FUTURE ENERGY AND CHEMICALS FROM BIO-BASED FEEDSTOCKS:

CATALYTIC CHALLENGES AND OPPORTUNITIES

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Catalysis and Alternative Feedstocks for the Biofuels Industry"
A New Industrial Chemistry and Engineering (NIChE) Workshop
by the Council for Chemical Research
September 21 - 22, 2011, University of Delaware Campus, Newark, DE

DEFINITIONS AND CAUTIONARY NOTE

Reserves: Our use of the term "reserves" in this presentation means SEC proved oil and gas reserves for all 2009 data, and includes both SEC proved oil and gas reserves and SEC proven mining reserves for 2007 and 2008 data.
Resources: Our use of the term "resources" in this presentation includes quantities of oil and gas not yet classified as SEC proved oil and gas reserves or SEC proven mining reserves. Resources are consistent with the Society of Petroleum Engineers 2P and 2C definitions.
Organic: Our use of the term Organic includes SEC proved oil and gas reserves and SEC proven mining reserves (for 2007 and 2008) excluding changes resulting from acquisitions, divestments and year-end pricing impact.
To facilitate a better understanding of underlying business performance, the financial results are also presented on an estimated current cost of supplies (CCS) basis as applied for the Oil Products and Chemicals segment earnings. Earnings on an estimated current cost of supplies basis provides useful information concerning the effect of changes in the cost of supplies on Royal Dutch Shell's results of operations and is a measure to manage the performance of the Oil Products and Chemicals segments but is not a measure of financial performance under IFRS.

The companies in which Royal Dutch Shell plc directly and indirectly owns investments are separate entities. In this presentation "Shell", "Shell group" and "Royal Dutch Shell" are sometimes used for convenience where references are made to Royal Dutch Shell plc and its subsidiaries in general. Likewise, the words "we", "us" and "our" are also used to refer to subsidiaries in general or to those who work for them. These expressions are also used where no useful purpose is served by identifying the particular company or companies. ''Subsidiaries'', "Shell subsidiaries" and "Shell companies" as used in this presentation refer to companies in which Royal Dutch Shell either directly or indirectly has control, by having either a majority of the voting rights or the right to exercise a controlling influence. The companies in which Shell has significant influence but not control are referred to as "associated companies" or "associates" and companies in which Shell has joint control are referred to as "jointly controlled entities". In this presentation, associates and jointly controlled entities are also referred to as "equity-accounted investments". The term "Shell interest" is used for convenience to indicate the direct and/or indirect (for example, through our 34% shareholding in Woodside Petroleum Ltd.) ownership interest held by Shell in a venture, partnership or company, after exclusion of all third-party interest.

This presentation contains forward-looking statements concerning the financial condition, results of operations and businesses of Royal Dutch Shell. All statements other than statements of historical fact are, or may be deemed to be, forward-looking statements. Forward-looking statements are statements of future expectations that are based on management's current expectations and assumptions and involve known and unknown risks and uncertainties that could cause actual results, performance or events to differ materially from those expressed or implied in these statements. Forward-looking statements include, among other things, statements concerning the potential exposure of Royal Dutch Shell to market risks and statements expressing management's expectations, beliefs, estimates, forecasts, projections and assumptions. These forward-looking statements are identified by their use of terms and phrases such as ''anticipate'', ''believe'', ''could'', ''estimate'', ''expect'', ''intend'', ''may'', ''plan'', ''objectives'', ''outlook'', ''probably'', ''project'', ''will'', ''seek'', ''target'', ''risks'', ''goals'', ''should'' and similar terms and phrases. There are a number of factors that could affect the future operations of Royal Dutch Shell and could cause those results to differ materially from those expressed in the forward-looking statements included in this presentation, including (without limitation): (a) price fluctuations in crude oil and natural gas; (b) changes in demand for the Shell's products; (c) currency fluctuations; (d) drilling and production results; (e) reserve estimates; (f) loss of market share and industry competition; (g) environmental and physical risks; (h) risks associated with the identification of suitable potential acquisition properties and targets, and successful negotiation and completion of such transactions; (i) the risk of doing business in developing countries and countries subject to international sanctions; (j) legislative, fiscal and regulatory developments including regulatory measures addressing climate change; (k) economic and financial market conditions in various countries and regions; (l) political risks, including the risks of expropriation and renegotiation of the terms of contracts with governmental entities, delays or advancements in the approval of projects and delays in the reimbursement for shared costs; and (m) changes in trading conditions. All forward-looking statements contained in this presentation are expressly qualified in their entirety by the cautionary statements contained or referred to in this section. Readers should not place undue reliance on forward-looking statements. Additional factors that may affect future results are contained in Royal Dutch Shell's 20-F for the year ended December 31, 2009 (available at www.shell.com/investor and www.sec.gov). These factors also should be considered by the reader. Each forward-looking statement speaks only as of the date of this presentation, 24 April 2011 Neither Royal Dutch Shell nor any of its subsidiaries undertake any obligation to publicly update or revise any forward-looking statement as a result of new information, future events or other information. In light of these risks, results could differ materially from those stated, implied or inferred from the forward-looking statements contained in this presentation.

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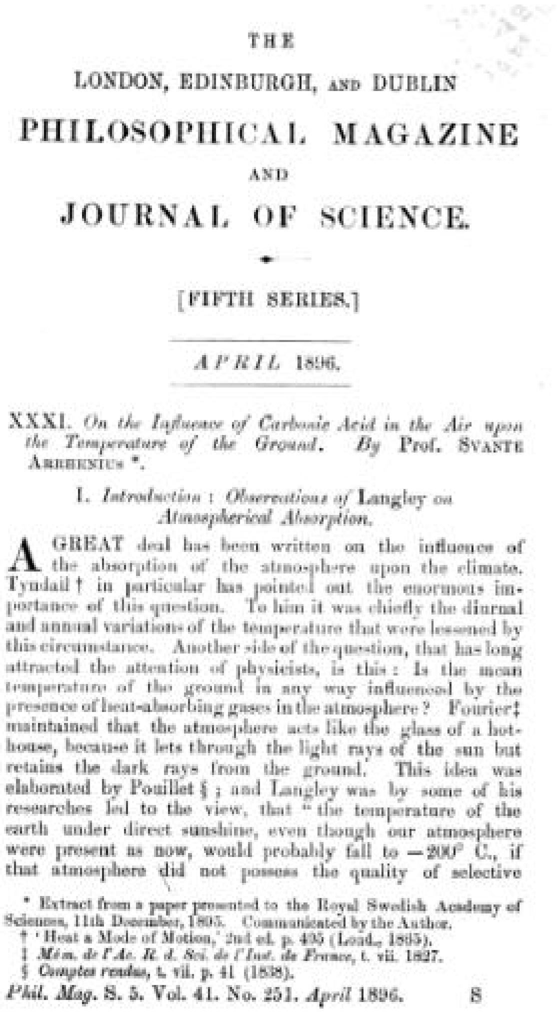
BIOFUELS AND BIO-BASED CHEMICALS

Why?

The way we produce and use energy today is not sustainable

A NEW DIRECTION IS NEEDED

The Effect of CO_2 on Global Temperatures isn't a Recent Discovery!



THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

I. *Introduction : Observations of* Langley *on Atmospherical Absorption.*

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall † in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere? Fourier ‡ maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet § ; and Langley was by some of his researches led to the view, that "the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to −200° C., if that atmosphere did not possess the quality of selective

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* Extract from a paper presented to the Royal Swedish Academy of Sciences, 11th December, 1895. Communicated by the Author.

† 'Heat a Mode of Motion,' 2nd ed. p. 405 (Lond., 1865).

‡ *Mém. de l'Ac. R. d. Sci. de l'Inst. de France*, t. vii. 1827.

§ *Comptes rendus*, t. vii. p. 41 (1838).

Phil. Mag. S. 5. Vol. 41. No. 251. *April* 1896. 8

- Svante Arrhenius, 1896

"For us, as a company, the debate about whether man-made climate change is happening is over.

The debate now is about what we can do about it. Businesses, like ours, need to turn CO_2 management into a business opportunity by leading the search for responsible ways to manage CO_2, and use energy more efficiently. But that also requires concerted action by governments to create the long-term, market-based policies needed to make it worthwhile for companies to invest.

With fossil fuel use and CO_2 levels continuing to grow fast, there is no time to lose."

Shell's position on Climate Change

- Among first energy companies to acknowledge the threat of climate change
  - —Take action ourselves!
  - —Call for coordinated action by governments, industry and energy users

- Technology is a key enabler:
  - —reduce CO2 emissions
  - —Capture and sequester CO_2 from current energy systems & technology

http://www.shell.com/home/content/responsible_energy/environment/climate_change/

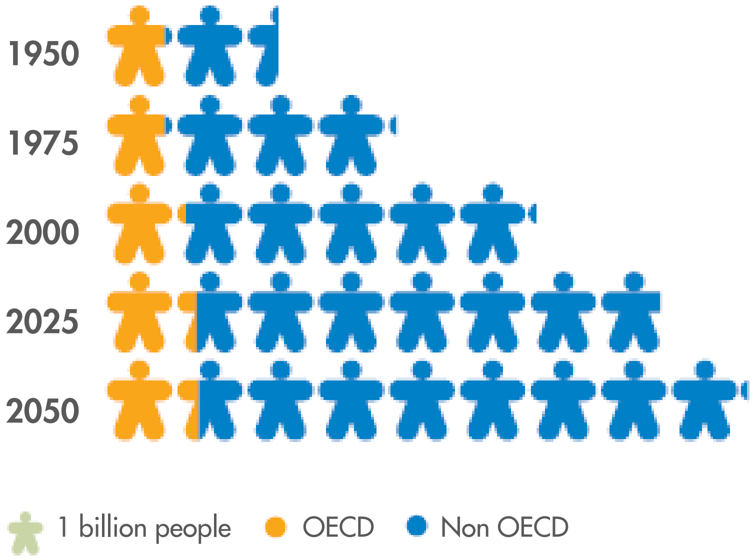
THE ENERGY CHALLENGE

Global demand for energy is growing.

Supplies of “easy oil cannot keep up with demand growth.

More energy means more CO_2 emitted at a time when climate change looms as a critical global issue

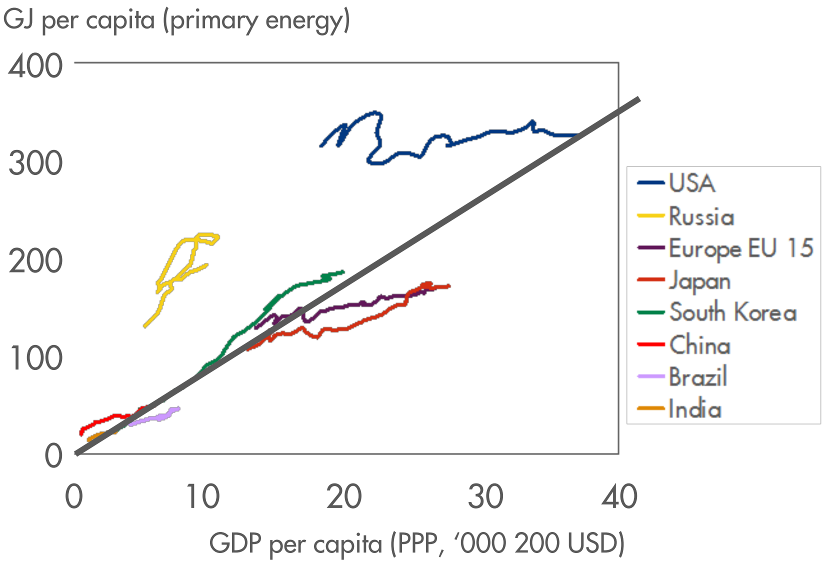
World population



Source: UN Population Division

Copyright of Royal Dutch Shell plc

Climbing the energy ladder

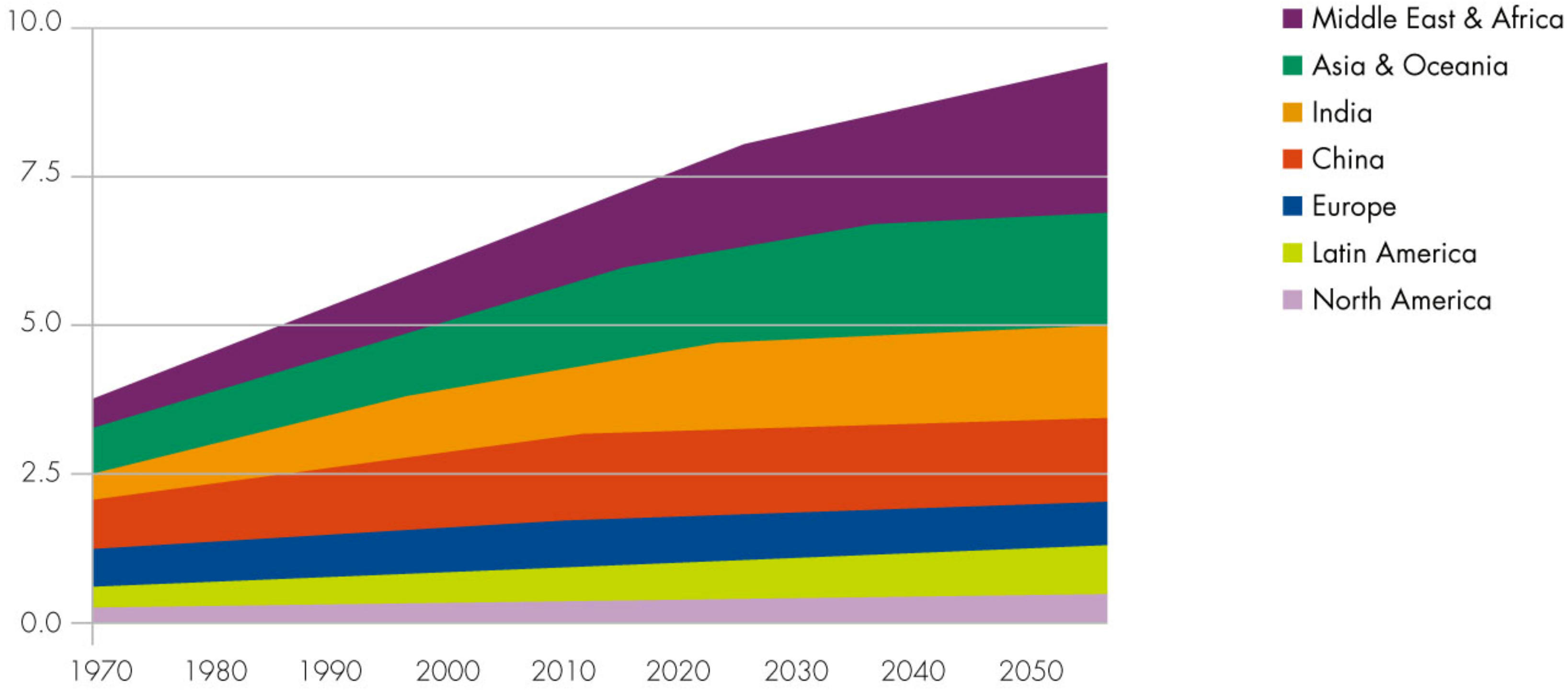


Data shown 1970-2005

Source: Energy Balances of OECD and Non-OECD Countries © OECD / IEA 2006

INCREASING POPULATION IS A KEY DRIVER OF ENERGY DEMAND

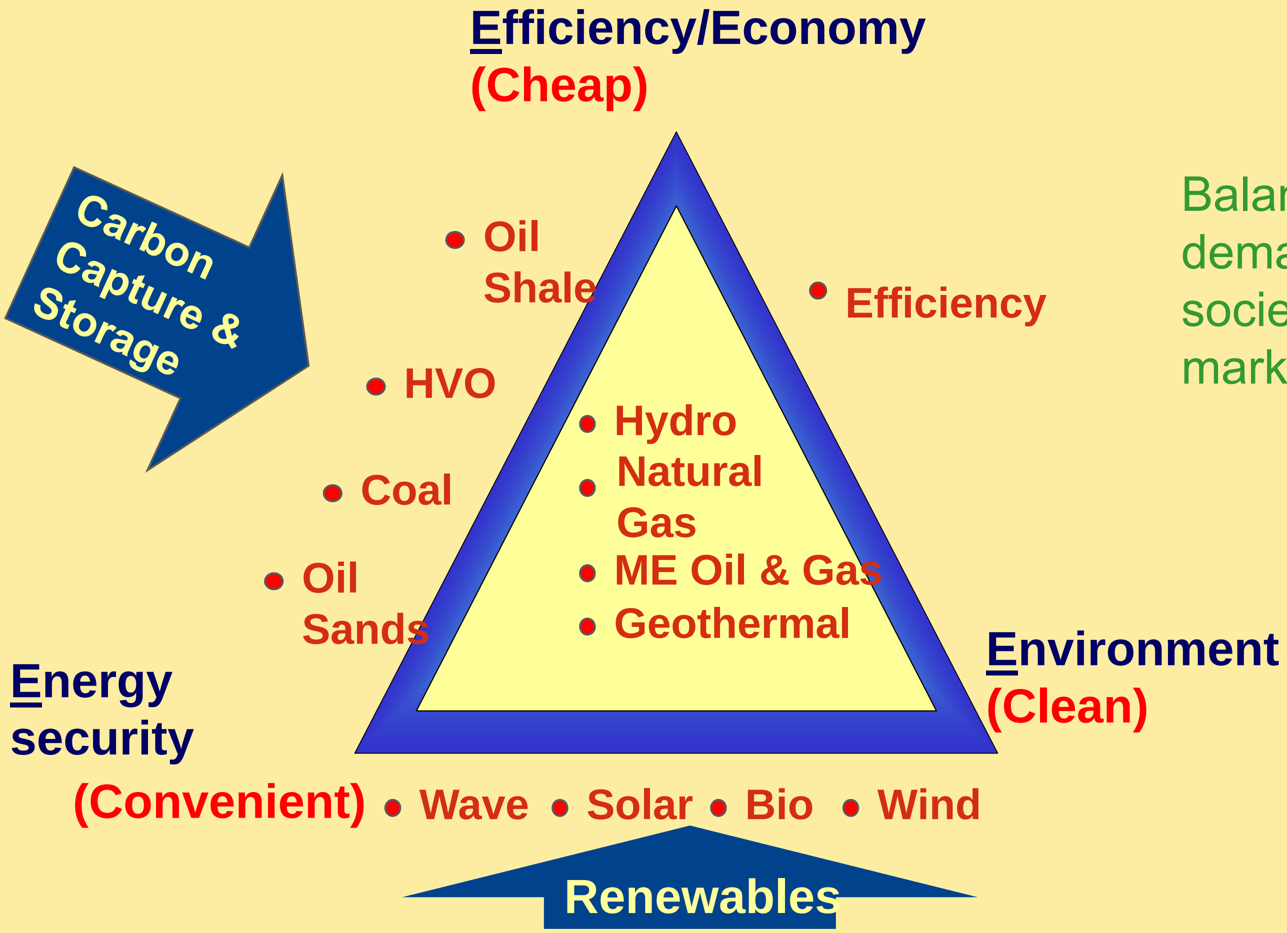
BILLION PEOPLE



Source United Nations Population Division, 2004 Revision

The Energy Challenge Trilemma:
Chemical Engineering is at forefront in providing systems solutions!

The “three Cs” or “three E’s”



Efficiency/Economy
(Cheap)

Carbon Capture & Storage

- **Oil Shale**
- **HVO**
- **Coal**
- **Oil Sands**

- **Efficiency**

- **Hydro**
- **Natural Gas**
- **ME Oil & Gas**
- **Geothermal**

Energy security
(Convenient)

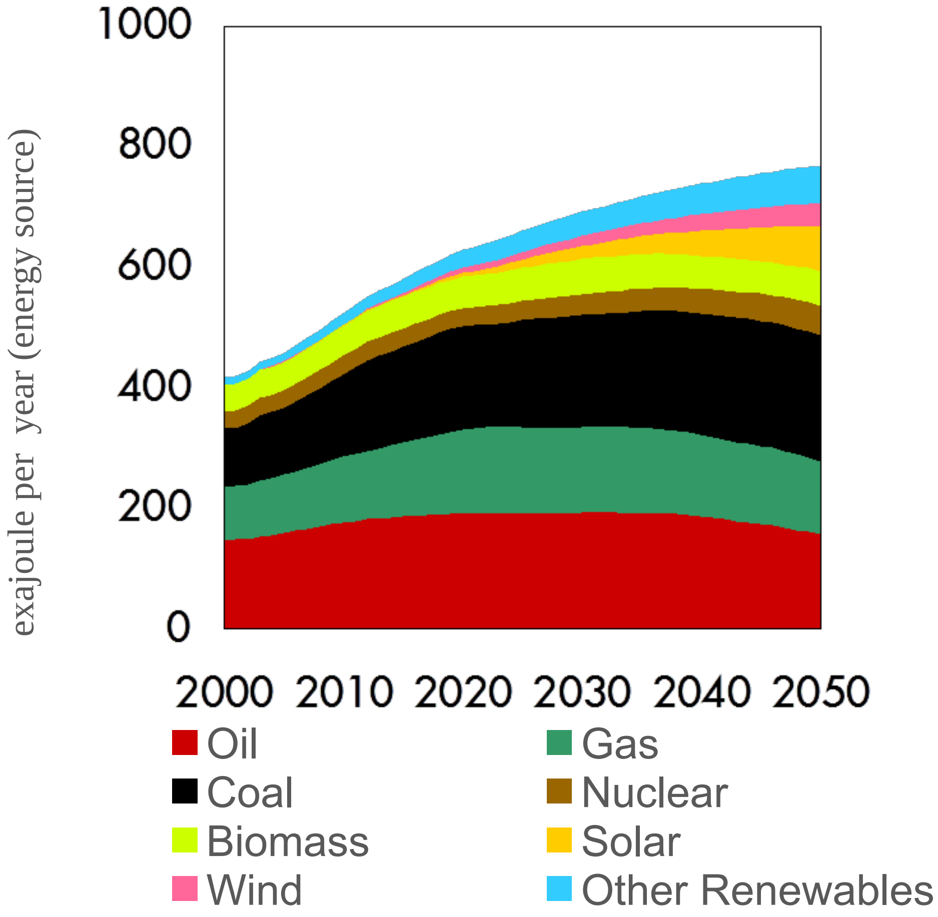
Environment
(Clean)

- **Wave**
- **Solar**
- **Bio**
- **Wind**

Renewables

Balancing demands of society and markets

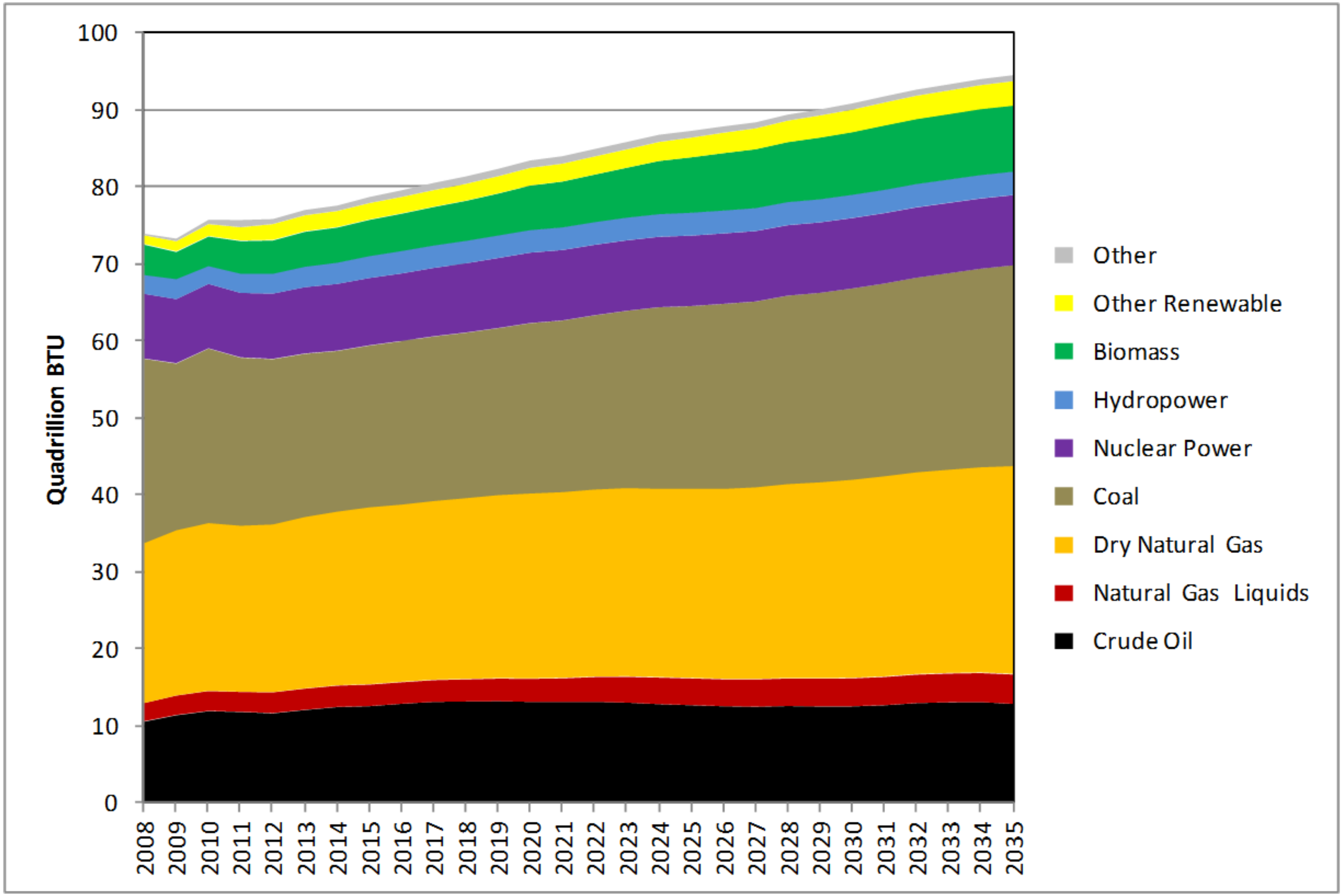
Shell "Blueprints" Scenario: What This Means for Energy


Total primary energy supply/demand

- Broader anticipation of challenges
- Critical mass of parallel responses to hard truths
- Effective carbon pricing established early
- Aggressive efficiency standards
- Growth shifts to electrification
- New infrastructure develops
- CCS emerges after 2020

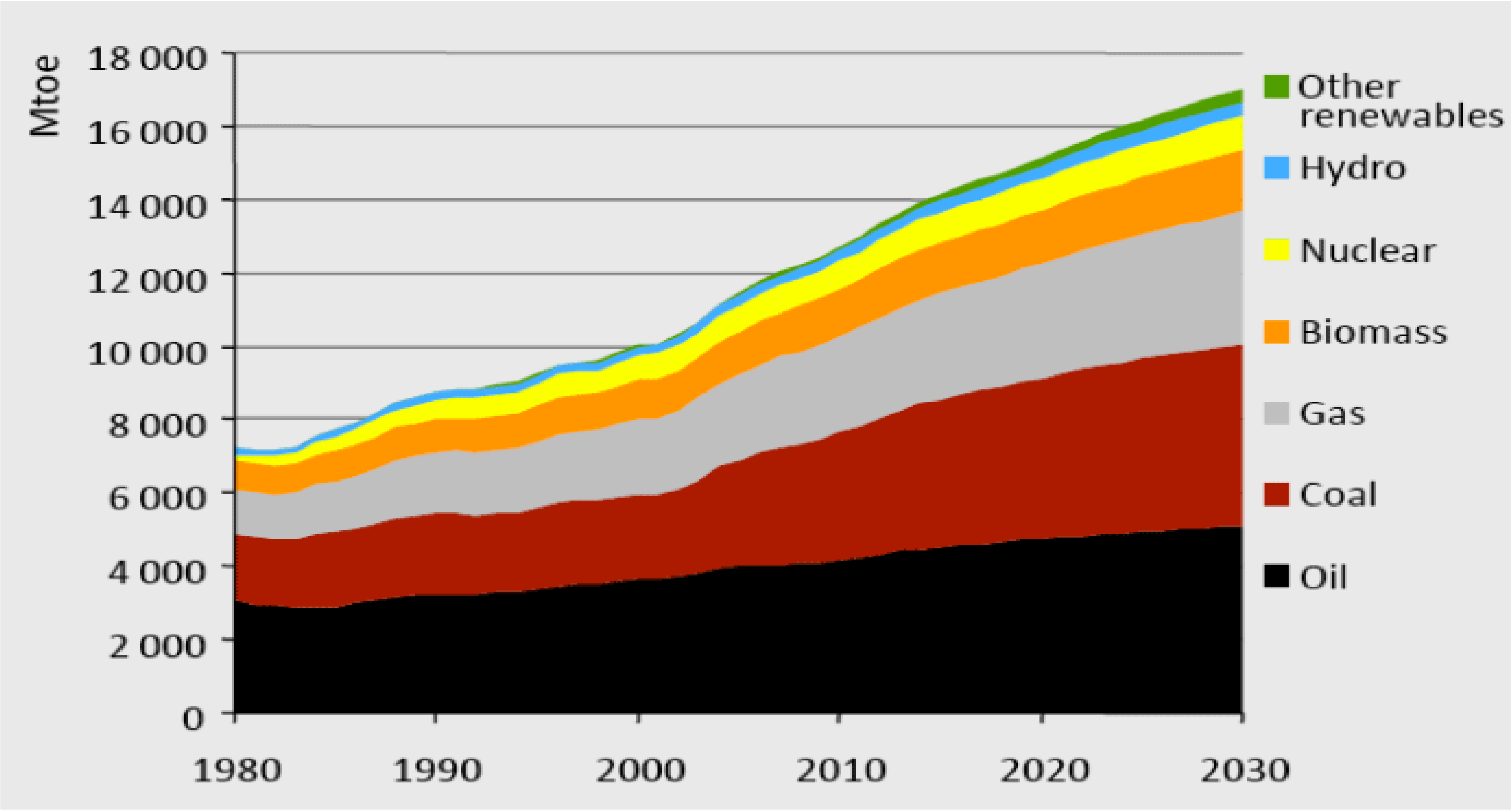
Source: Shell International BV and Energy Balances of OECD and Non-OECD Countries©OECD/IEA 2006

Future Energy Supply for US (predicted)



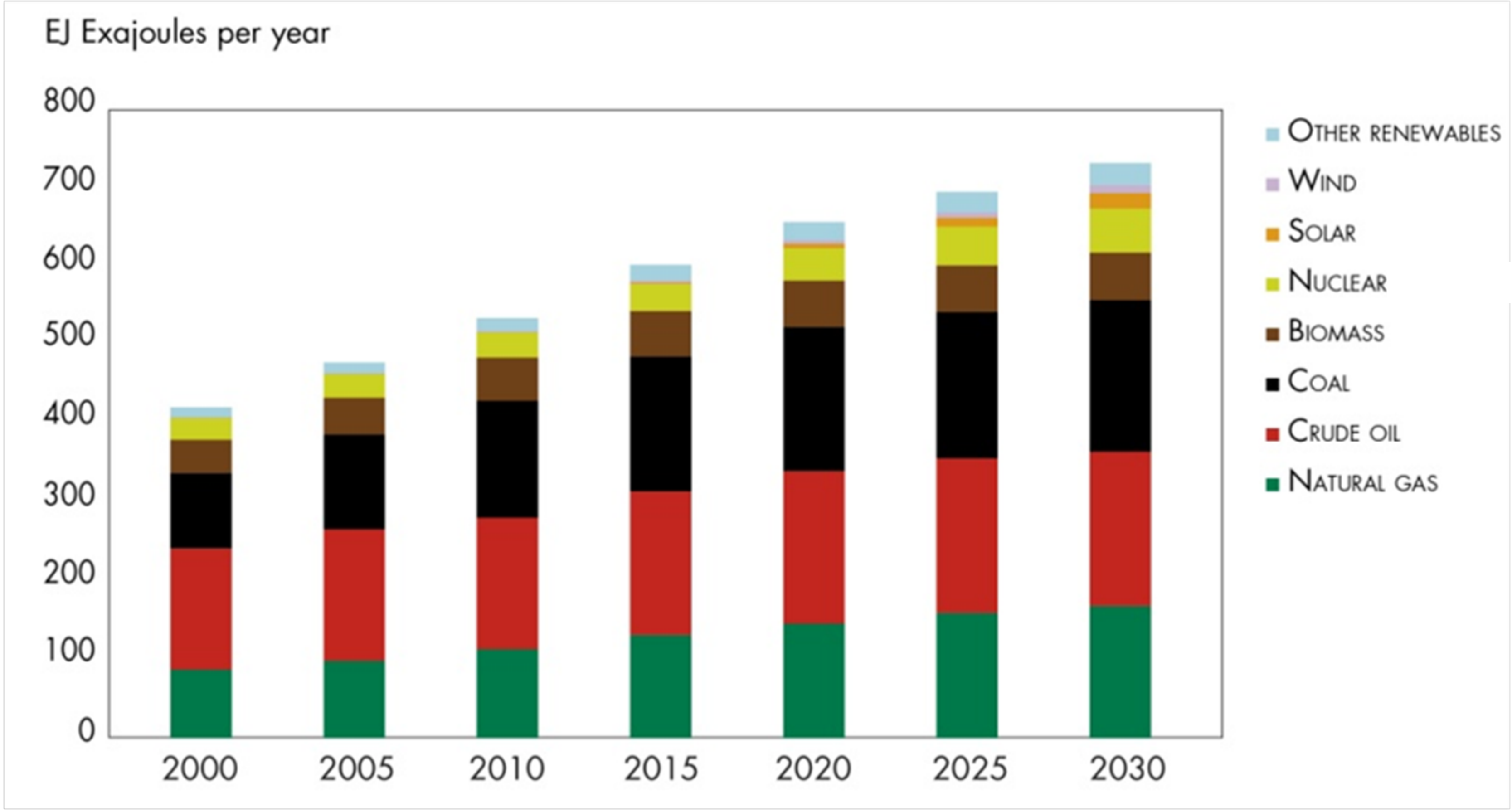
U.S. DOE, Biomass Multi-Year Program Plan, April 2011

Shell Scenarios: future global energy supply



From Warren Fernandez 2011

Global: Total Primary Energy to 2030

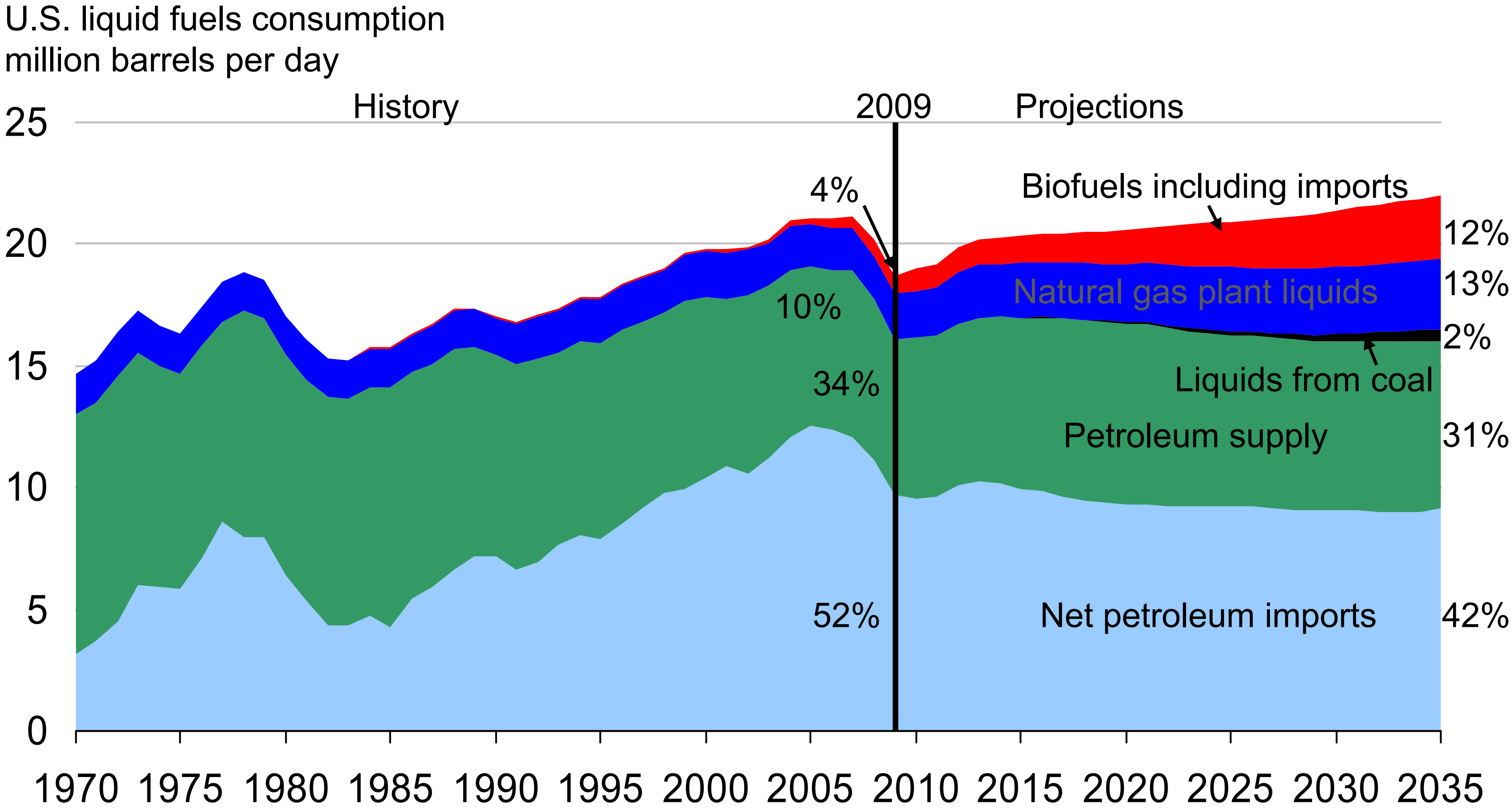


Shell Energy Scenarios to 2050 www.Shell.com

NO SINGLE ALTERNATIVE TO OIL BASED ROAD TRANSPORT FUELS

- All fuel options will be needed
- Countries and regions will choose portfolios of fuel solutions based on cost, security of supply, existing infrastructure and CO_2 emissions
- Not just fuels: Improvements in CO_2 emissions through vehicle efficiency, fuel technology and driving habits
- The internal combustion engine and liquid fuels will continue to play an important role
- Electric and hydrogen will play an important role if technical and infrastructure challenges can be overcome
- Natural gas will continue to find a niche in local markets

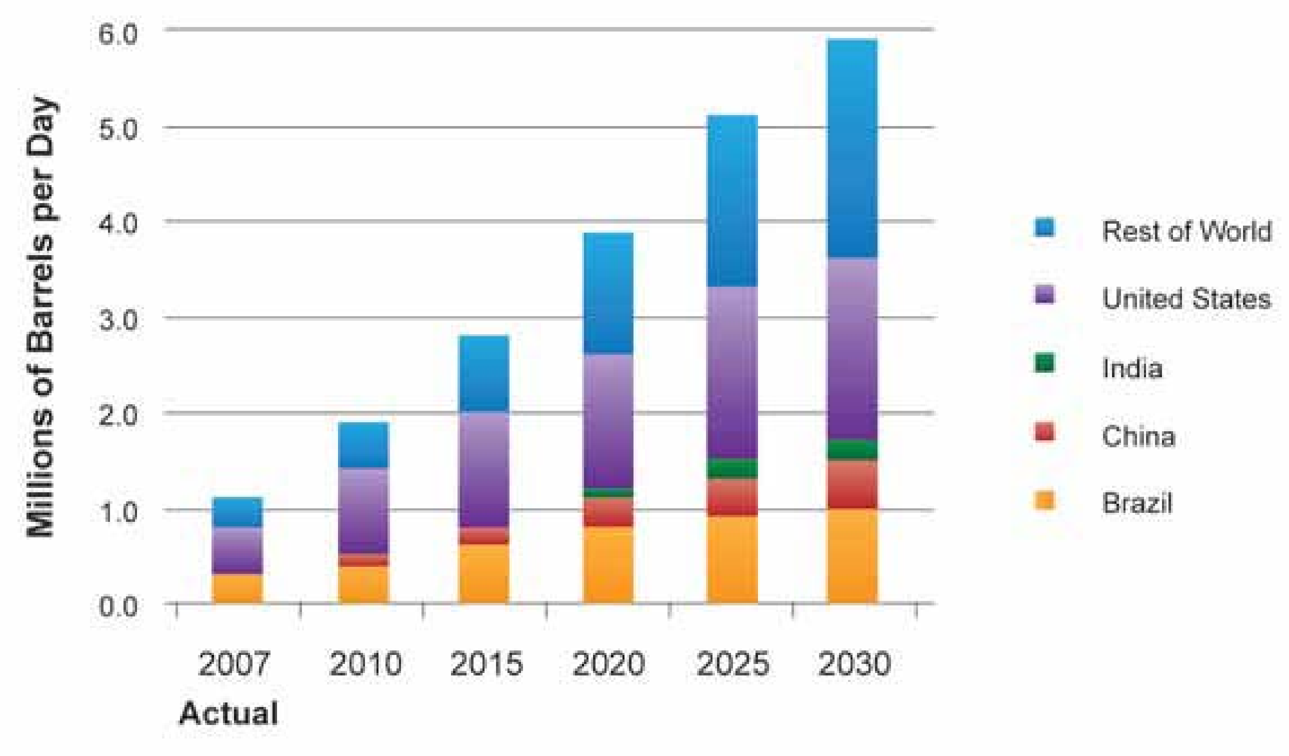
U.S. imports of liquid fuels fall due to increased domestic production—including biofuels—and greater fuel efficiency



Richard Newell, December 16, 2010

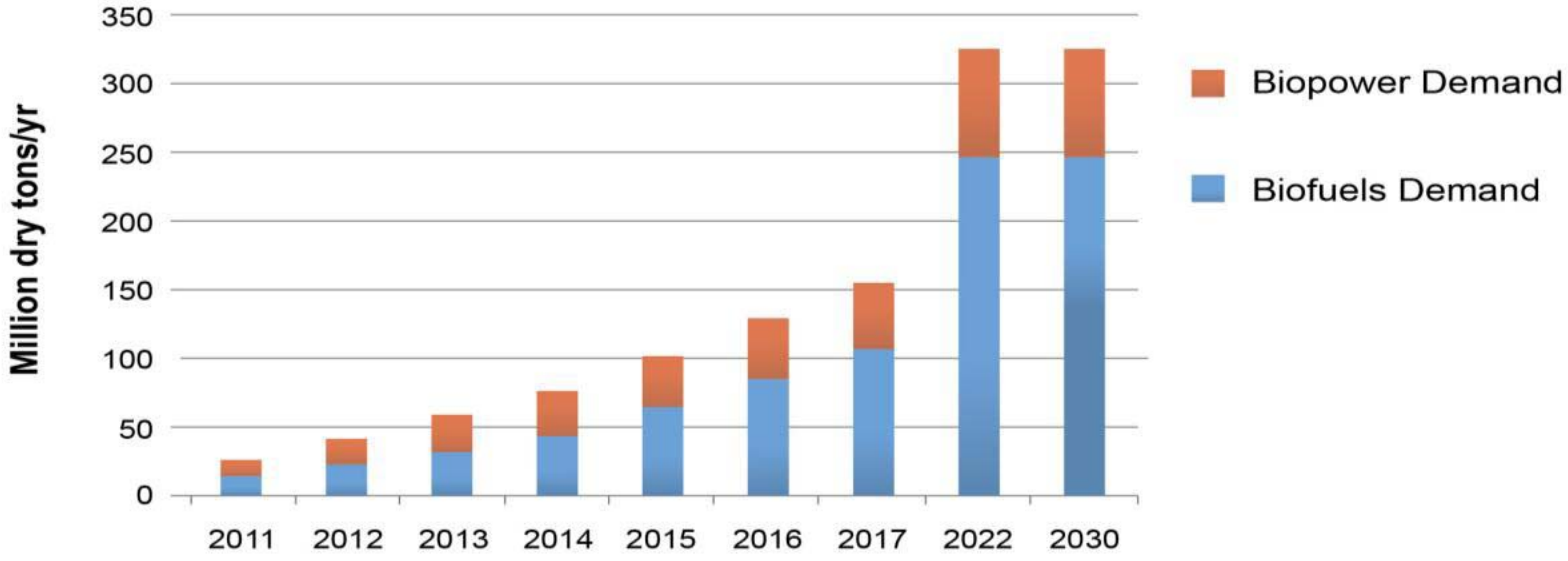
Source: EIA, *Annual Energy Outlook 2011*

Global Production of Biofuels



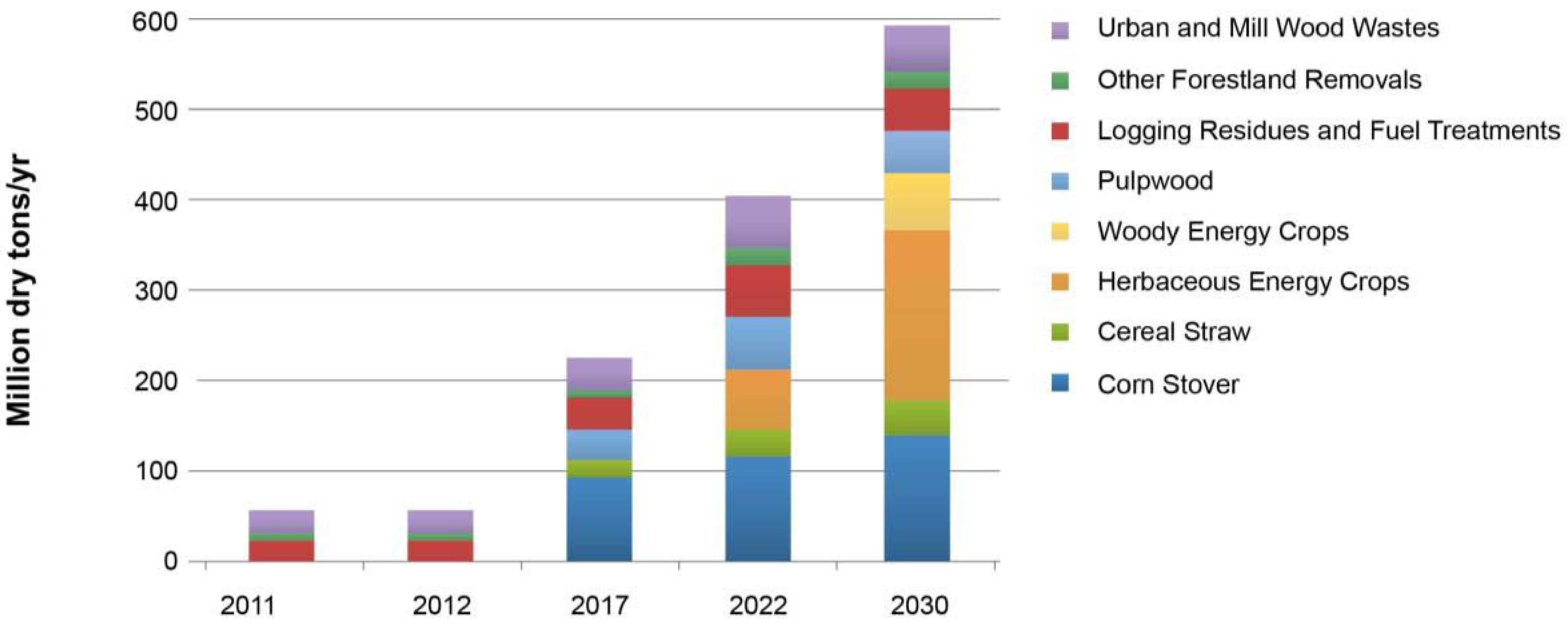
- U.S. DOE, Biomass Multi-Year Program Plan, April 2011
- Biofuels, Biopower, and Bioproducts: Integrated Biorefineries , Description An overview of integrated biorefineries and Biomass Program efforts to develop, build, operate, and validate integrated biorefineries on various scales. www.eere.energy.gov/biomass/pdfs/ibr_portfolio_overview.pdf .

US Bioenergy Demand



U.S. DOE, Biomass Multi-Year Program Plan, April 2011

Projected Feedstock Availability at Specified Minimum Grower Payments



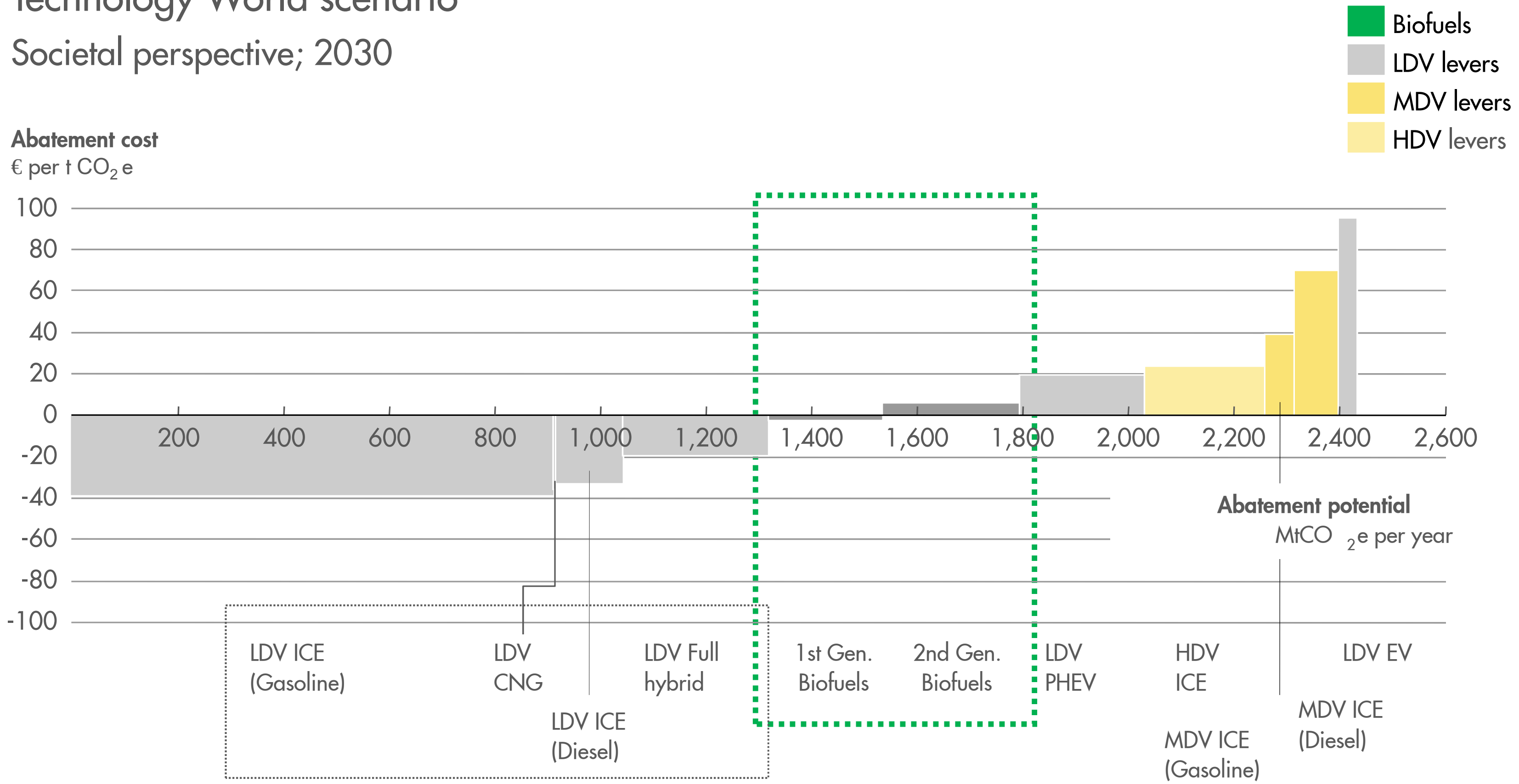
U.S. DOE, Biomass Multi-Year Program Plan, April 2011

BIOFUELS VS. ENERGY EFFICIENCY: REDUCING CO_2 EMISSIONS TODAY

- Today's biofuels are the most realistic commercial solution to take CO_2 out of the transport fuels sector over the next twenty years

Global CO_2 abatement cost curve for the Road Transport sector - Mix Technology World scenario

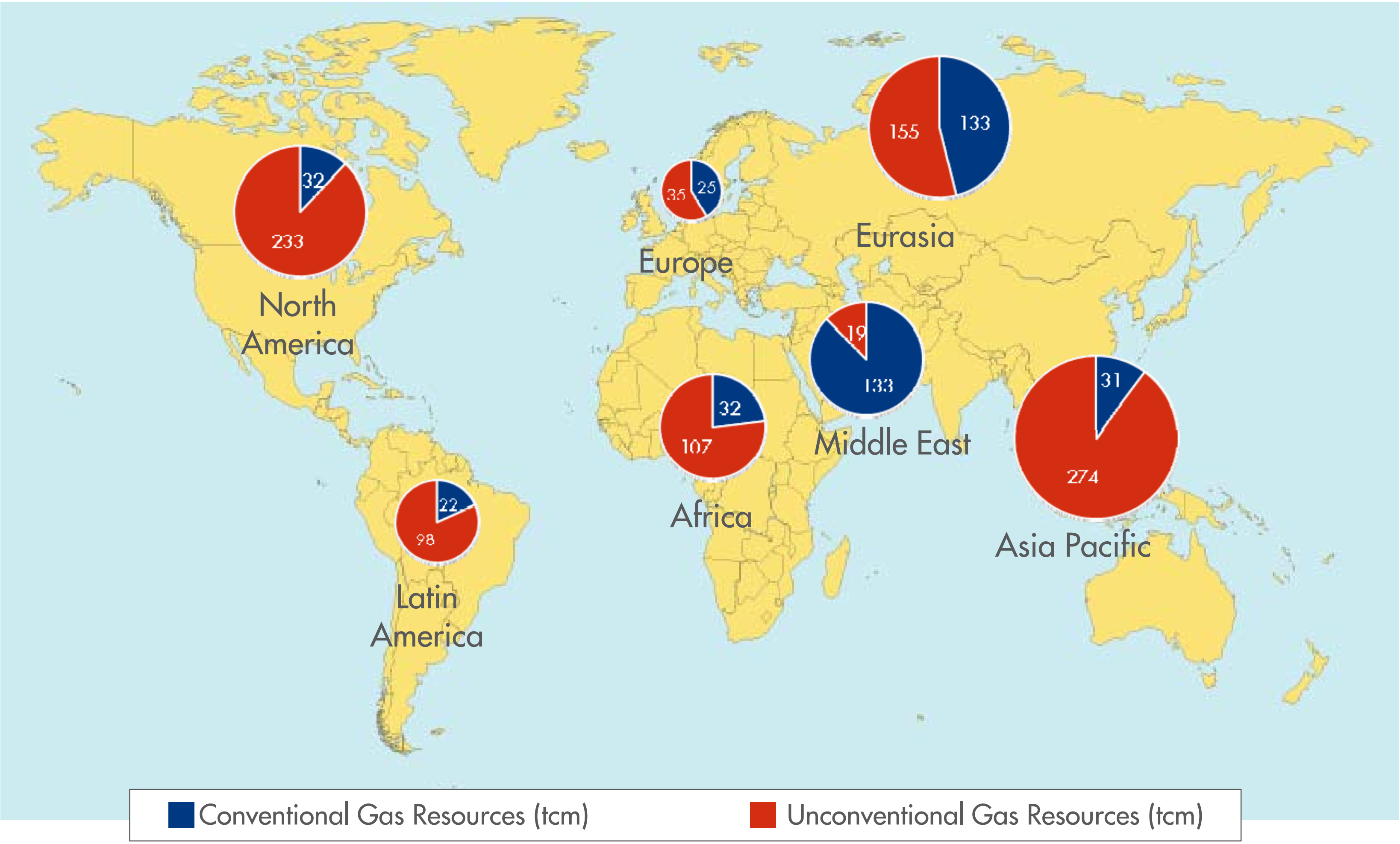
Societal perspective; 2030



Note: The curve presents an estimate of the maximum potential of all technical GHG abatement measures below €100 per t CO_2e in a penetration scenario if each lever was pursued aggressively. It is not a forecast of what role different abatement measures and technologies will play.

Source: Global GHG Abatement Cost Curve v2.0

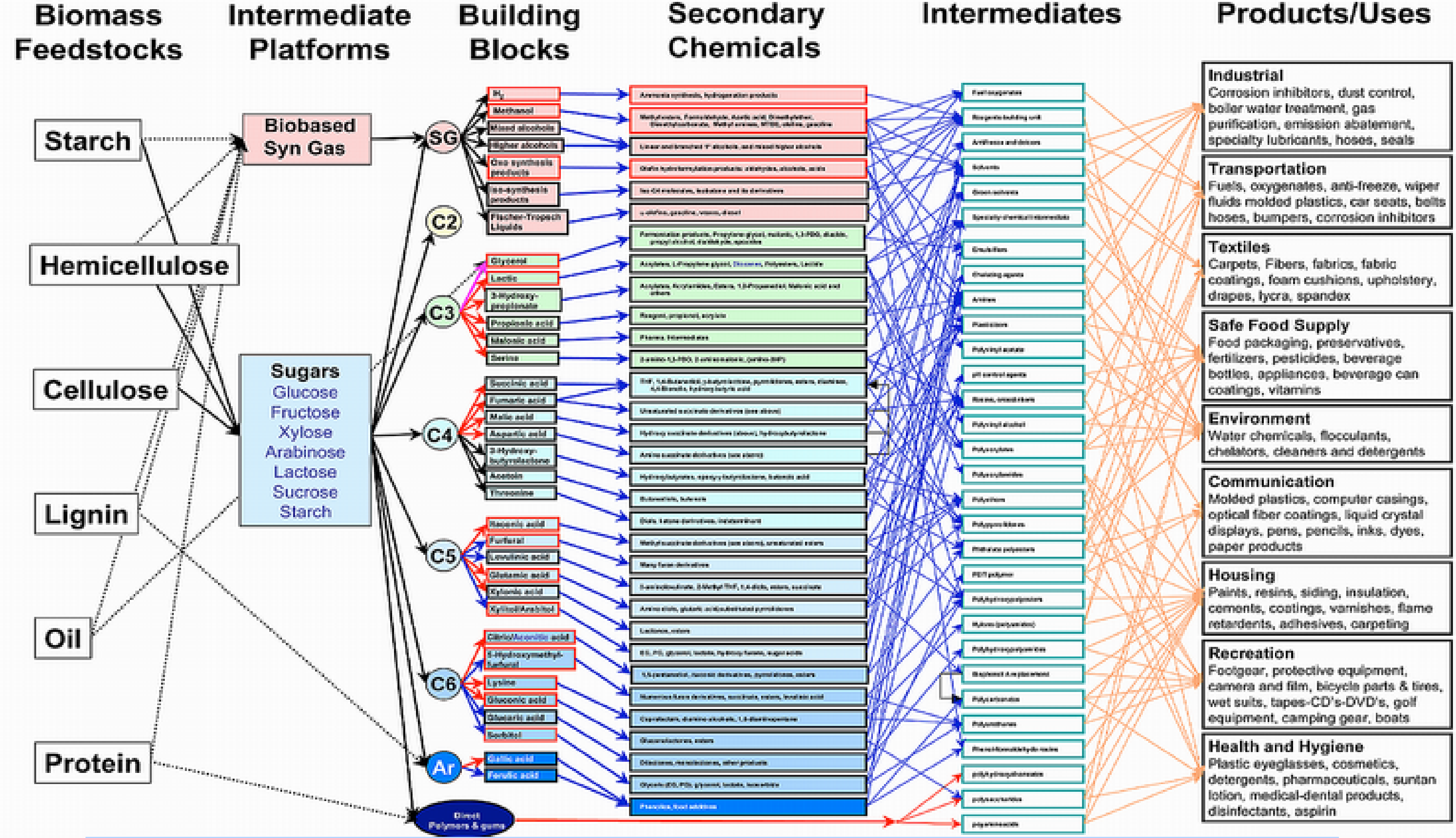
Alternatives: Natural Gas is Abundant: Huge Global Resources



IEA estimates 250 years global supply at current production levels

Source: IEA World Energy Outlook, WoodMackenzie, Shell Interpretation

Multiple routes to Chemicals from Bio-Based feedstocks



Industrial
Corrosion inhibitors, dust control, boiler water treatment, gas purification, emission abatement, specialty lubricants, hoses, seals

Transportation
Fuels, oxygenates, anti-freeze, wiper fluids molded plastics, car seats, belts hoses, bumpers, corrosion inhibitors

Textiles
Carpets, Fibers, fabrics, fabric coatings, foam cushions, upholstery, drapes, lycra, spandex

Safe Food Supply
Food packaging, preservatives, fertilizers, pesticides, beverage bottles, appliances, beverage can coatings, vitamins

Environment
Water chemicals, flocculants, chelators, cleaners and detergents

Communication
Molded plastics, computer casings, optical fiber coatings, liquid crystal displays, pens, pencils, inks, dyes, paper products

Housing
Paints, resins, siding, insulation, cements, coatings, varnishes, flame retardents, adhesives, carpeting

Recreation
Footgear, protective equipment, camera and film, bicycle parts & tires, wet suits, tapes-CD's-DVD's, golf equipment, camping gear, boats

Health and Hygiene
Plastic eyeglasses, cosmetics, detergents, pharmaceuticals, suntan lotion, medical-dental products, disinfectants, aspirin

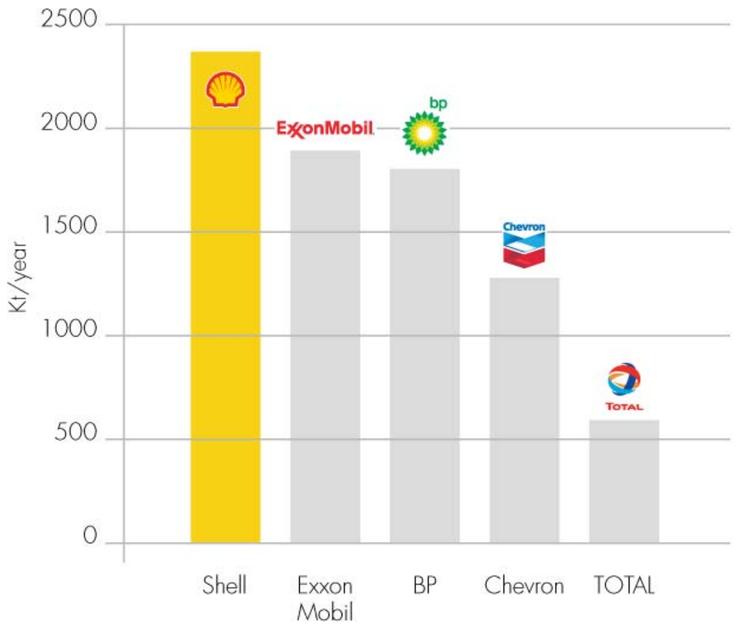
•Top Value Added Chemicals from Biomass: Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas Produced by the Staff at Pacific Northwest National Laboratory (PNNL) National Renewable Energy Laboratory (NREL) Office of Biomass Program (EERE) For the Office of the Biomass Program T. Werpy and G. Petersen, Editors, August 2004.

Advantaged chemicals production derived from fuels feedstocks.

Shell: BIO-FUELS today and future

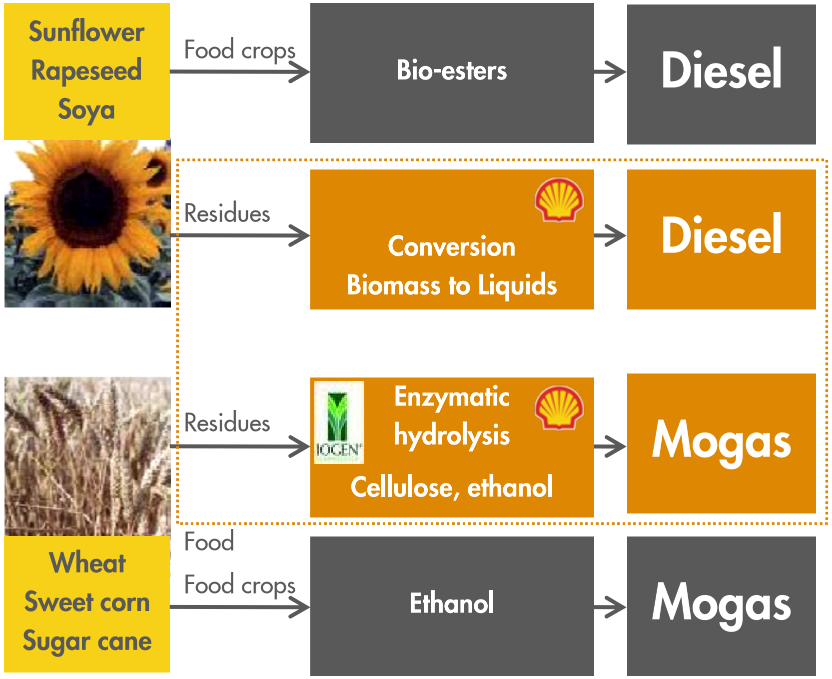
BIOFUELS DISTRIBUTION TODAY

Bio-component Volume
(Ethanol, FAME)
Kt/year



Sources: Shell analysis, EUCAR/JRC/CONCAWE

Advanced biofuels deliver substantial CO_2 benefits and use residues not food crop



Sunflower
Rapeseed
Soya

Food crops → **Bio-esters** → **Diesel**

Residues → **Conversion Biomass to Liquids** → **Diesel**

Residues → **Enzymatic hydrolysis Cellulose, ethanol** → **Mogas**

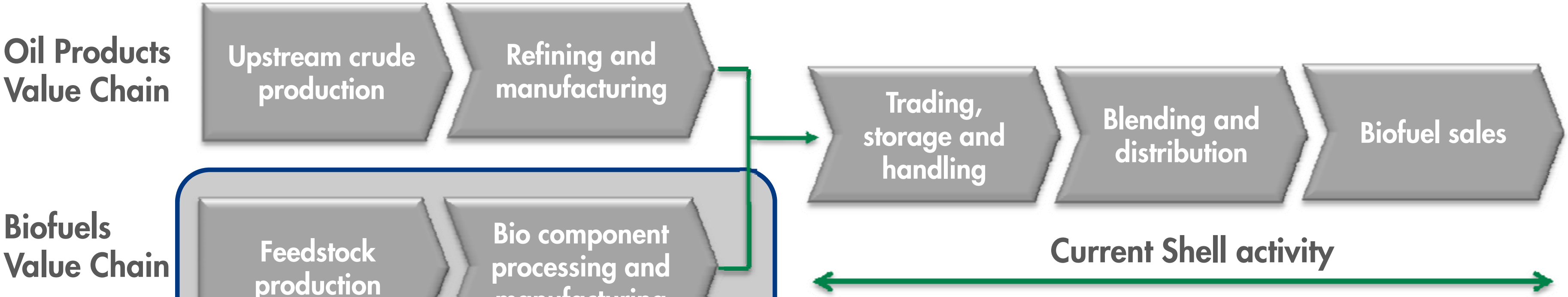
Wheat
Sweet corn
Sugar cane

Food
Food crops → **Ethanol** → **Mogas**

IOGEN L-C ETHANOL
VIRENT™ "BIOFORMING"
Codexis: ENZYMES
COSAN RAIZEN

SHELL: A LEADER IN TODAY'S BIOFUELS

- 30-year history of biofuels development and investment
- Growing investment in infrastructure to store, blend and distribute biofuels
- World's largest distributor of biofuels – 9.6 billion litres in 2010
- Recently moved into the production of conventional biofuels
- Building capacity in biofuels that provide best combinations of performance and low 'well-to-wheel' CO_2 performance from more sustainable feedstocks



Oil Products Value Chain

Upstream crude production

Refining and manufacturing

Biofuels Value Chain

Feedstock production

Bio component processing and manufacturing

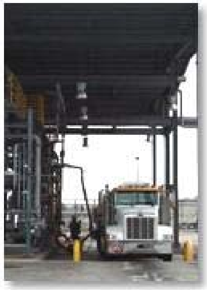
Trading, storage and handling

Blending and distribution

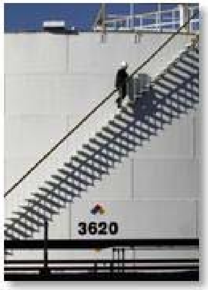
Biofuel sales

Current Shell activity

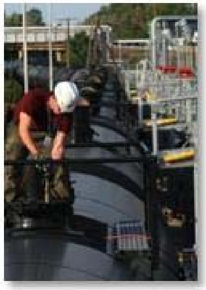
Raizen - (Shell Cosan Joint Venture)



Carson,
Los Angeles



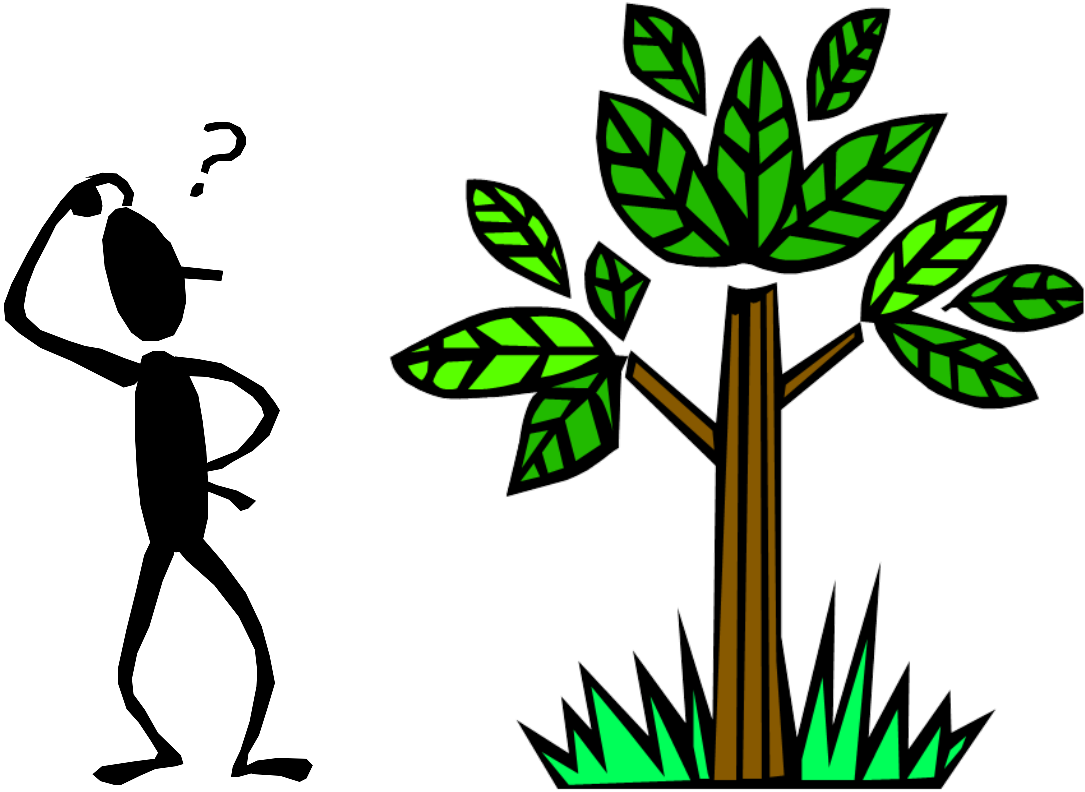
Providence,
Rhode Island



Sewaren,
New Jersey

BIOFUELS AND BIOBASED CHEMICALS

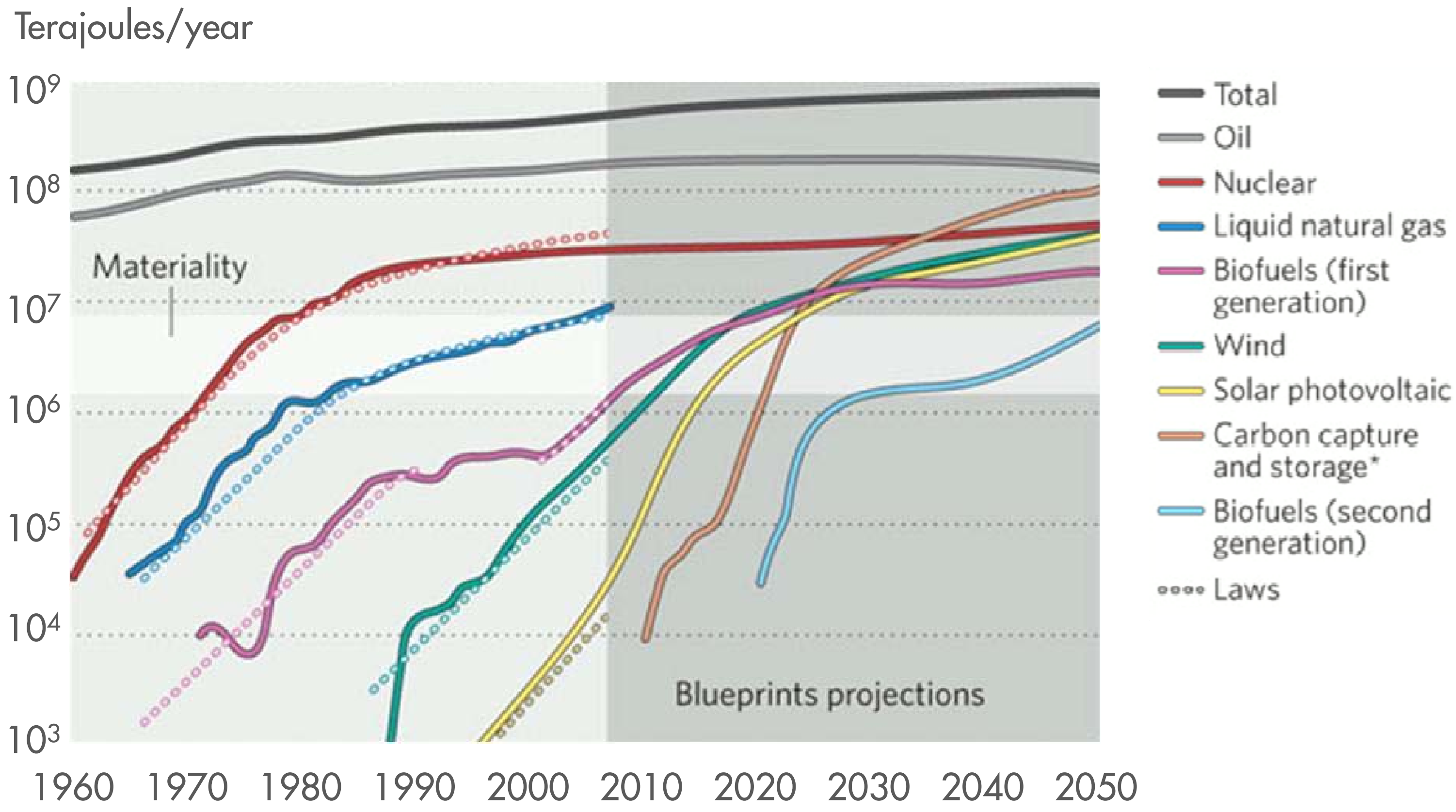
How ?



- *Grand Challenges*

ENERGY TECHNOLOGY CHANGE TAKES TIME

Global production of primary energy sources.

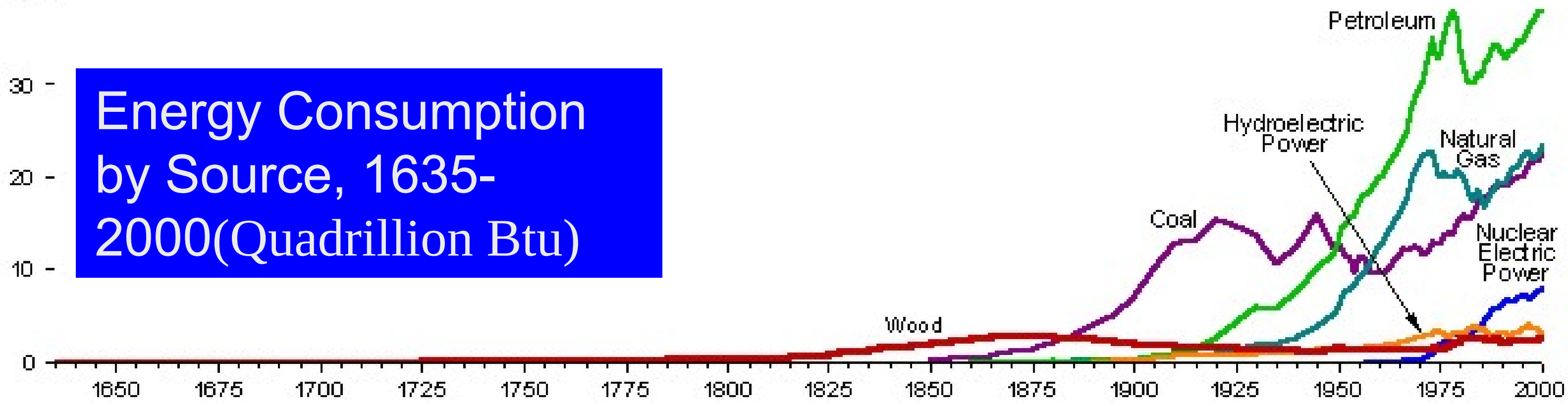


Source: Historic Data: Energy Balances of OECD Cuntries (IEA, 2009), Energy Balanaces of Non-OEDD Countries (IEA, 2009). Projections: Shell International, from the article: *No quick switch to low-carbon* energy by Gert Jan Kramer & Martin Haigh *Nature* 462, 568-569(3 December 2009)

*Coal and natural gas used in power generation with carbon capture and strorage

Challenges: Back to the Future for Energy

http://www.eia.doe.gov/emeu/aer/eh/frame.html



Energy Consumption by Source, 1635-2000(Quadrillion Btu)

Coal replaces woody biomass to start industrial revolution

Steam replaces wind / clipper ships (1850's)

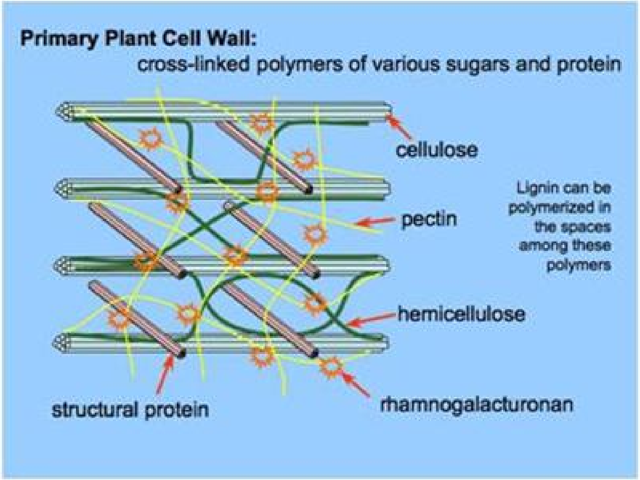
Petroleum replaces coal as preferred transportation fuel (1900's)

Electric / natural gas driers replace the solar clothes drier 1960.

Petroleum & natural gas previously replaced the "alternative energies" now considered as "future energy"!   Replacement was due to economics and convenience!

Bio-Domain Challenges & Opportunities

Sustainable bio-systems, collection, and storage.



Characterization and manipulation of biological systems

Thermo-catalytic & biomolecular conversion of low density feedstocks rich in oxygen and water.

Process design, optimization, and scale up.

TODAY'S ROAD TRANSPORT BIOFUELS

- The most widely used transport biofuels are ethanol and biodiesel
- Ethanol is usually made by fermenting crops high in sugar
- Biodiesel (FAME) is made from vegetable oil crops through transesterification
- Hydro-treating (HVO) uses a different process to biodiesel and can be blended at higher concentrations

Bio-based feed

Sugar cane

Corn

Wheat

Rape seed

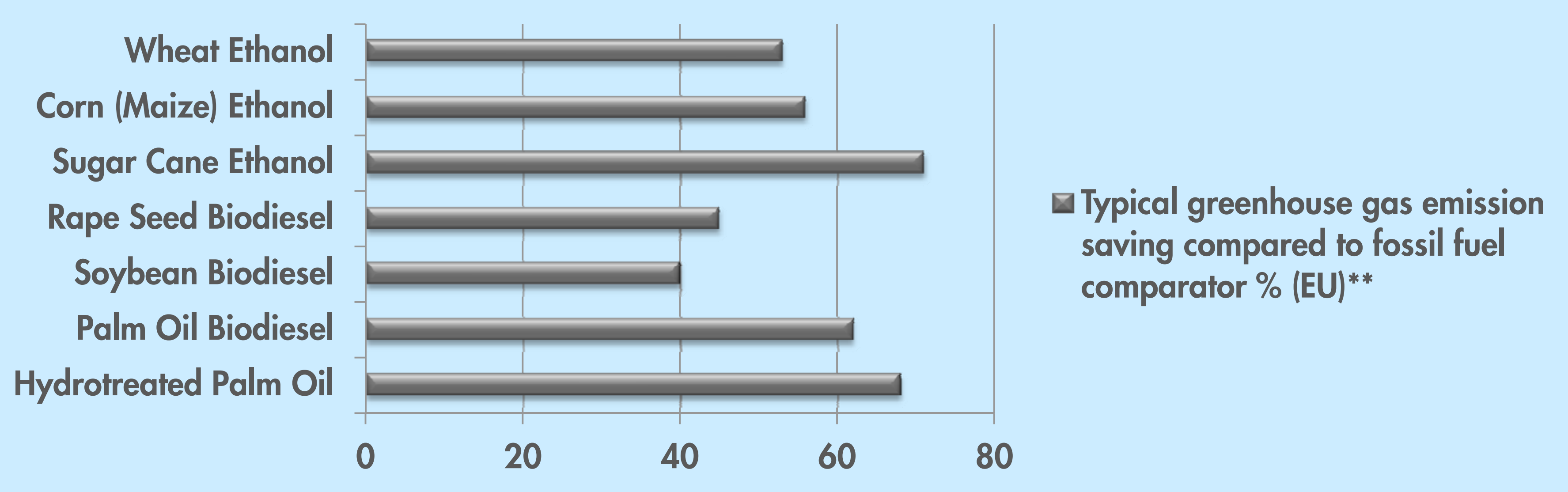
Palm oil

Soya bean

Process	Product
Fermentation	Ethanol (blend with gasoline)
Transesterification	FAME (blend with diesel)
Hydro-treating	HVO (blend with diesel)

BIOFUELS REDUCE CO_2 TODAY AND DIVERSIFY FUEL SUPPLY

- Biofuels are a low 'well-to-wheel'* CO_2 sustainable alternative to gasoline and diesel available today
- But CO_2 emission reductions depend on whole journey to combustion – feedstock production, process used, distribution and use in vehicles
- Biofuels diversify transport fuel pool and offer prospect of improved energy security
- Biofuels can be used in existing liquid transport fuel infrastructure
- For some countries biofuels can offer economic and rural development opportunities



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*Well-to-Wheel CO_2 analysis calculates the CO_2 emissions relating to a particular fuel pathway. The calculation divides the pathway into two parts: (i) 'Well-to-Tank' (WtT) CO_2 emissions – from the production and distribution of the fuel feedstocka and the actual fuel (ii) 'Tank-to-Wheel' CO_2 emissions – from the use of the fuel in the vehicle

** Directive 2009/28/EC of the European Parliament and of the Council

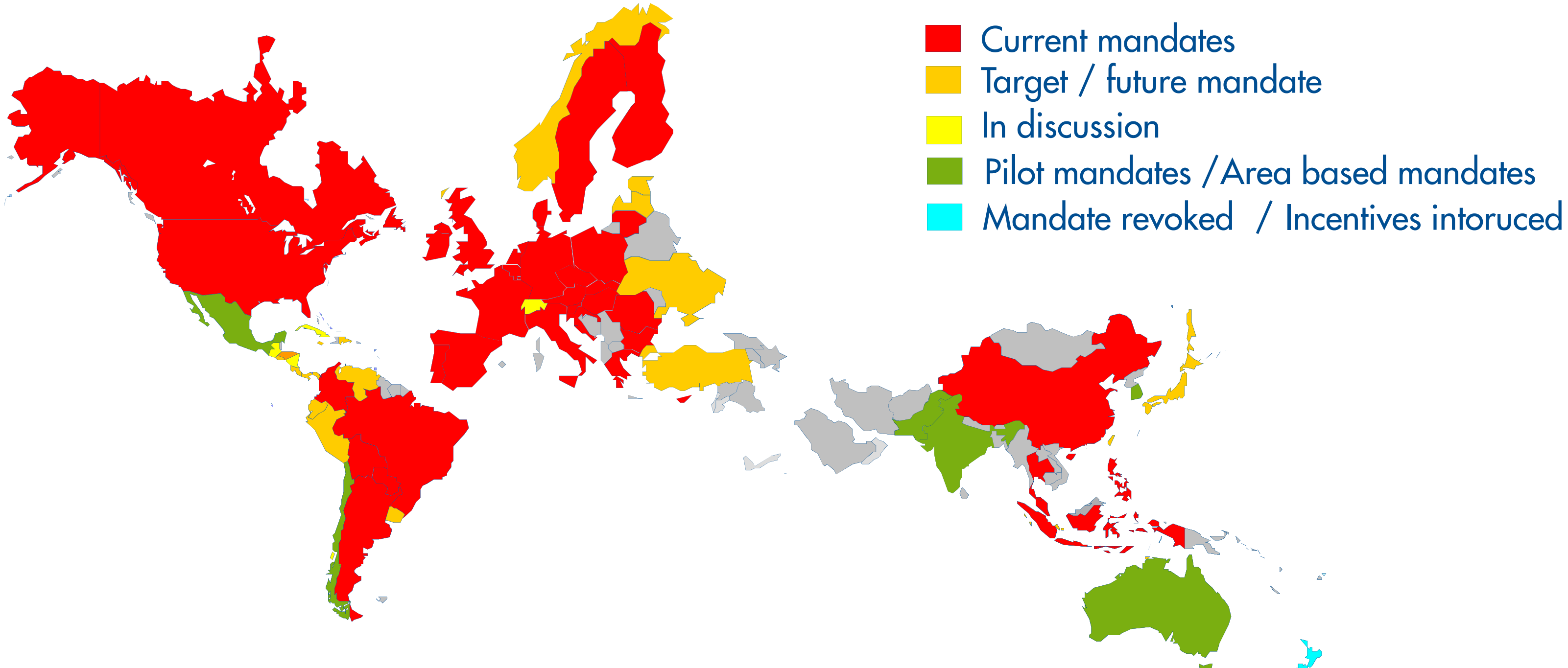
GOVERNMENT POLICIES CREATE A MARKET FOR BIOFUELS

More than 65 countries have or are developing renewable fuels mandates

Legislative priorities differ – energy security, support for domestic agriculture, environment

Policies have created an international market for biofuels. Shell is working to meet obligations & benefit from opportunities

The International Energy Agency has estimated that biofuels could represent 30% of the world's road transport fuel mix by 2050



How: PROMOTING CO_2 AND SUSTAINABILITY STANDARDS

- Advocating for the adoption of 'well-to-wheel' CO_2 standards to reward low CO_2 biofuels
- Need for a single robust approach for calculating 'well-to-wheel' carbon intensity of fuels
- Engaging industry, governments, intergovernmental agencies and policy makers to encourage sustainability standards in the biofuels supply chain
- Participating in industry initiatives working on voluntary guidelines for particular feedstocks
- Pledged support for international multi-stakeholder coalition seeking to enforce a moratorium on rainforest and peatland clearance for palm oil in Southeast Asia

RSPO
Roundtable on Sustainable Palm Oil

EPFL
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

RTRS Round Table on Responsible Soy

BSI

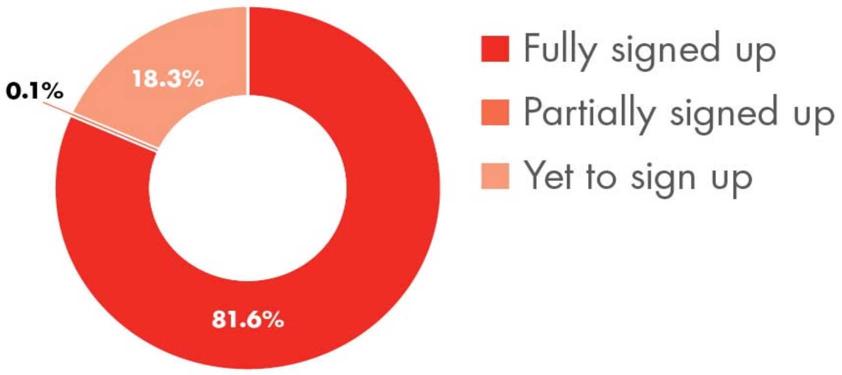
SUSTAINABILITY OF SHELL'S BIOFUELS SUPPLY CHAIN

Championing sustainability standards in our own biofuels supply chain

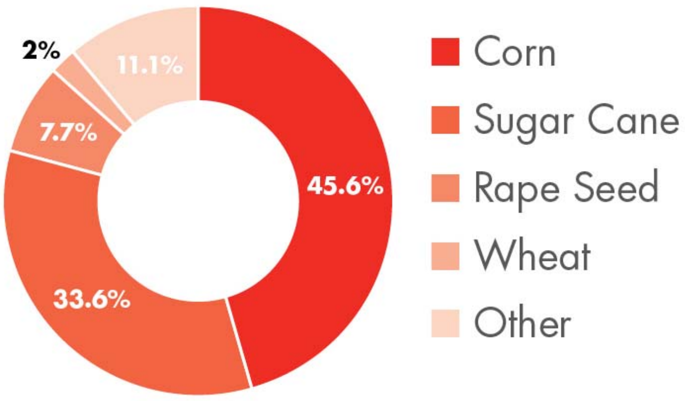
Rules and practices to help assess risks, implement controls, monitor compliance and report our progress

Sustainability clauses in new and renewed term contracts:

- feedstocks not knowingly linked to violation of human rights or produced in areas of high biodiversity value
- suppliers develop and implement supply chain traceability systems
- suppliers join relevant international bodies developing sustainability criteria particular feedstocks



Shell's Biocomponent Purchases Covered by Sustainabilty Clauses



Shell Global Biocomponent Feedstock Purchase Q4 2009

SHELL-COSAN JOINT VENTURE: Raizen

- Brazilian sugar cane – lowest CO_2 most sustainable and cost competitive of today's biofuels
- 2 billion litres of ethanol production capacity per year – with room to grow
- Robust sustainability principles, standards and operating procedures

Ethanol fuel in Shell's retail network

Automated sugarcane harvesting

IOGEN ENERGY: CELLULOSIC ETHANOL FROM STRAW

- Shell and Iogen Corporation 50:50 equity partners in Joint Venture company Iogen Energy since 2002
- Joint technology programme developing the processing technology to make ‘cellulosic’ ethanol from lignocellulose (straw) using enzymes
- World’s first commercial demonstration cellulosic ethanol plant opened in 2004 (Ottawa, Canada):
  - Produced more than 500,000 litres in 2009
  - Month long retail demonstration in Ottawa, June 2009
- CO_2 emissions of enzymatic cellulosic ethanol from straw could be up to 90% less than gasoline
- Full-scale commercial plant under assessment with focus on a site in Saskatchewan, Canada

IOGEN®
CORPORATION

CODEXIS: DEVELOPING NEW ENZYMES

Shell has held a14.7% equity stake in Codexis, California since 2007

Joint technology development programme to 'evolve' natural enzymes into improved variant enzymes capable of performing to specification

Codexis is working closely with Shell and Iogen Energy to enhance the efficiency of enzymes used in the Iogen cellulosic ethanol production process

Researching new enzymes to convert biomass directly into components similar to gasoline and diesel

CODEXIS®

VIRENT: SUGARS TO HYDROCARBONS

Joint technology development programme to convert plant sugars directly in to a range of high performance liquid transport fuels rather than ethanol, since 2008

Uses catalysts to convert plant sugars into hydrocarbons

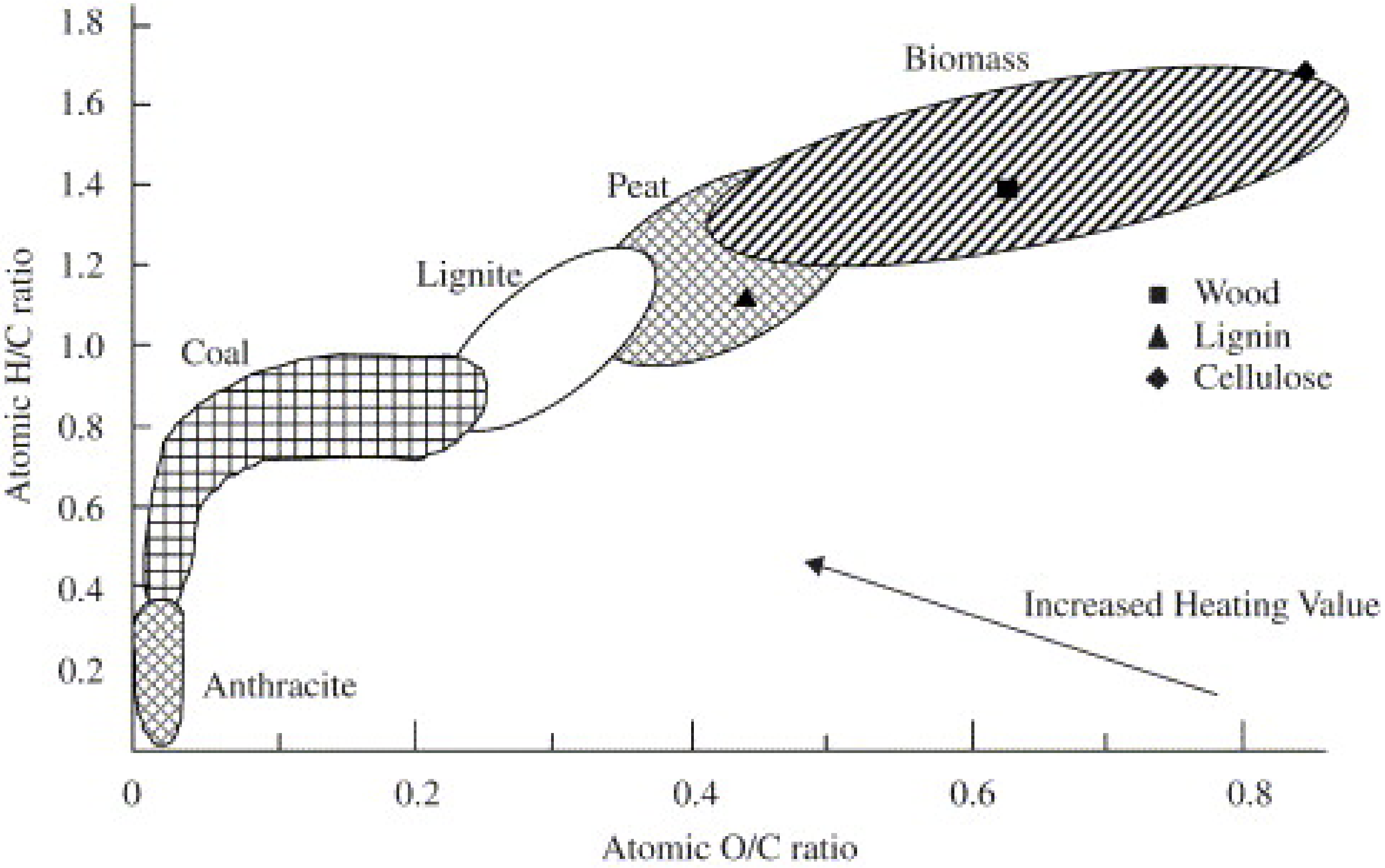
Sugars can be sourced from crops and non-food sources

Fuels have higher energy content than ethanol (or butanol) and deliver better fuel efficiency

Could result in biofuels that can be used at high blend rates in standard gasoline engines

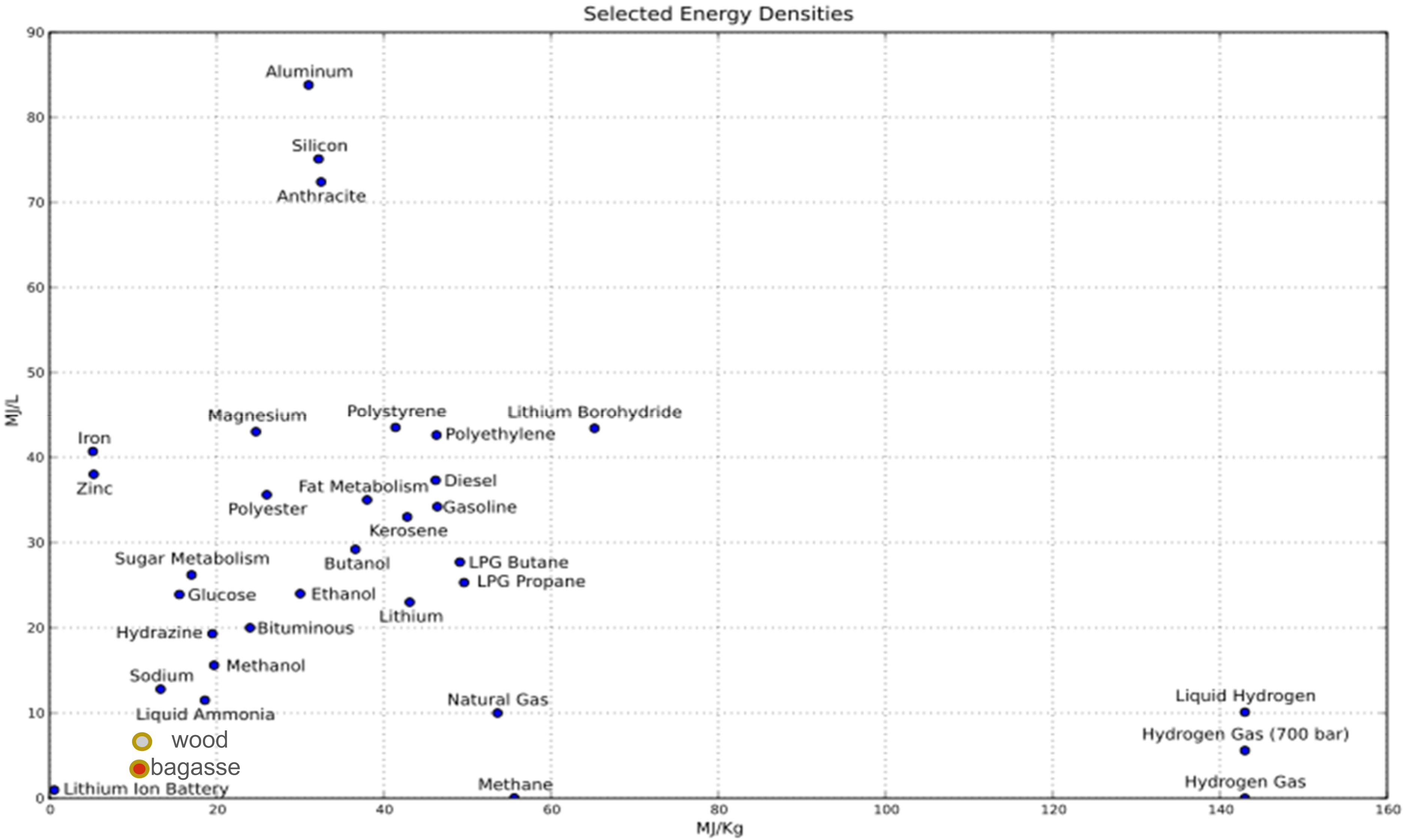
Potentially eliminates requirement for specialized infrastructure, new engine designs and blending equipment

OXYGEN CONTENT OF BIOMASS:



NTNU Combustion Handbook:
http://www.handbook.ifrf.net/handbook/cf.html?id=23

Energy Density: volumetric and mass



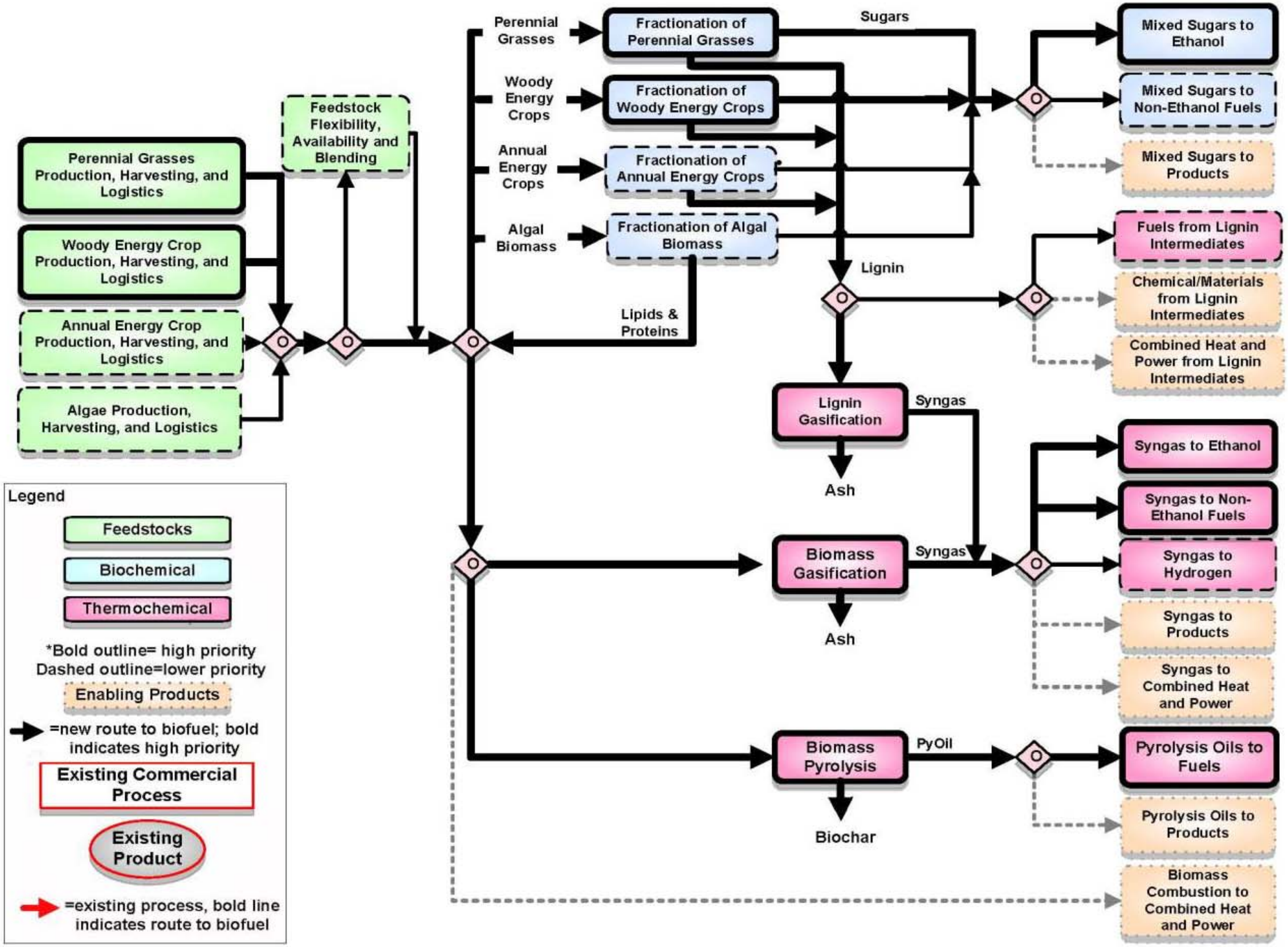
www.wikipedia.org

Challenges in Bio-based feeds: Energy Density

Sugar cane

Collection radius and transport efficiency

Energy Crops Pathways:



Perennial Grasses Production, Harvesting, and Logistics

Woody Energy Crop Production, Harvesting, and Logistics

Annual Energy Crop Production, Harvesting, and Logistics

Algae Production, Harvesting, and Logistics

Feedstock Flexibility, Availability and Blending

Perennial Grasses

Woody Energy Crops

Annual Energy Crops

Algal Biomass

Fractionation of Perennial Grasses

Fractionation of Woody Energy Crops

Fractionation of Annual Energy Crops

Fractionation of Algal Biomass

Lipids & Proteins

Sugars

Mixed Sugars to Ethanol

Mixed Sugars to Non-Ethanol Fuels

Mixed Sugars to Products

Lignin

Fuels from Lignin Intermediates

Chemical/Materials from Lignin Intermediates

Combined Heat and Power from Lignin Intermediates

Lignin Gasification

Syngas

Ash

Biomass Gasification

Syngas

Ash

Syngas to Ethanol

Syngas to Non-Ethanol Fuels

Syngas to Hydrogen

Syngas to Products

Syngas to Combined Heat and Power

Biomass Pyrolysis

PyOil

Biochar

Pyrolysis Oils to Fuels

Pyrolysis Oils to Products

Biomass Combustion to Combined Heat and Power

Legend

Feedstocks

Biochemical

Thermochemical

*Bold outline= high priority
Dashed outline=lower priority

Enabling Products

=new route to biofuel; bold indicates high priority

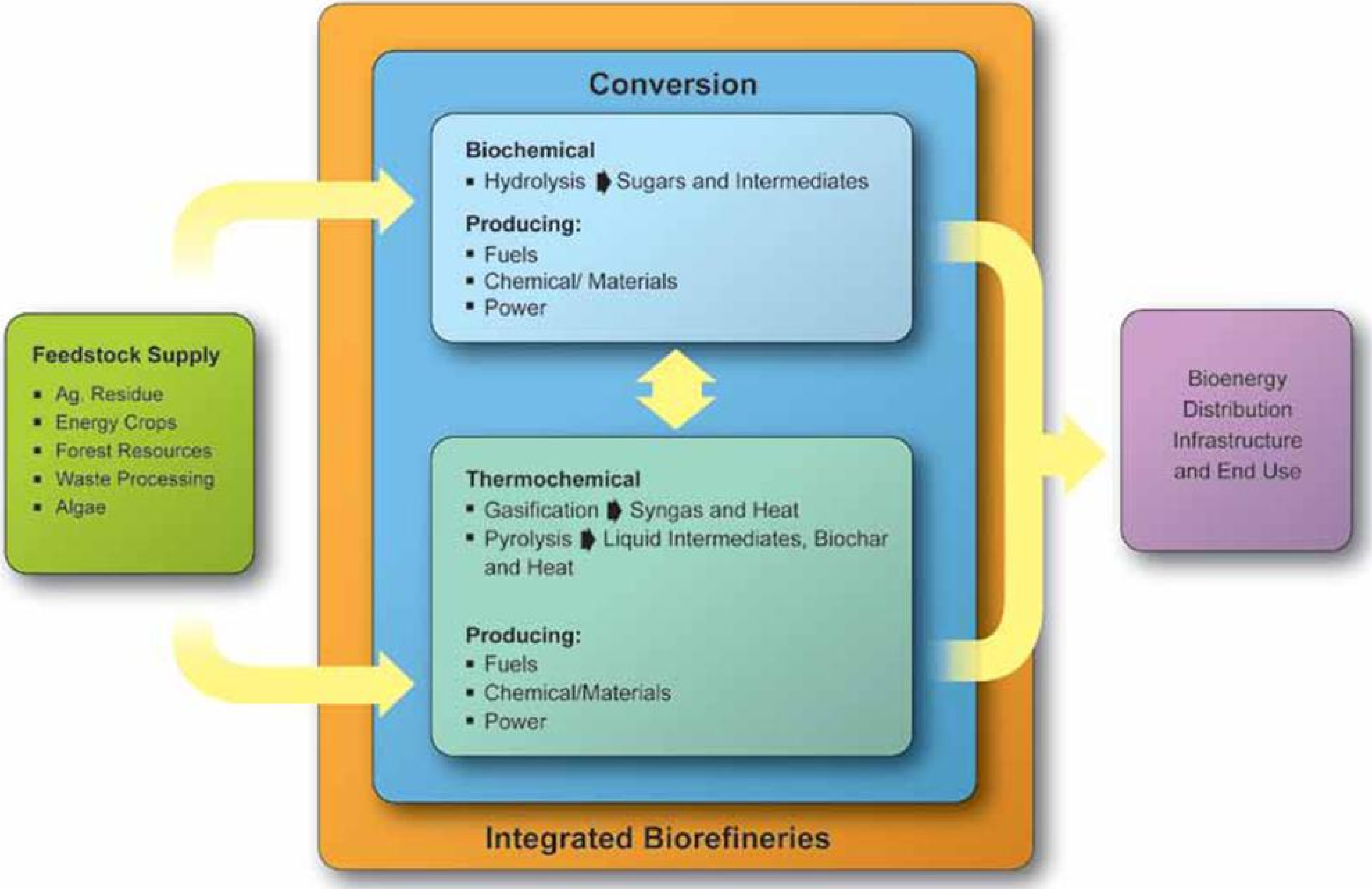
Existing Commercial Process

Existing Product

=existing process, bold line indicates route to biofuel

U.S. DOE, Biomass Multi-Year Program Plan, April 2011, Appendix A

BIOCHEMICAL / BIOMOLECULAR VS. THERMOCATALYTIC ROUTES



Feedstock Supply

- Ag. Residue
- Energy Crops
- Forest Resources
- Waste Processing
- Algae

Conversion

Biochemical

- Hydrolysis ➧ Sugars and Intermediates

Producing:

- Fuels
- Chemical/ Materials
- Power

Thermochemical

- Gasification ➧ Syngas and Heat
- Pyrolysis ➧ Liquid Intermediates, Biochar and Heat

Producing:

- Fuels
- Chemical/Materials
- Power

Integrated Biorefineries

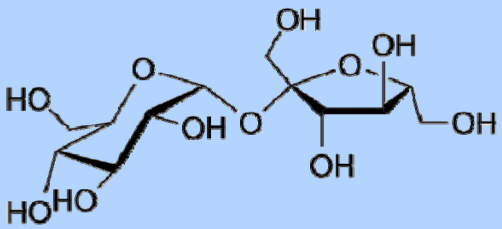
Bioenergy
Distribution
Infrastructure
and End Use

U.S. DOE, Biomass Multi-Year Program Plan, April 2011

Catalytic Challenges in Biofuels and Bio-Based Chemicals

Biobased feedstocks = Carbohydrates = $[C(H2O)]_n$

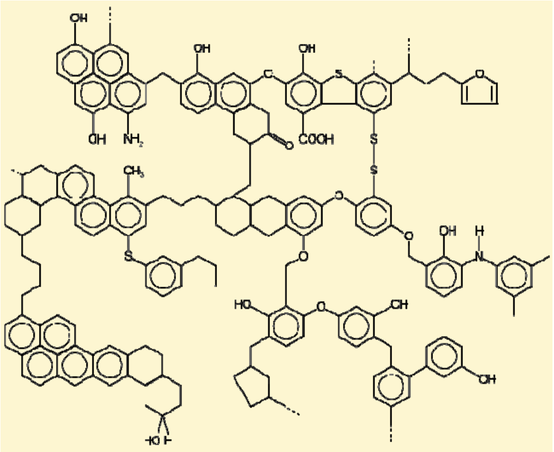
Oxygen is a challenge for thermocatalytic conversion!



Sucrose is composed of two monosaccharides: D-glucose (left) and D-fructose (right).

Amylose is a linear polymer of glucose mainly linked with α(1→4) bonds. It can be made of several thousands of glucose units. It is one of the two components of starch, the other being amylopectin.

Coal



CRUDE OIL	
Element	**Percent range**
Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.05 to 1.5%
Sulfur	0.05 to 6.0%
Metals	< 0.1%

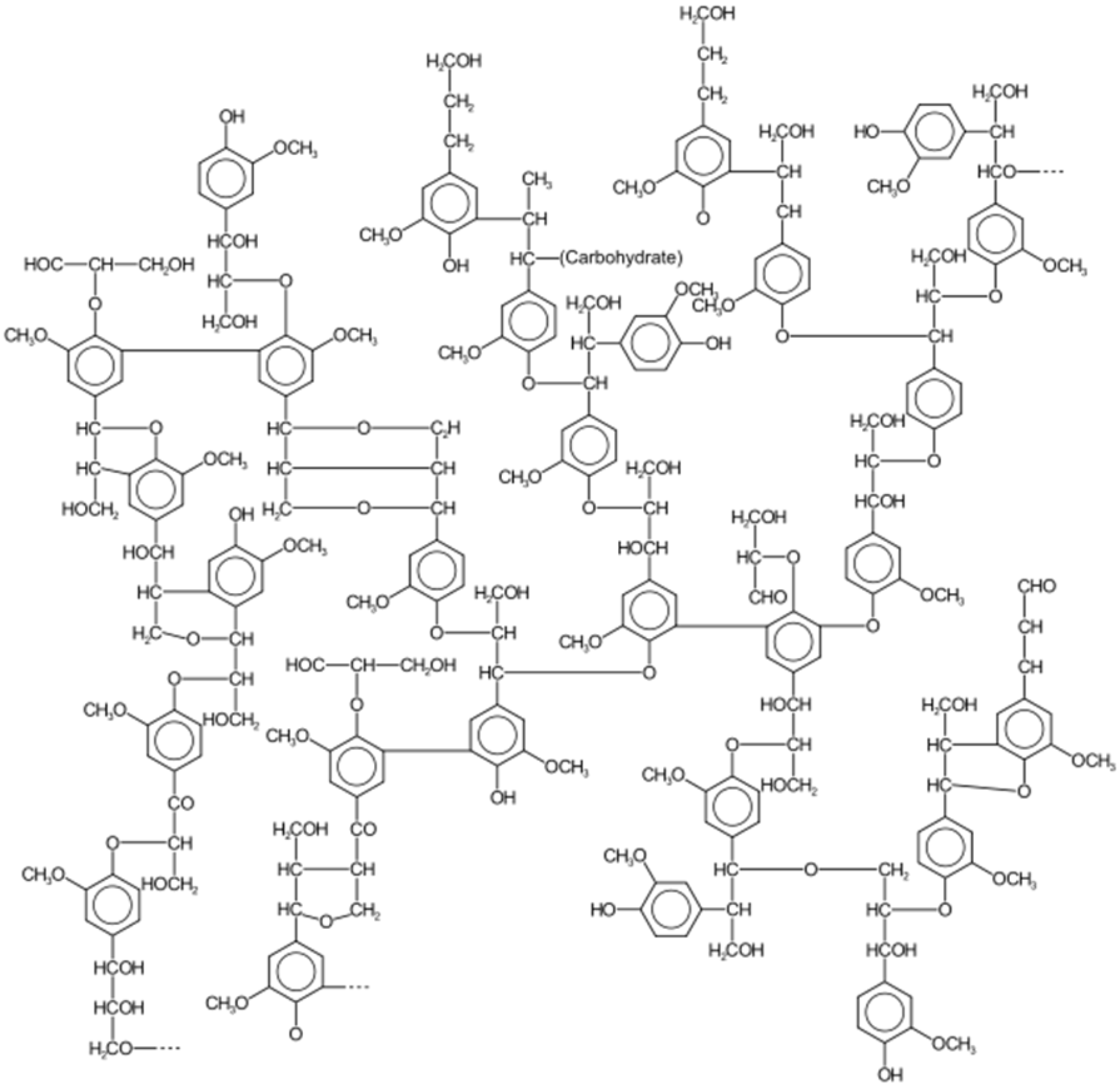
The Challenge of Lignin:

"You can make anything
from lignin, except money. "

– old industry saying
(per J. Lane, Biofuels Digest 2011)

CHALLENGES:

- Selective reaction pathways other than gasification to syngas?
- Folded structure: bonds and immobilizes / deactivates enzymes for cellulose hydrolysis.
- Fouling of surfaces during processing.
- Primary component of "healthy topsoil"

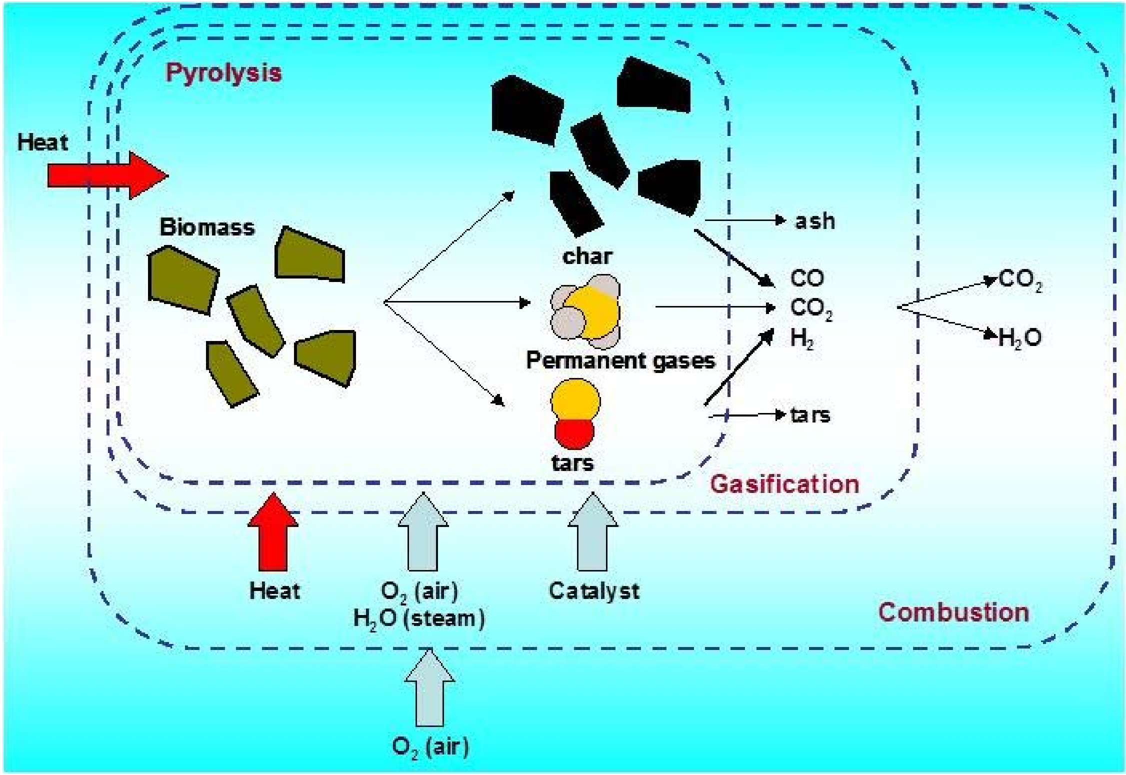


Biomass Gasification - Background

- Biomass ($CH_{1.4}O_{0.6}$) is more like a carbohydrate (CH_2O) not exactly an hydrocarbon (CH_2) or coal (CH) or NG (CH_4)
- Contains more oxygen and volatile content (50-80%) than coal (~20%)
- Has lower sulfur & ash content (contains lower melting ash ~ 850 °C)
- Is more reactive (than coal) hence gasification can be conducted at lower temperatures

Typical steps in Biomass gasification

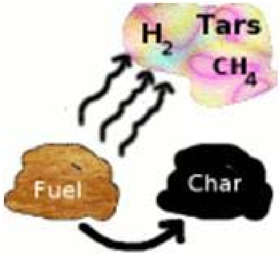
- **Pyrolysis:** thermal decomposition at lower temperatures in the absence of O_2 to produce volatiles and char
- **Gasification:** partial combustion of the volatiles/bio-oils, char in the presence of an oxidant at higher temperatures to produce syngas
- **Combustion:** combustion of the char in-situ or separately to provide heat for endothermic reactions



Source: V. Swaaij, et al, Thermal conversion of biomass into secondary products, 12th European conference on Biomass and Waste, Amsterdam 2002

Biomass Gasification

- Partial combustion of the volatiles, bio-oils, char etc in the presence of an oxidant at higher temperatures to produce syngas.
- Typical equivalence ratio of 0.2-35 (fraction of the theoretical O_2 required for combustion)
- Typical cold gas efficiencies 70 – 80 %
- Biomass gasifers can be classifed based on various categories –



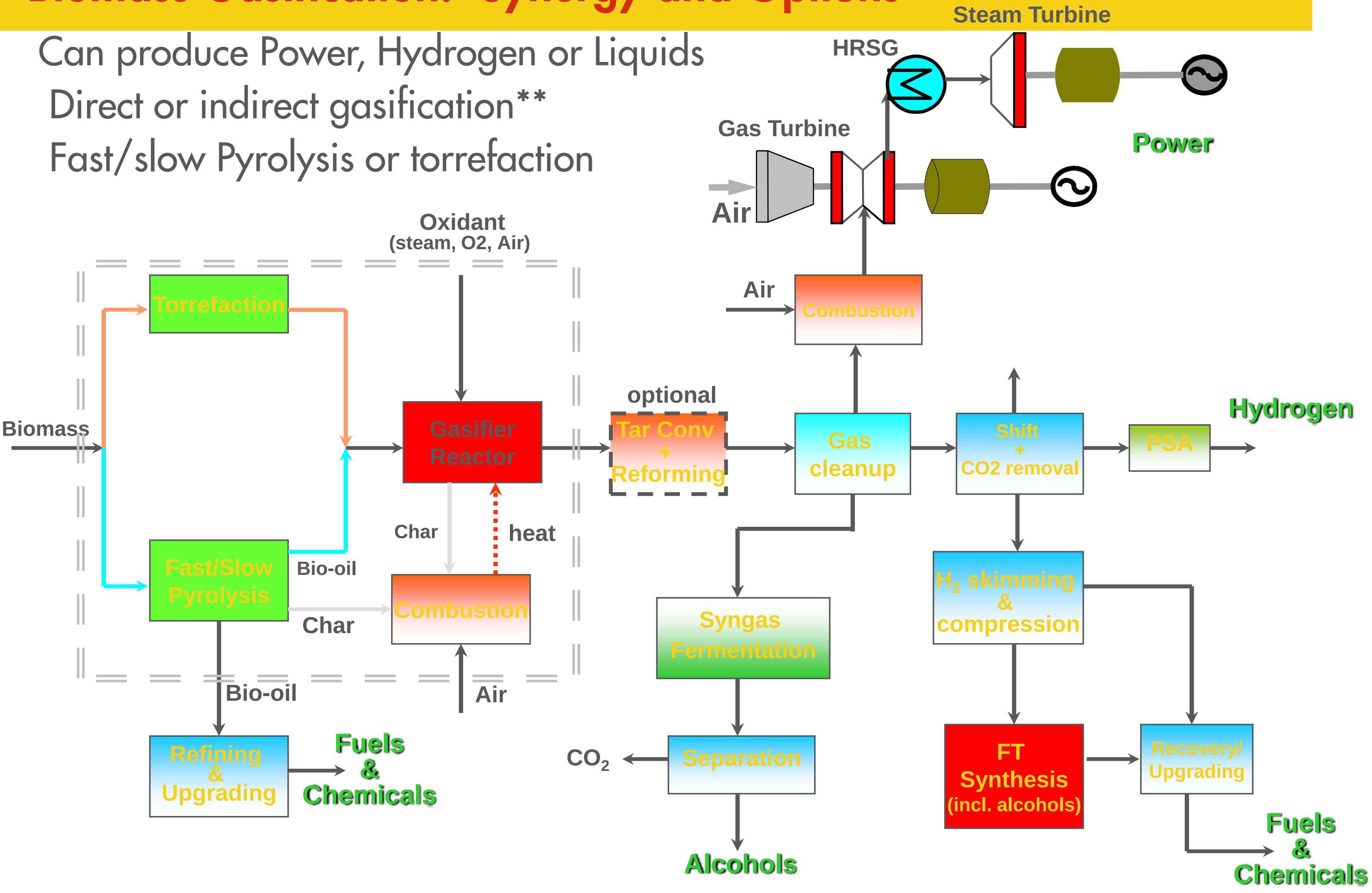
- **Oxidizing agent**: Air, Steam, or O_2
- **Heat for gasification**
  - ***Direct gasification*** (autothermal)
    - with air usually for power (BIGCC)
    - Oxygen for hydrogen or liquids (BTL) or alcohols
  - ***Indirect gasification*** with air (allothermal) – different gasification and combustion zones
    - Use of hot solids or sand to provide the heat (similar to the FCC concept)
    - Heat duty via tubular furnace heat exchangers (similar to SMR concept)
- **Types of Reactors**
    - Fixed/moving – updraft, downdraft, cross-draft
    - Fluidized or entrained
    - Others - like rotary kiln, cyclone, plasma etc
- **Gasifer pressure** – atmospheric, pressurized

Biomass Gasification: Synergy and Options

Can produce Power, Hydrogen or Liquids

Direct or indirect gasification**

Fast/slow Pyrolysis or torrefaction



Biomass Gasification: Catalyst Challenges

1. The catalysts must be effective in the removal of tars.
2. If the desired product is syngas, the catalysts must be capable of reforming methane.
3. The catalysts should provide a suitable syngas ratio for the intended process.
4. The catalysts should be resistant to deactivation as a result of carbon fouling and sintering.
5. The catalysts should be easily regenerated.
6. The catalysts should be strong.
7. The catalysts should be inexpensive.

David Sutton, Brian Kelleher, Julian R.H. Ross, Review of literature on catalysts for biomass gasification, ***Fuel Processing Technology, 73***, 2001.155–173

Challenges for Biomass Gasification

Viable for electrical power: a good use of biomass!
- Key issue is low cost production of clean gas.

Challenged for BTL:
- feed handling
- feed sizing for optimal gasification (wet)
- gas cleanup vs. operating temperature
- ongoing R&D

Tar elimination & efficiency are key design issues for use in power generation or BTL

Thermal Pretreatment

Pyrolysis (400-500 ^{o}C)

- **Fast pyrolysis**
  - Rapid heating to produce char (25 wt %) and volatile vapors (75 wt%), followed by cooling of the vapors to yield bio-oils (unstable, acidic, corrosive and need further treatment)
  - Short residence times in a fluidized bed reactor with dry biomass feed (10-15 wt% moisture)
- **Slow Pyrolysis**
  - Longer residence time in a heater kiln device
  - Produces more char (than fast pyrolysis) that can be used for soil enhancements, etc

Torrefaction (200-300 ^{o}C)

- Biomass is a low energy density solid (35-65 % of coal) with higher moisture content
- Issues with grinding, feeding and other mechanical properties (esp. for higher pressures)
- Presents logistic challenges with feedstock distribution and storage
- Torrefaction – is mild pyrolysis to reduce moisture content and reduces mass ~ 30 wt%
  - Maintains most of the energy content (~90%) and energy density is similar to coal
  - The torrified material can be easily pulverized – easier for handling and feeding system

Biomass pretreatments

-- Mechanical milling

– Acid

-- Base

-- Organic solvents

--- Steam explosion

--   Ammonia explosion

--   Ionic liquids

-- Near critical water

-- Gas Expanded Liquids

Ultrasound / microwave

Micro-organism digestion (of lignin)

- Energy costs
- Chemicals / enzyme costs
- Inhibitor formation

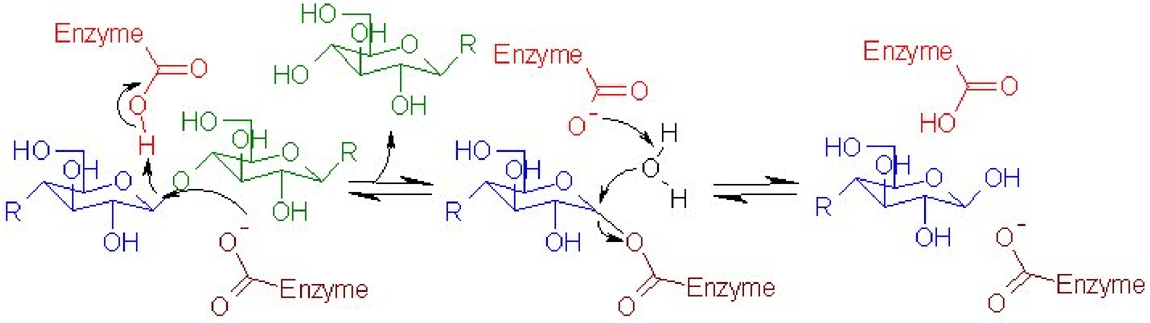
Biomolecular Processing: Biomass Pretreatment Challenges:

- Selective pretreatment of biomass to provide access substrates for enzymatic hydrolysis and fermentation.

  → Elimination of inhibitors for hydrolysis by enzymes
- Avoid formation of fermentation inhibitors :
  - Furfural
  - 5-hydroxymethylfurfural (HMF)
  - lignin degradation products: phenolic acids, alcohols, and ketones.
  - Organic acids
  - Acetate from deacetylation of hemicellulose
- Removal of fermentation inhibitors = expensive

Challenge: Overcome Inhibitors for hemicellulose / cellulose hydrolysis

- Lignin: “non productive” enzymatic binding
- End-product and intermediate inhibition:
  - Monomeric & oligomeric sugars (e.g. glucose and cellobiose)
- Enzyme deactivation with time, Temperature
- Xylo-oligomers
- High ionic strength (from pretreatment)
- Distribution of reactivities of starting material (C5 vs. C6 sugars)



Q.Qing, B. Yang, C. E. Wyman, Bioresource Technology 101 (2010) 9624–9630

Co-fermentation of C5 and C6 sugars … and co-hydrolysis

- Natural micro-organisms not effective in C5 fermentation. Low substrate and product tolerance.

- New GMO's but phenotypically unstable
  - Bacteria exhibit poor substrate and ethanol tolerances
  - Some yeasts are capable of utilizing C5 sugars
    - "Consolidated Bioprocessing" holds promise: one-step bioprocessing with Saccharomyces cerevisiae (enzyme production, saccharification, fermentation)- Seth Snyder (Argonne)

Process intensification for biomolecular conversion

- **SHF (Separate Hydrolysis and Fermentation):**

  Cellulase production / enzymatic hydrolysis/ fermentation = separate processes.

- **SSF (Simultaneous Saccharification and Fermentation)**

  Combines cellulose hydrolysis and fermentation in one step.

- **SSCF (Simultaneous Saccharification and Co-Fermentation):**

  Enzyme hydrolysis is integrated with fermentation of hexose and pentose sugars but with cellulase produced in separate step.

- **CBP (Consolidated BioProcessing):**

  Combines cellulase production, enzyme hydrolysis, and co-fermentation of C5 and C6 sugars in a single step.

iomolecular vs. Thermochemical Catalysts

Parameter	***Biological Catalysts***	***Chemical Catalysts***
Products	Alcohols	A Wide Range of Hydrocarbon Fuels
Reaction Conditions	Less than 70 C, 1 atm	100-1200 C, 1-250 atm
Residence Time Selectivity	2-5 days Tunable (> 95%)	0.01 second to 1 hour Variable. Need improved selectivity.
Catalyst Cost	$0.50/gallon lignocellulosic ethanol; $0.04/gallon sugar cane / corn ethanol	$0.01/gallon gasoline petroleum
Sterilization Recyclability	Needed Difficult	Not needed Easy with solid catalyst

NSF. 2008. *Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries.* Ed. George W. Huber, University of Massachusetts Amherst. National Science Foundation. Chemical, Bioengineering, Environmental, and Transport Systems Division. Washington D.C.

Catalytic Grand Challenges in Bio-Based Fuels and Chemicals.

Biomolecular catalysts

- Cost
- Recycle / reuse / *in situ* production?
- Selectivity
- Activity
- Yields (selectivity & conversion vs. inhibition)
- Inhibitor tolerance
- Stability (thermal, chemical, phenotype)

Thermochemical

- Water stability
- Oxygen conversion / Hydrogen activation / tar elimination
- Poison tolerance
- Selectivity across complex substrates
- Stability during regeneration