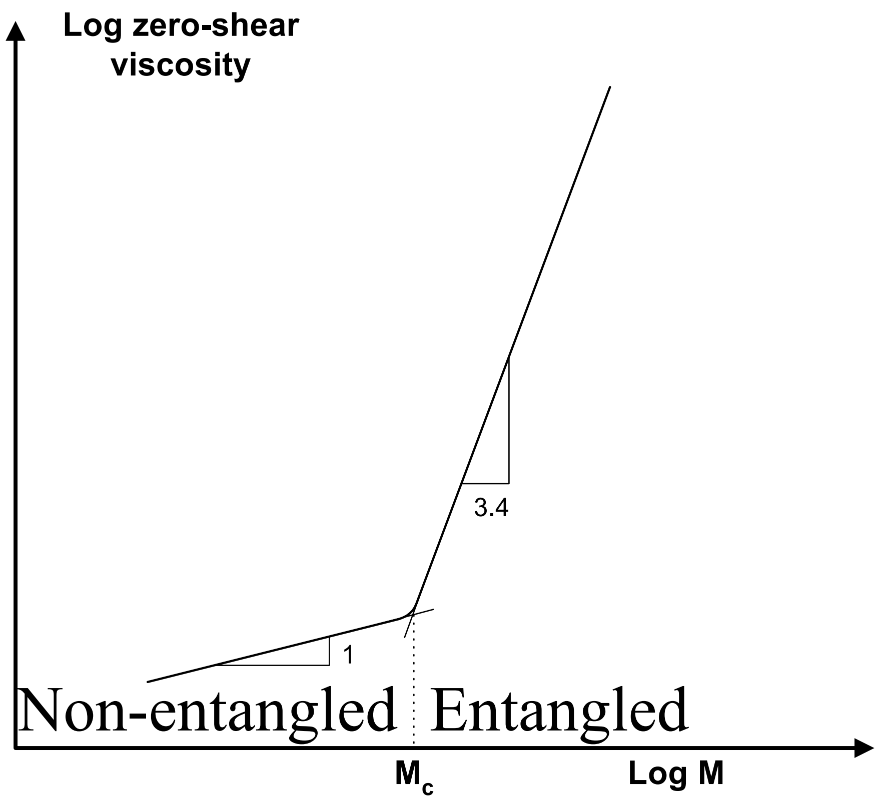
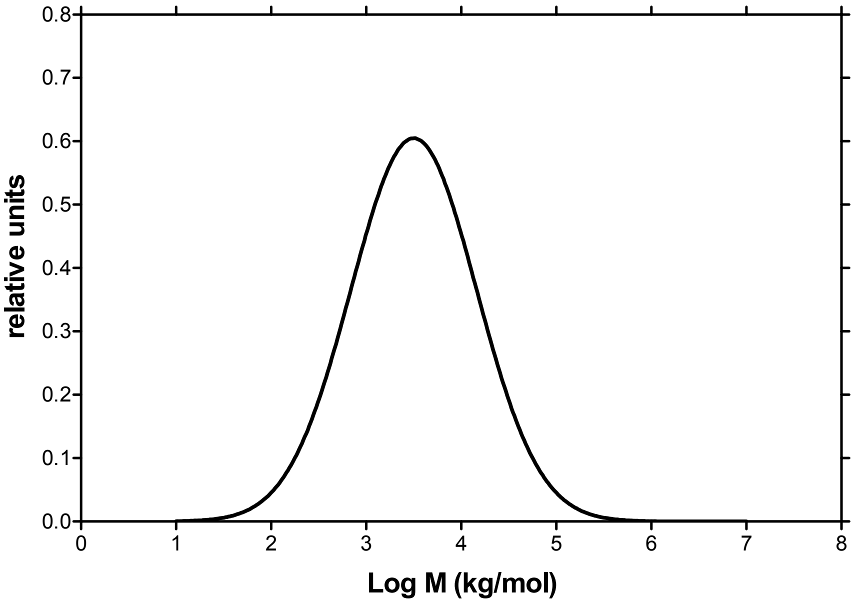
Molecular structure & Rheology

- M_c critical entanglement molecular weight
  - dramatic rheology change
  - due to chain entanglement



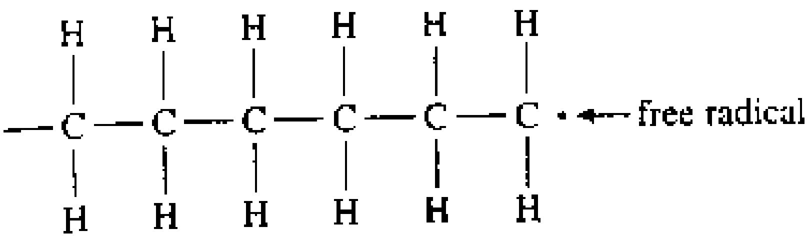
Polymer Architecture

- Molecular Mass Distribution (MMD)
  - Degree of Polymerisation
    - Number of monomers in a polymer
  - Monodisperse MMD
    - Polymers have same molecular mass
  - Polydisperse MMD
    - Polymers have different molecular mass
  - Homogenous MMD
    - Same polymer architecture independent of molecular mass
  - Heterogenous MMD
    - Mixture of different polymer architectures

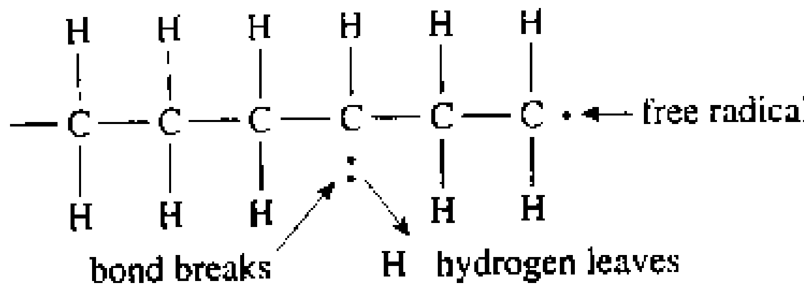


Polyethylene

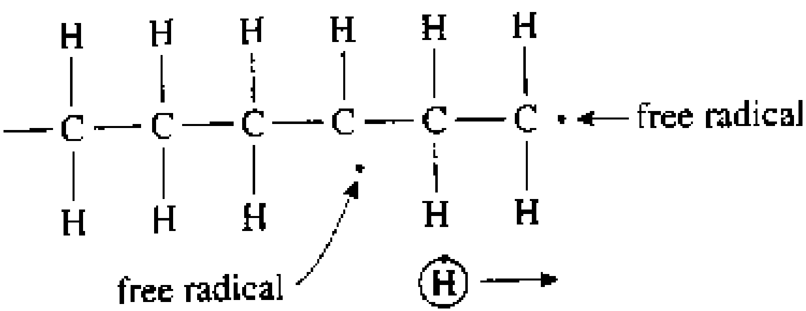
Synthesis:
Chain-growth - free radical polymerisation

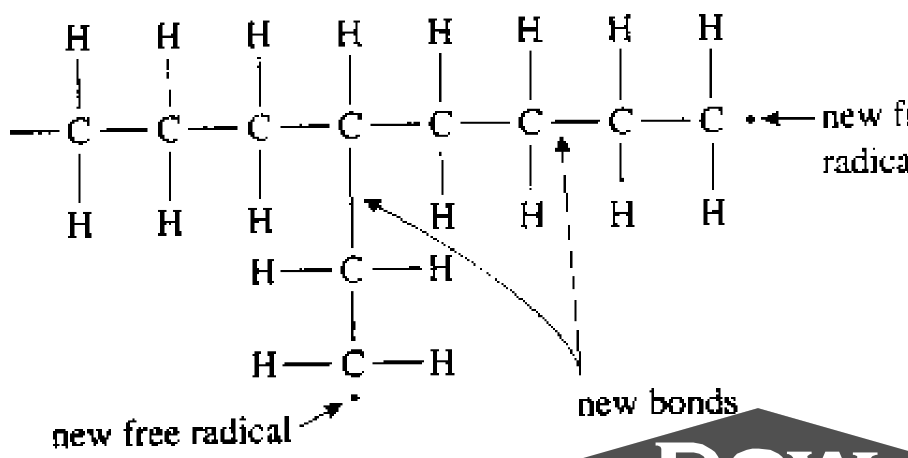


(a) Growing polymer chain

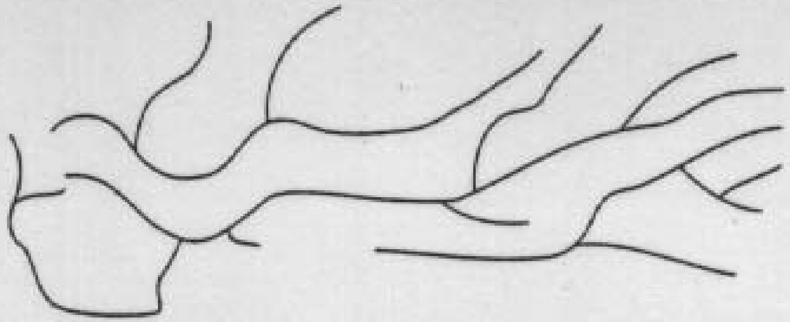


(b) Rupture of carbon-hydrogen bond



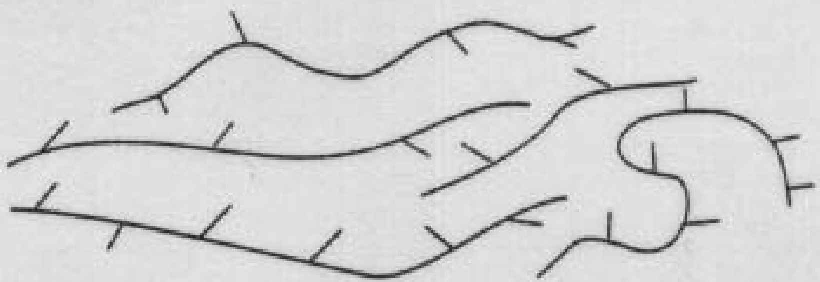


Polyethylene



(a) Low density polyethylene (LDPE)

(b) High density polyethylene (HDPE)



(c) Linear low density polyethylene (LLDPE)

Polymer Architectures

Polyethylene

	High-Pressure		Low-Pressure		
Process	Autoclave	Tubular	Solution	Gas phase	Slurry
P (bar)	1000 - 3000	1000 - 3000	20 - 100	20 - 100	1 - 20
T (°C)	> 200	>200	100 -200	50-100	50-100
Catalyst	air peroxides	air peroxides	Ziegler-Natta metallocene	Ziegler-Natta metallocene	Ziegler-Natta metallocene
Reaction	radical	radical	coordination	coordination	coordination
Polymer	random tree SCB+LCB	random tree SCB + LCB	linear, comb homopolymer copolymers SCB + LCB	linear, comb homopolymer copolymers SCB + LCB	linear,comb homopolymer copolymers SCB + LCB
Mw/Mn	10 -30	10-30	2-10	2-10	5 - 30
Density (kg/m^3)	915 - 935	915 - 935	865 - 965	890 - 965	935 - 965
Name	LDPE	LDPE	ULDPE VLDPE LLDPE HDPE	VLDPE LLDPE HDPE	MDPE HDPE UHMPE

Manufacturing Technologies

DOW

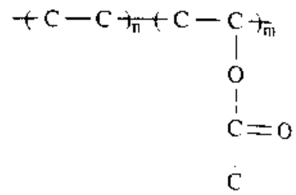
Polyethylene

Crystallinity & Short Chain Branching effects on Properties

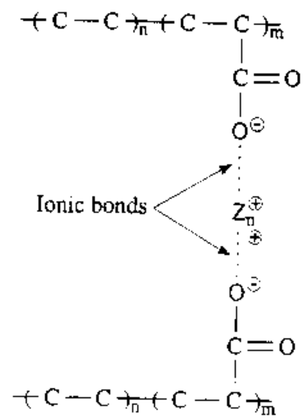
Property	How Increased Branching Affects the property
Density/crystallinity	Decreases
Melting point	Decreases
Creep resistance	Decreases
Tensile strength	Decreases
Stiffness	Decreases
Hardness	Decreases
Impact toughness	Increases
Transparency	Increases
Oxidative resistance	Decreases
UV stability	Decreases
Solvent resistance	Decreases
Permeability	Increases
Shrinkage	Decreases

Polyethylene Co-polymers

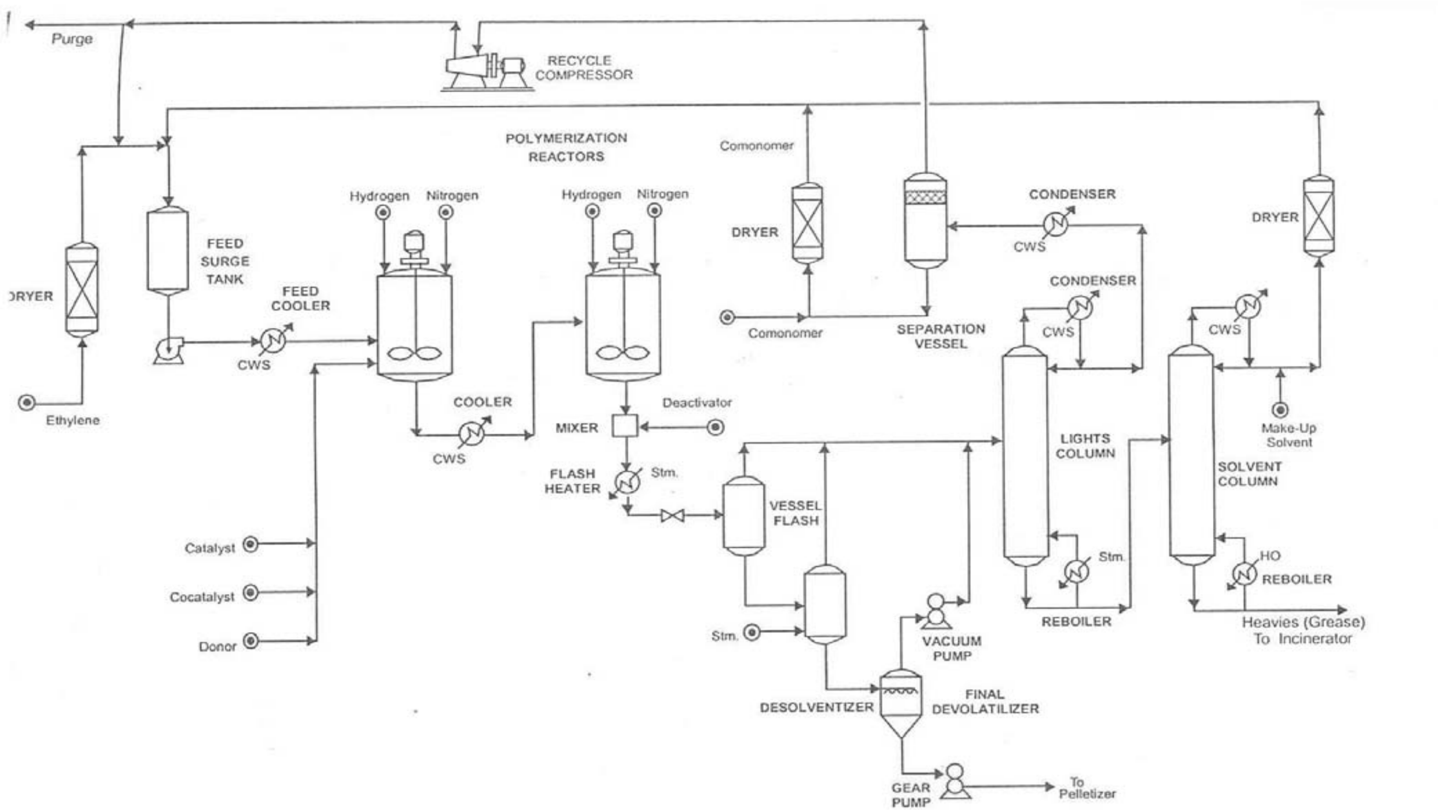
- Ethylene Vinyl Acetate (EVA)
  - High pressure process
  - 5-50% wt VA
  - High Clarity film
  - Hot melts



- Ethylene Acrylic Acid (EAA)
  - High pressure process
  - 3-20% AA
  - Ionomers

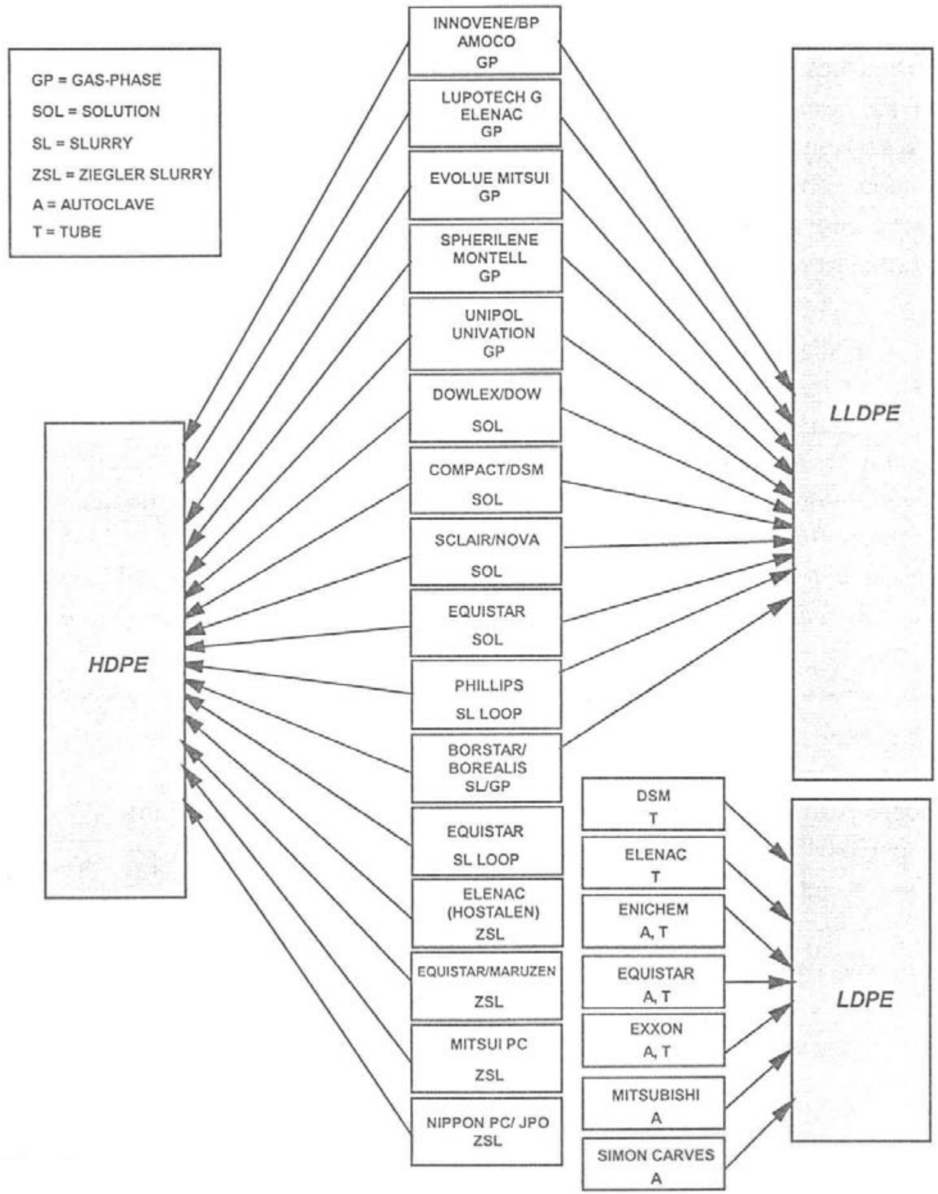


Polyethylene Manufacturing



DOWLEX SOLUTION LLDPE
PROCESS REACTION AND
SOLVENT RECOVERY

LICENSING TECHNOLOGY COMPETITION



Polyethylene

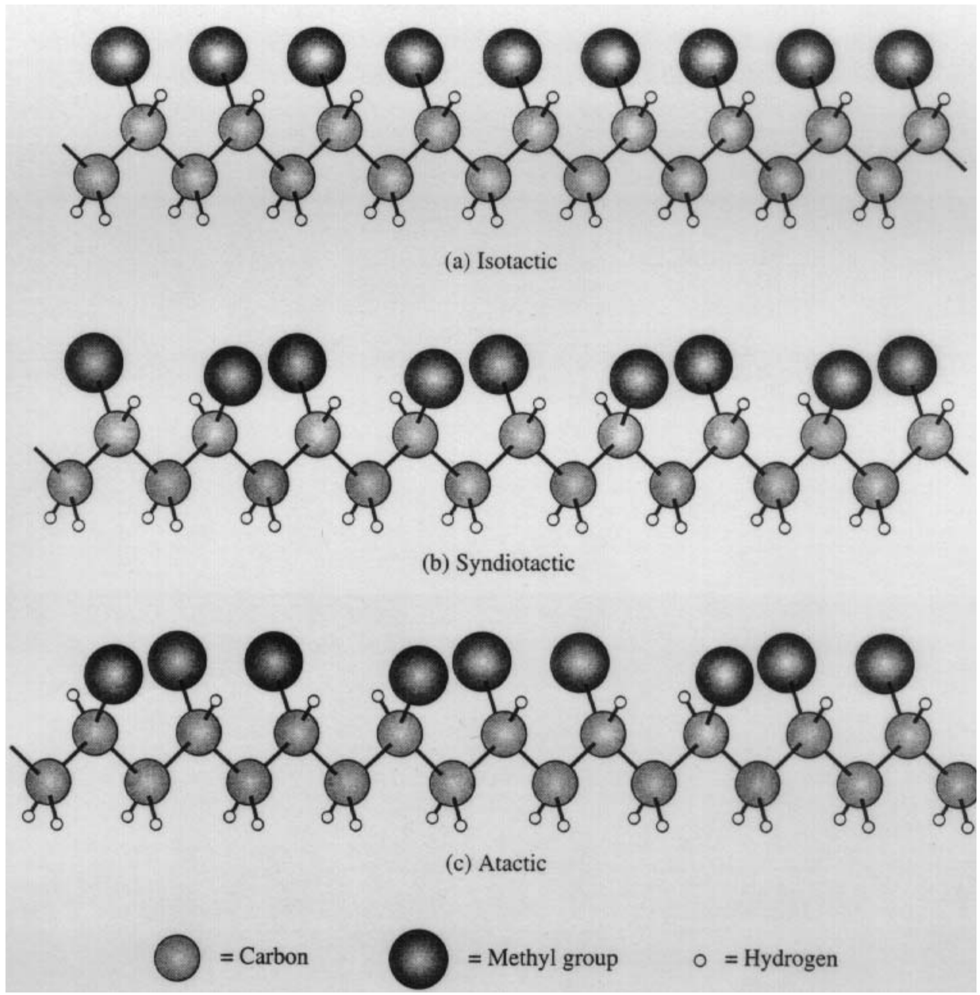
The first polyethylene was produced more or less by chance in March 1933 under ***very high pressure*** (1400 bar) in an experimental plant run by the British company ***ICI***. It took a further two years before the developers succeeded in polymerising ethylene in a controlled process using modified apparatus. Polyethylene melts at 115°C to 120°C and has a relatively low density (***PE-LD***) of 0.918. Even in 1939 a plant with an annual output of several hundred tons was insufficient to meet the rapidly rising demand. In 1953 ***Karl Ziegler*** developed a new production method by which polyethylene could be polymerised at ***atmospheric pressure*** using suitable catalysts in a suspension. This not only eliminated the technical problems associated with extremely high pressures, it also produced material of substantially higher density (***PE-HD***) with a more crystalline structure and a higher melting point, i.e. a very much stronger material. Polyethylene is an excellent ***electrical insulator***. It can be used for a multitude of different purposes ranging from ***household appliances***, ***packaging*** and ***industrial equipment*** to ***toys***.

Polypropylene

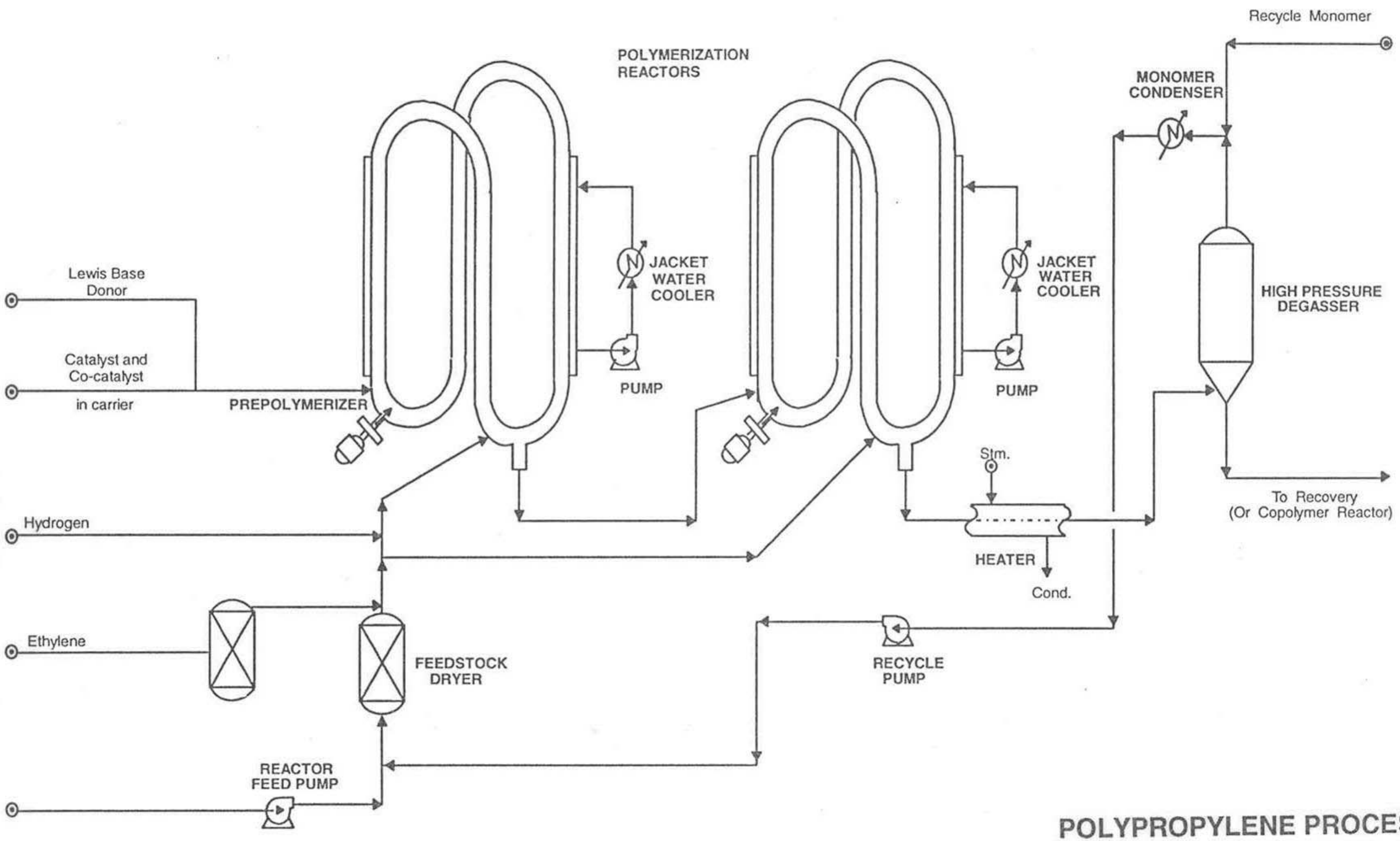
Polypropylene is the youngest of the bulk plastics. It has evolved at breathtaking speed and established itself in a very wide range of fields. This plastic was developed in 1954 by ***Giulio Natta*** in cooperation with researchers at the firm of ***Montecatini***, where the material was also first produced on an industrial scale. Polypropylene is very similar to high-density polyethylene, but has a ***lower density*** and is more ***rigid and harder***. It is the hardest of all polyolefin polymers and retains this quality even at temperatures ***above 100°C***. It is exceptionally resistant to friction, and its heat resistance is outstanding. It possesses excellent dielectrical properties, is a ***good insulator*** and has especially ***high long-term flexural strength*** (10 million bending stress reversals). There are many different types of polypropylene on the market. They can be used in a wide variety of applications, including ***medical appliances*** and ***household goods***, ***toys***, ***automotive components*** and ***sports equipment***, ***food packaging***, ***agricultural equipment***, ***signs***, ***furniture***, and components for the chemicals industry.

Polypropylene

Stereo-Isomers



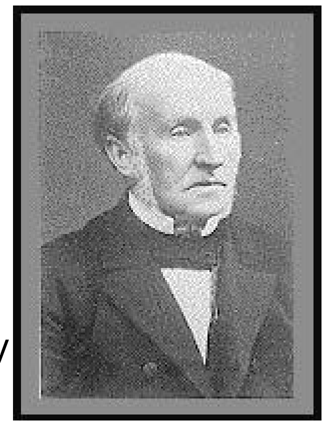
Polypropylene Manufacturing

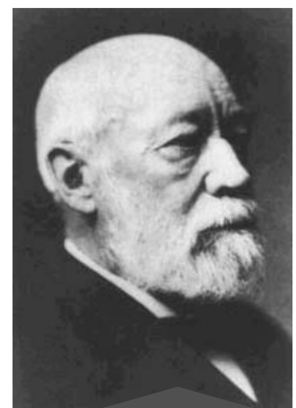


POLYPROPYLENE PROCESS
MONTELL PROCESS (LOOP REACTOR)

History of Plastics

- Naturally occurring substances (Rubber, Cellulose)
  - 17-18th Century
    - Hevea (Ecuador) - Gutta-Percha (Indonesia/Malaya) Rubber
  - 1823: C. Macintosh (Mackintosh)
    - Waterproof sheet of layers of fabric and rubber
  - 1838: C. Goodyear
    - Sulfur vulcanization of rubber
  - 1862: A. Parkes
    - “Parkesine” - nitrated cellulose for replacing Ivory
  - 1869: J.W. Hyatt
    - Celluloid



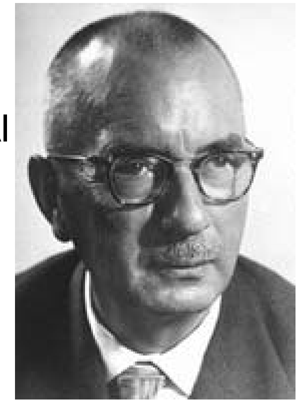


History of Plastics

- Thermoplastics
  - 1909: H. Stobbe & G. Posnyak
    - Polystyrene
    - Commercial development in 1925 by IG Farben and commercialised in US by The Dow Chemical Company in 1938
  - 1913: F. Klatte
    - Polyvinylchloride - revisited in 1927
  - 1927 - 1938: O. Röhm
    - Plexiglass - Polymethylmetacrylate
  - 1934: E. Fawcett & R. Gibson
    - High pressure research gave Polyethylene
    - Commercial in 1939 as cable insulation material
  - 1937: W. Carothers
    - Step-growth polymerisation
    - Polyamide - Nylon
  - 1941: J. Whinfield & J. Dickson
    - Polyethylene Terephtalate - Terylene fibres

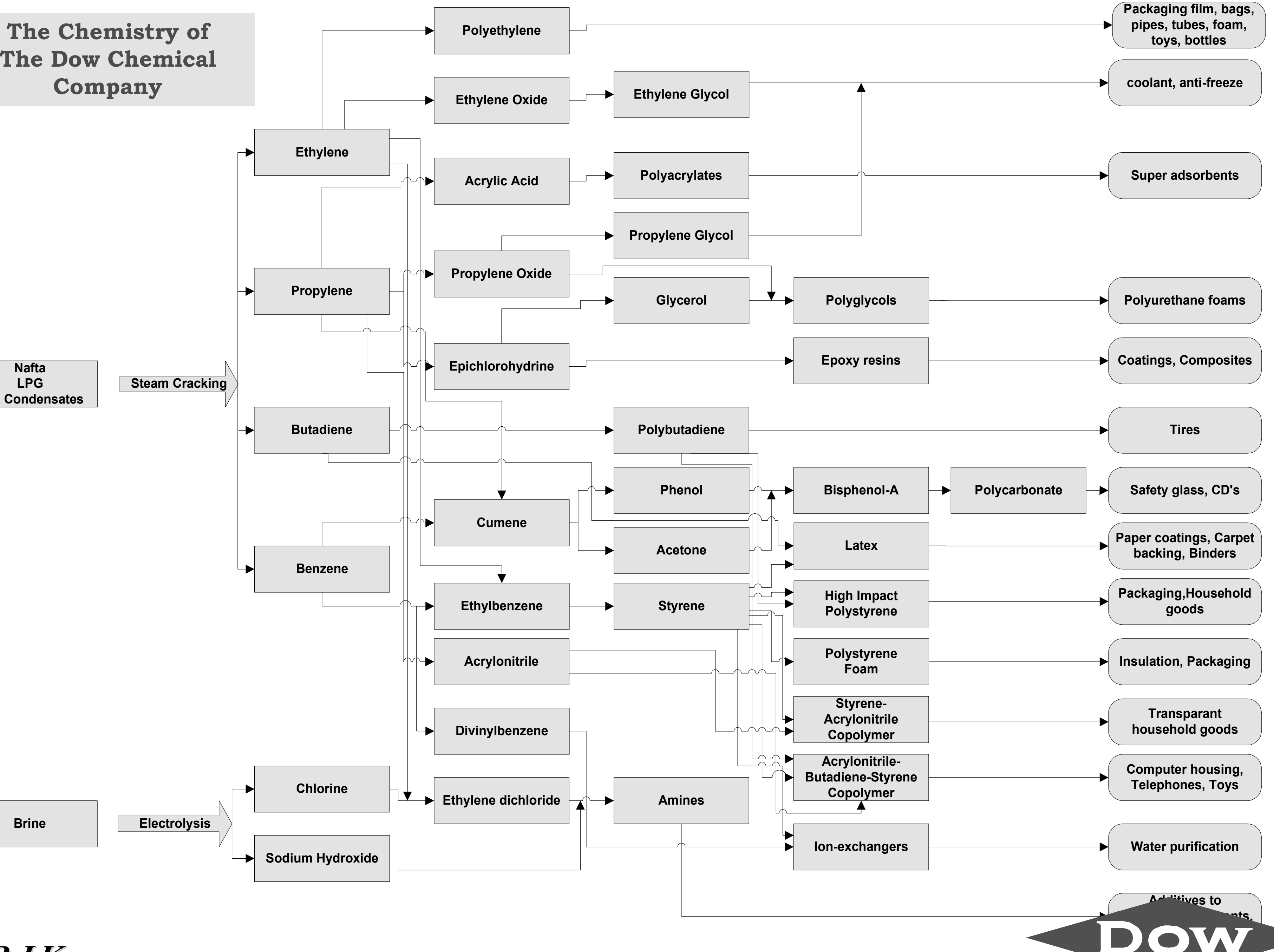
DOW

History of Plastics

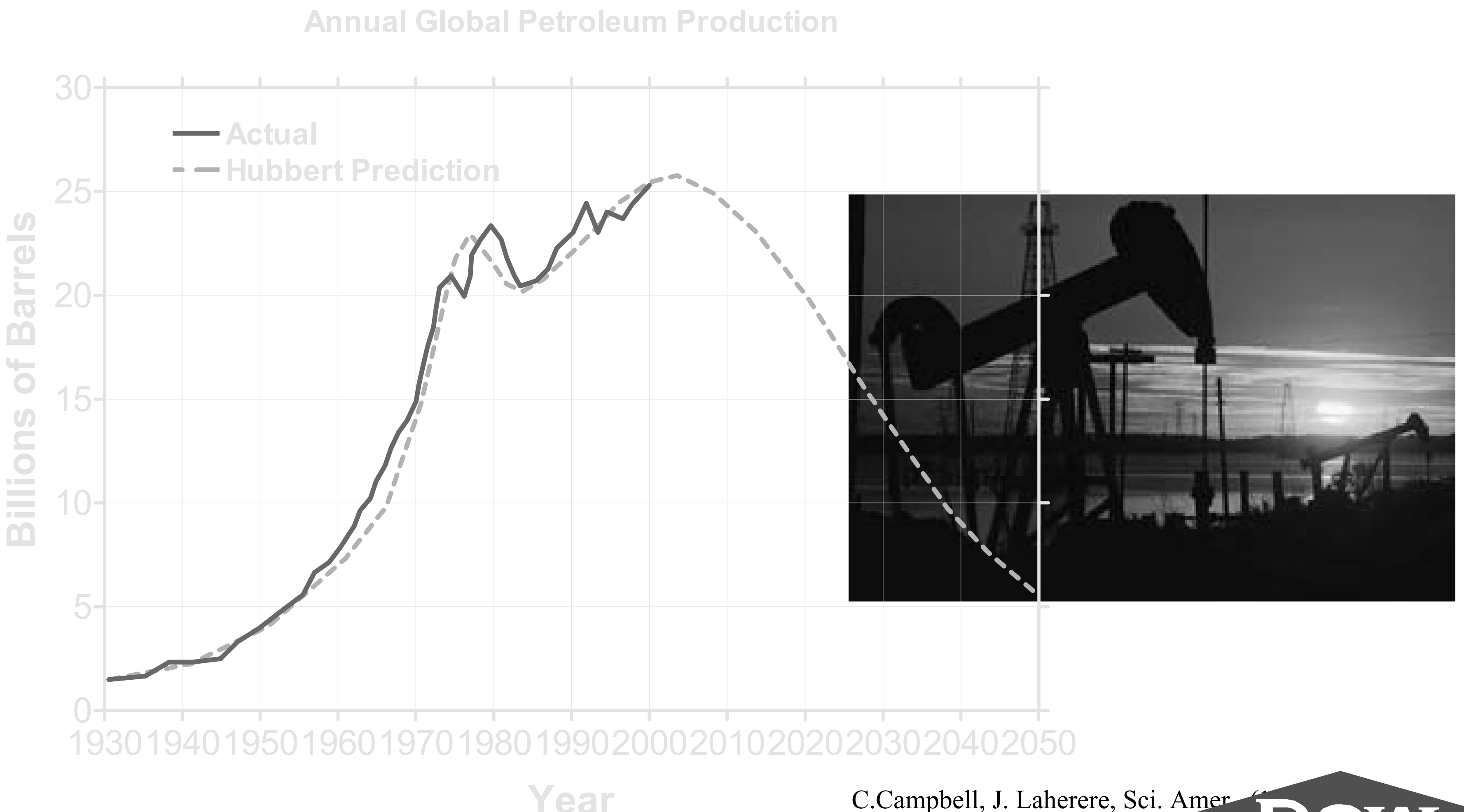


- 1940's: K. Ziegler
  - Coordination chemistry - Zr, Ti + alkyl-Al
  - Low pressure Polyethylene
- 1954: G. Natta
  - Polypropylene
- 1956: H. Schnell - D. Fox
  - Polycarbonate
  - General Electric Co. - commercial in 1959 - Lexan
- 1955-1970: Composite materials
- 1960-1980: Manufacturing technology
- 1980-2000: Specialty plastics & new catalysts

The Chemistry of The Dow Chemical Company



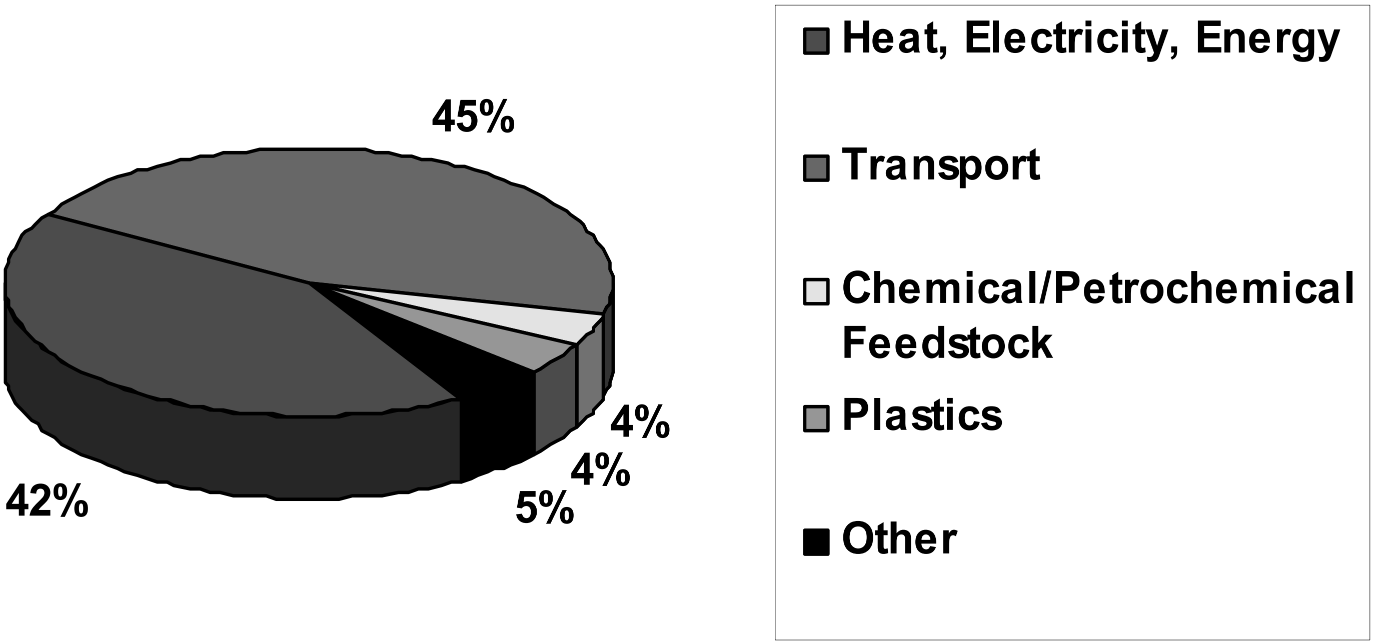
Challenges of Today



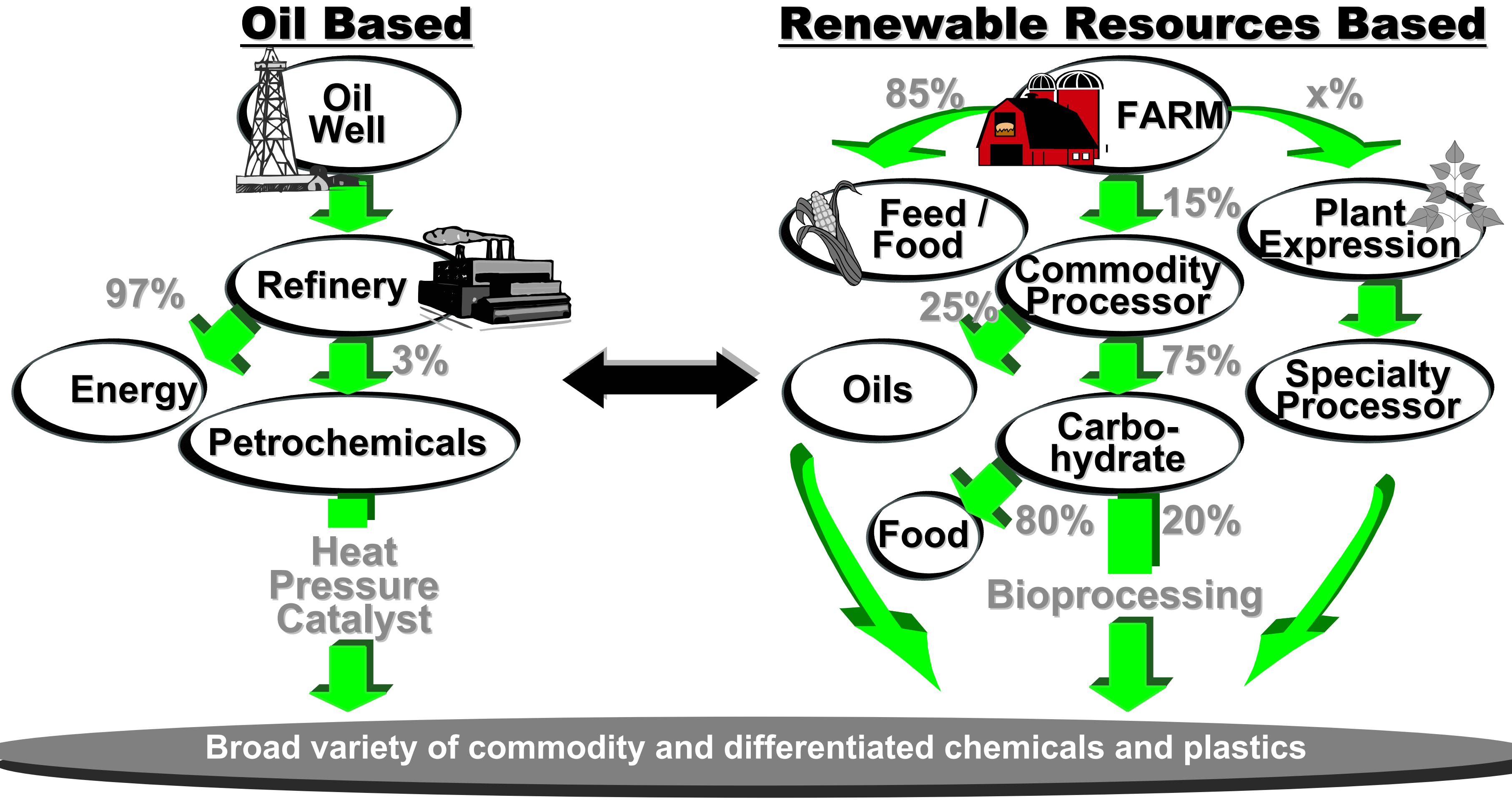
C.Campbell, J. Laherere, Sci. Amer.

Challenges of Today

Relative use of Petroleum



Emerging Future: Duality in Feedstocks and Processes

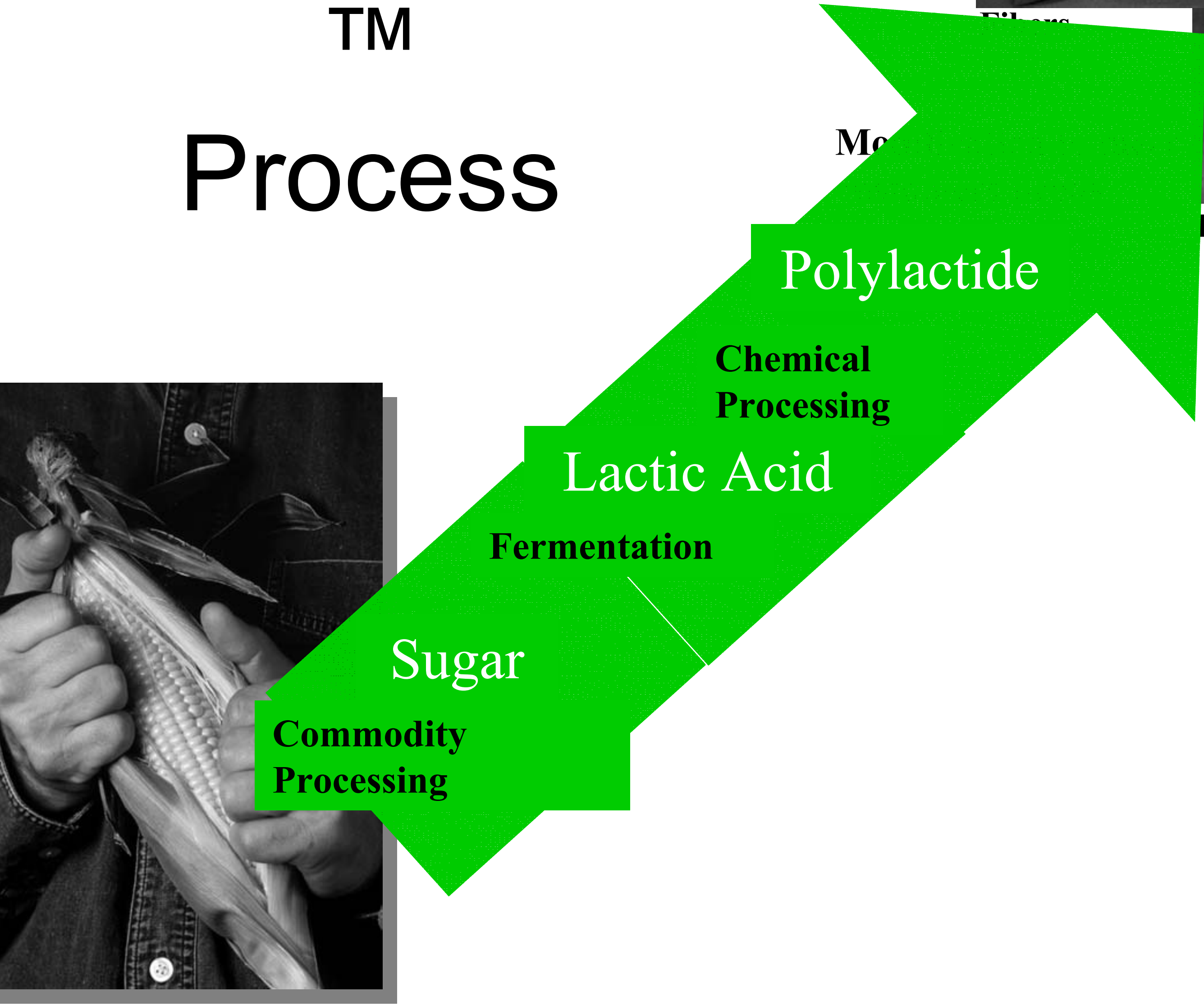


KEY COMPETENCIES
• Catalysis • Chem Engineering • Material Science

KEY COMPETENCIES
• Biotech Basics • Bioprocessing • Chem Engineering • Material Science

NatureWorks
TM

Process

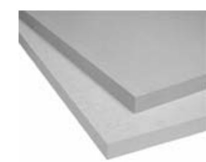


Future Challenges

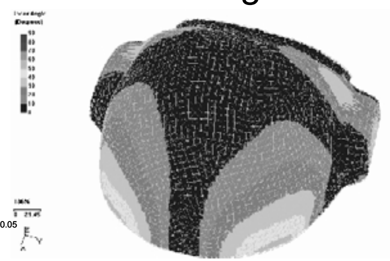
length

Processing
End-User Application

Wind Mill Blades, PCB Laminates, Refrigerator Insulation, Industrial Building Using Steel-Faced Sandwich Panels

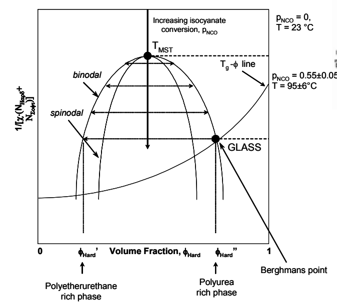


Finite Element Modeling
Design



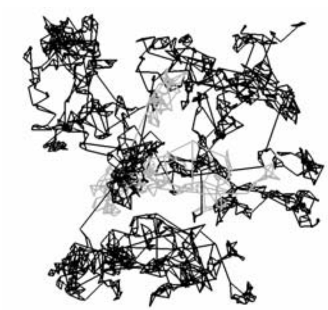
Helicopter pilot helmet - predicted shear angles for carbon/epoxy prepreg

Continuum Models



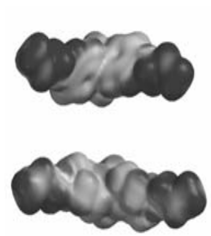
Microstructural phase transition in flexible polyurethane foam formation

Molecular Dynamics
Monte Carlo



Cluster linkage in poly(urethane-urea) networks

Quantum Modeling



Diepoxides undergoing reaction with hardener

time

Stake holder Value

The Business Goal ?

Stake Holder Value Creation

Conclusions

- From product push to product pull
  - Sustainability
  - Stakeholder value creation
- R&D is essential to growth
  - Controlled performance
  - Integration – Multi-disciplinary
- Global reach & local integration
- People