-fuels production
- Catalytic pyrolysis of biomass for bio-oil production
  - Fluid-bed reactor
  - Production of gas, liquid and solid fuels

Fischer-Tropsch Fuels @ LEFH

BTL: Biomass To Liquid



Biodiesel Production @ LEFH

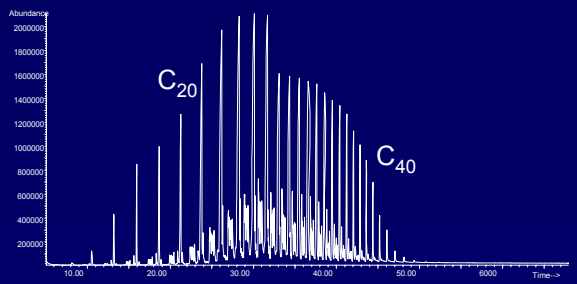
FT-wax Hydrocracking

- Pilot plant for FT-wax upgrade to FT-fuels
  - Fully automated unit
- Determination of optimal catalysts and operating conditions for BTL-diesel
  - Commercial catalysts
  - T, P, LHSV, hydrogen-to-wax ratio
- Production of specific quantity of BTL-fuels for engine tests
  - EU Research program in cooperation with European car manufacturers, oil industries, research institutes

FT-wax Hydrocracking

FT-wax

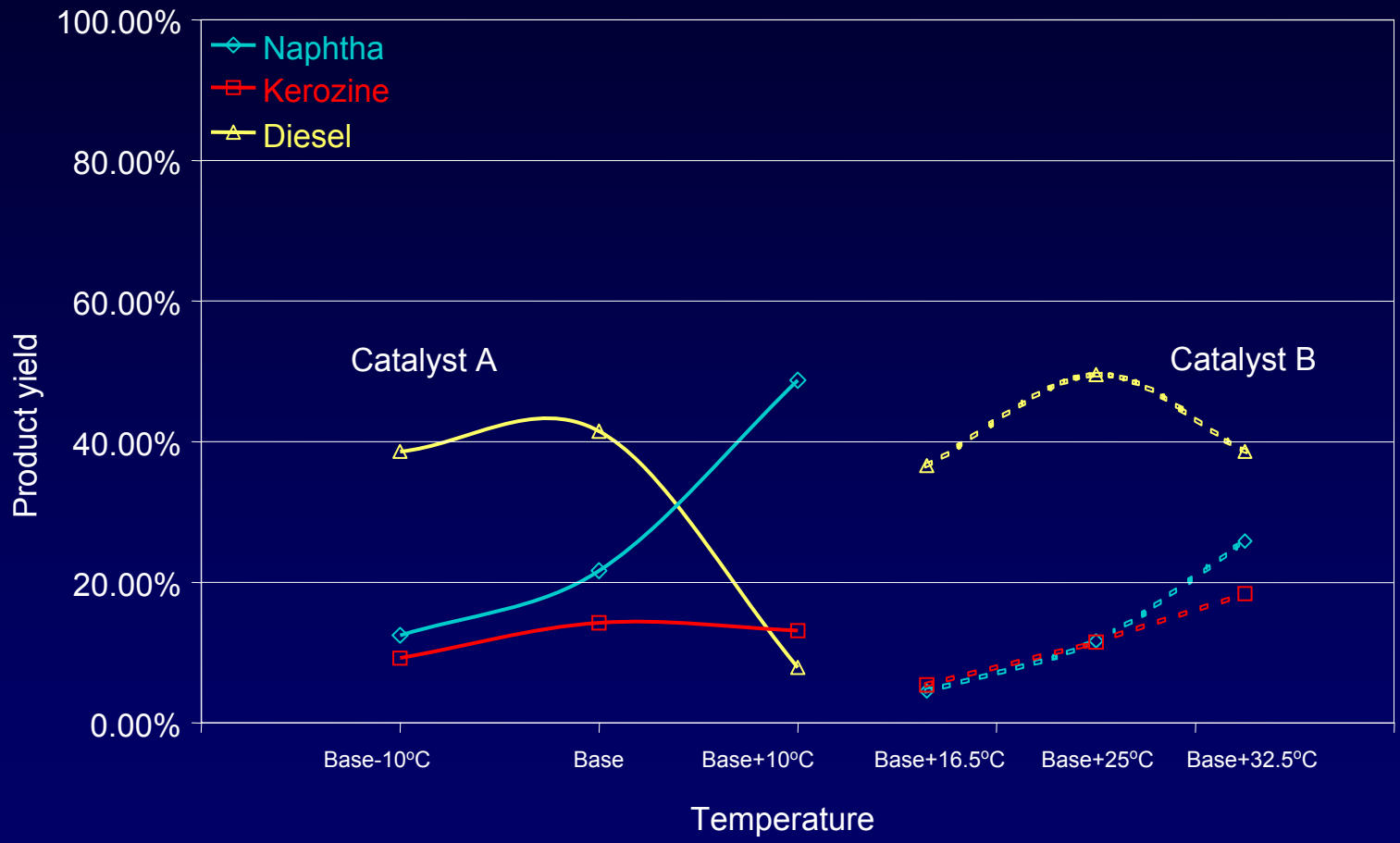
- Highly paraffinic
  - C_{20}-C_{45}
- Physicochemical properties
  - » API = 45.26
  - » s.g. = 0.8
  - » S = 3.9ppm
  - » Viscosity = 2.25 cst



FT-fuels

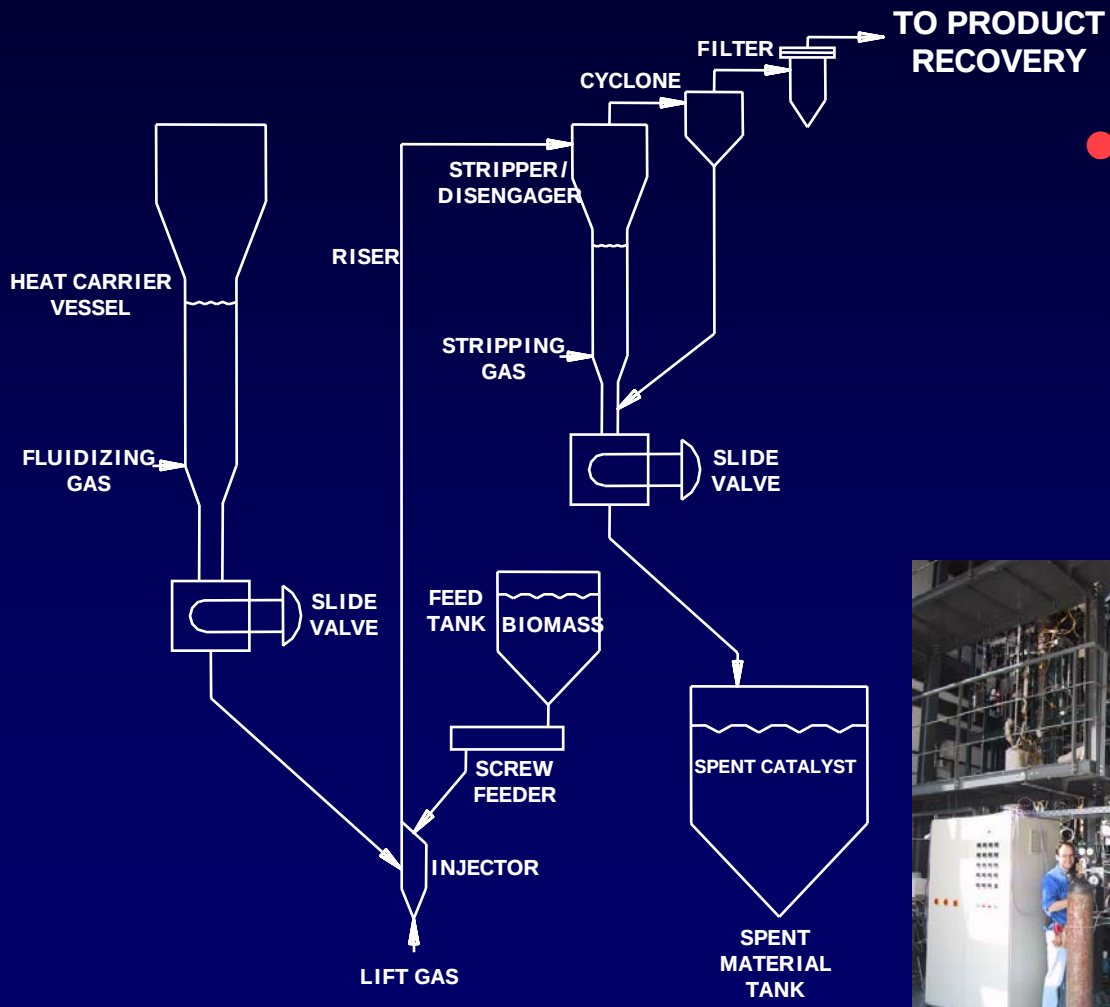
- Wide range
  - BTL Naphtha (80-150˚C)
  - BTL Kero (150-200˚C)
  - BTL Diesel (200-320˚C)
- Aims to optimize diesel yield
  - Respecting specifications
    - » Density 0.78 gr/ml
    - » Cetane index 76
    - » Aromatic compounds 0%

Catalysts & Operating Conditions



Operating conditions determine BTL product yields

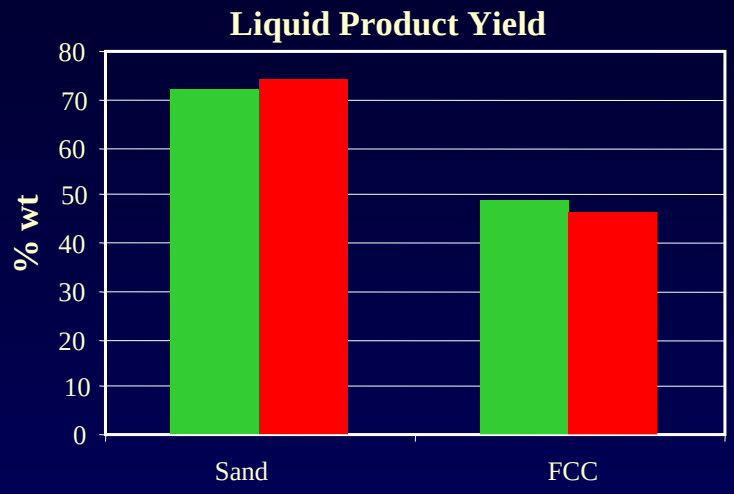
Biomass Pyrolysis @ LEFH

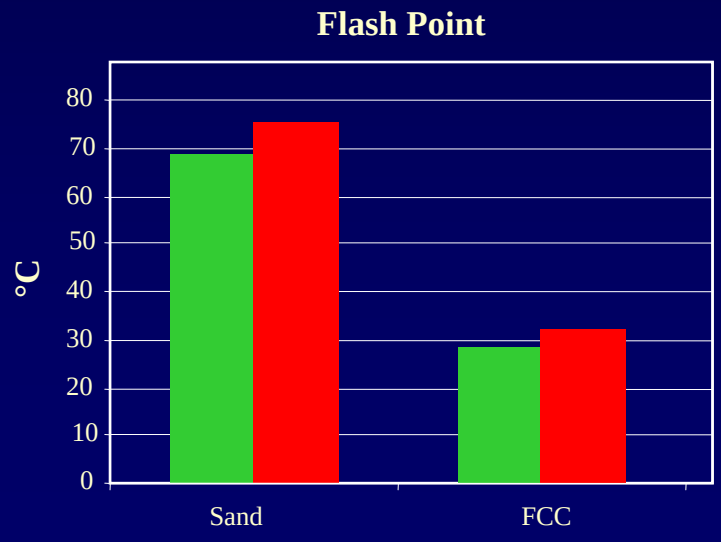


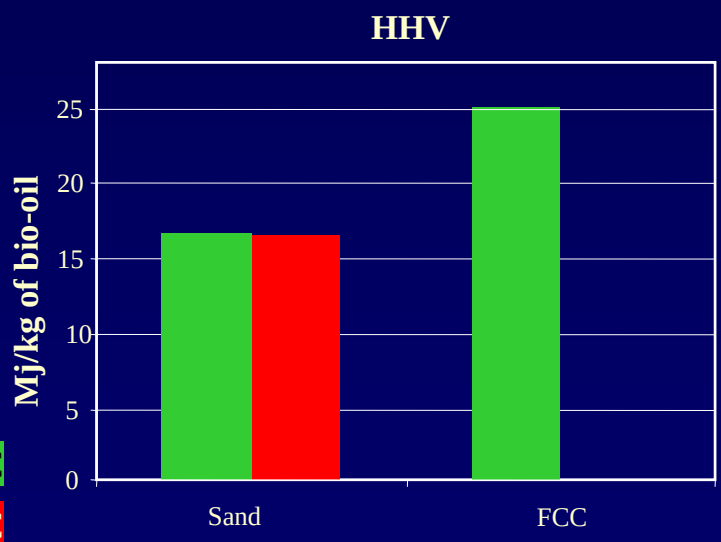
- Pilot plant
  - Thermochemical pyrolysis of biomass for production of liquid, solid and gas fuels
  - Heat carrier
    - New catalysts
    - Sand

Sand vs. FCC Catalyst

- For bio-oil production thermal pyrolysis is recommended
  - Catalytic pyrolysis gives lower bio-oil yield







T=450oC

T=500oC

Biomass Pyrolysis Products

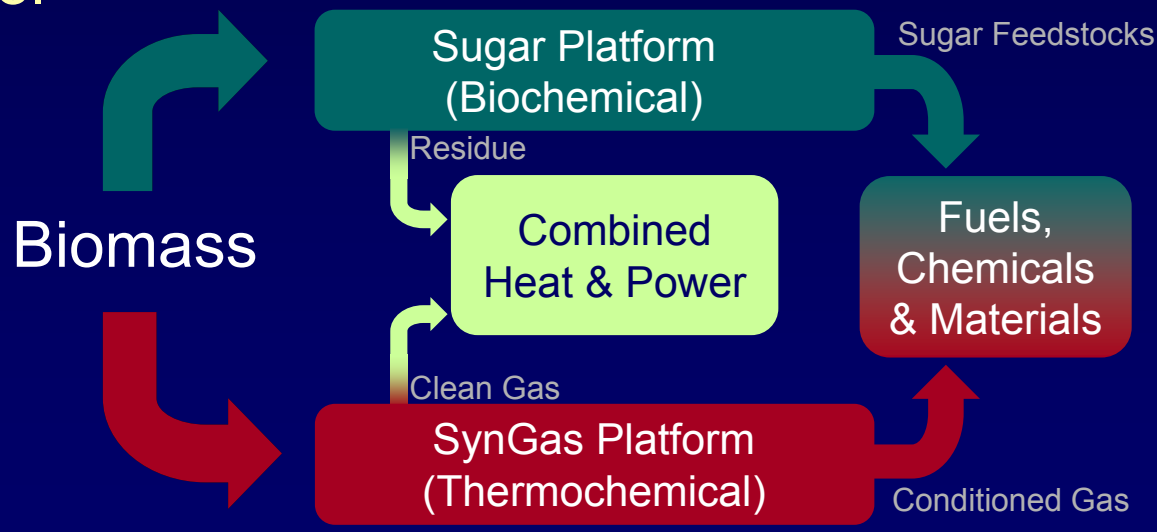
- 75% of biomass is converted to liquid product (bio-oil)
- Secondary products
  - Gas products (mainly CO) ~ 8-10% wt
  - Coke ~ 15% wt
- Parameters affecting bio-oil yield
  - Catalyst (activity)
  - Pyrolysis temperature
    - » Higher temperatures give lower bio-oil yields
- Bio-oil properties
  - Higher density, low flash point, lower viscosity

What is a Biorefinery?

- Production facility which integrates biomass conversion processes to produce fuels, energy and chemicals
  - Takes advantage of differences of biomass components and intermediates to maximize value derived from biomass feedstock
  - Parallel production of chemicals and fuels
  - Energy production (for internal usage or for sale as electricity)
- Specialized according to Biomass type
  - Include similar processes
    - » Ex. forest biorefineries

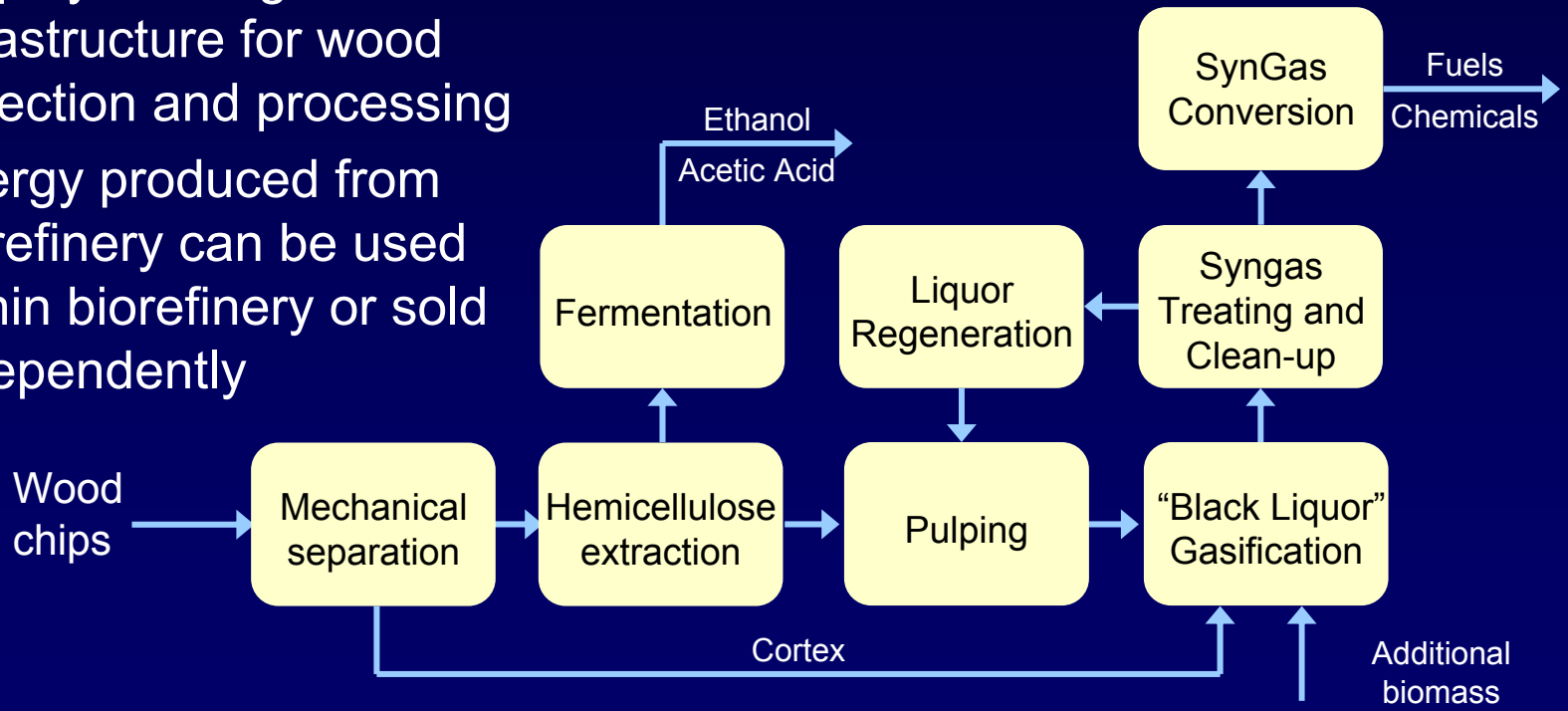
Typical Biorefineries

- Transform main cellulose and semi-cellulose ingredients into sugars, which undergo fermentation
- Process large biomass quantities
  - Up to 240 tons/day
- Do not generate excess pollutants
- Mainly produce ethanol
- Produced SynGas can be further processed for other biofuels production

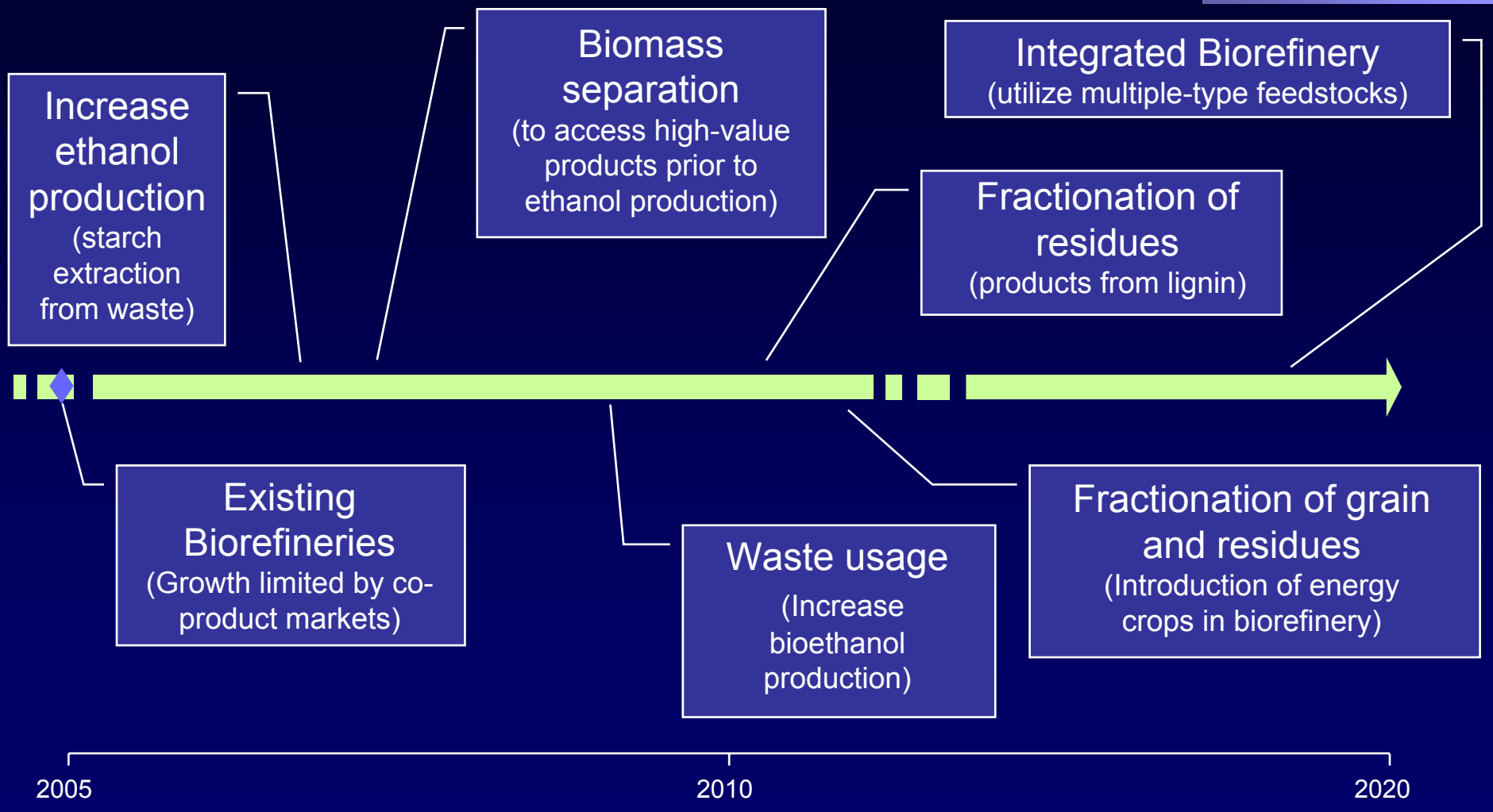


Forest Biorefineries

- Included in paper industry plants
  - Presently paper industry waste (40-60% biomass of forestry origin) is used as burning fuel
  - Employ existing infrastructure for wood collection and processing
  - Energy produced from biorefinery can be used within biorefinery or sold independently



Biorefinery Development



Source: US Department of Energy

"The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as the petroleum and coal tar products of the present time"

Rudolph Diesel, 1912

Integrated Biorefinery