

Recent Developments in Renewable Resource-based Resins

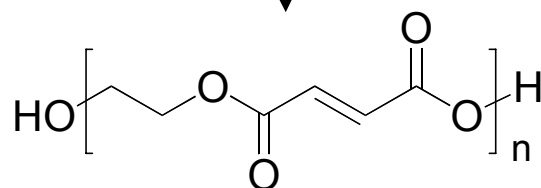
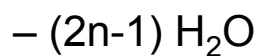
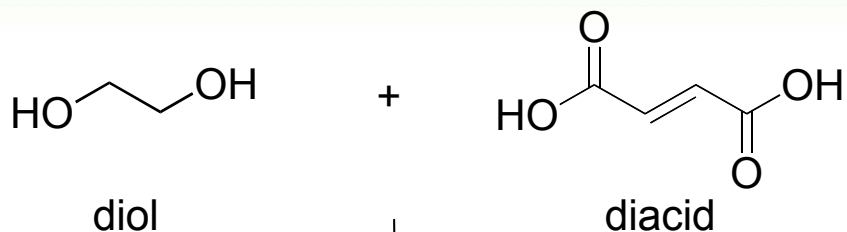
**SPE Automotive Composites Conference & Exposition
September 16-18, 2008**

**Darcy Culkin
Ashland Inc.**

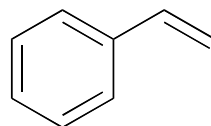
Outline

- ❖ Background and Motivation for Renewable Resource-based Unsaturated Polyester Resins
- ❖ Development and Application of Renewable Resource-based Resins
- ❖ Opportunities for “Green” Growth

Unsaturated Polyester Resins



unsaturated polyester



vinyl monomer
(reactive diluent)

Unsaturated Polyester Resin

peroxide initiator
cross-linking reaction

Thermoset Plastic

Renewable Resource Definitions

Renewable Resource

Any natural resource that is depleted at a rate slower than the rate at which it regenerates. Renewable resources can be replaced by natural ecological cycles or sound management practices.

Renewable Energy Sources

- Solar
- Wind
- Geothermal
- Hydroelectric
- Biomass
- Waste

Renewable Product Sources

- Water
- Oxygen
- Aquatic life
- Animals
- Biomass (Trees, Crops, Grass)
- Soil

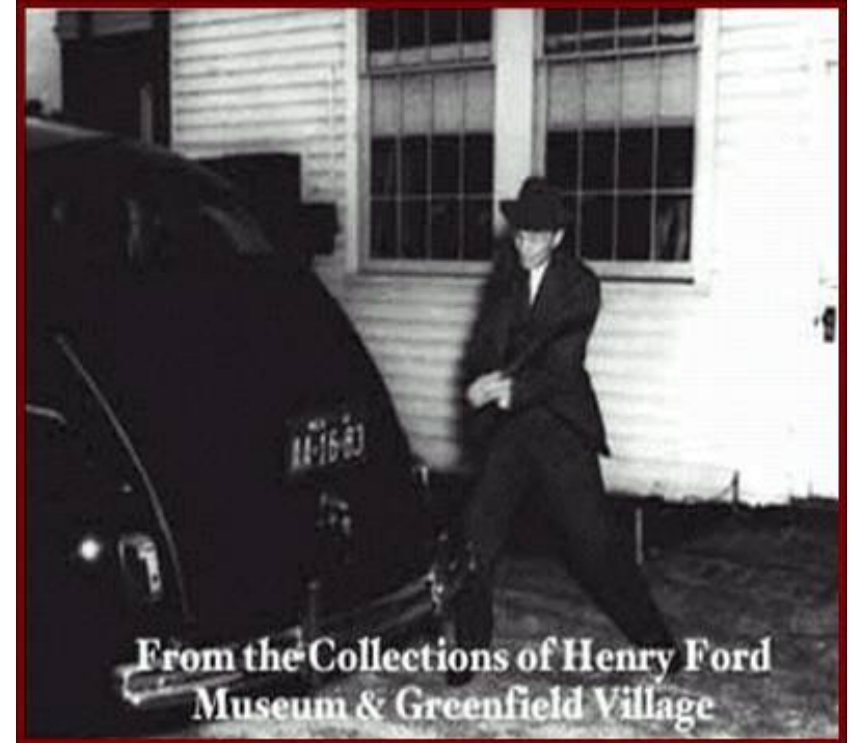
Non-Renewable Resource

Has no mechanism to replenish itself or it is depleted at a rate greater than the rate at which it regenerates.
Examples: Coal, crude oil, natural gas

Biomass as a renewable feedstock
is a growing field of chemistry.

Renewable Resource-based Plastics

"I believe that industry and agriculture are natural partners" Henry Ford (1863-1947)

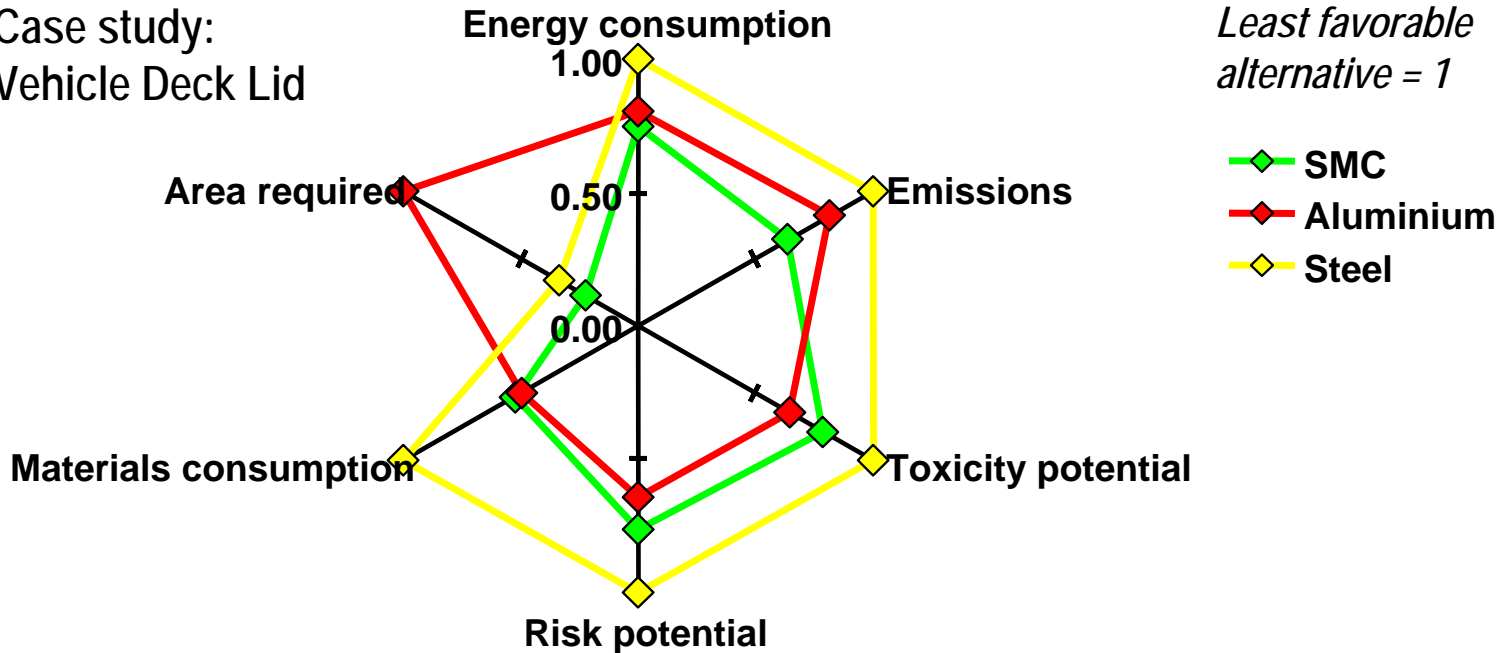


- Ford introduced an all-plastic motor car body in 1941.
- The plastic body panels were made of 70% cellulose fiber and 30% phenolic resin extended with soybean meal, a by-product of the soybean oil extraction process.

Reduced Environmental Impact

- ❖ Composites: lower environmental impact solution vs. other types of materials

Case study:
Vehicle Deck Lid



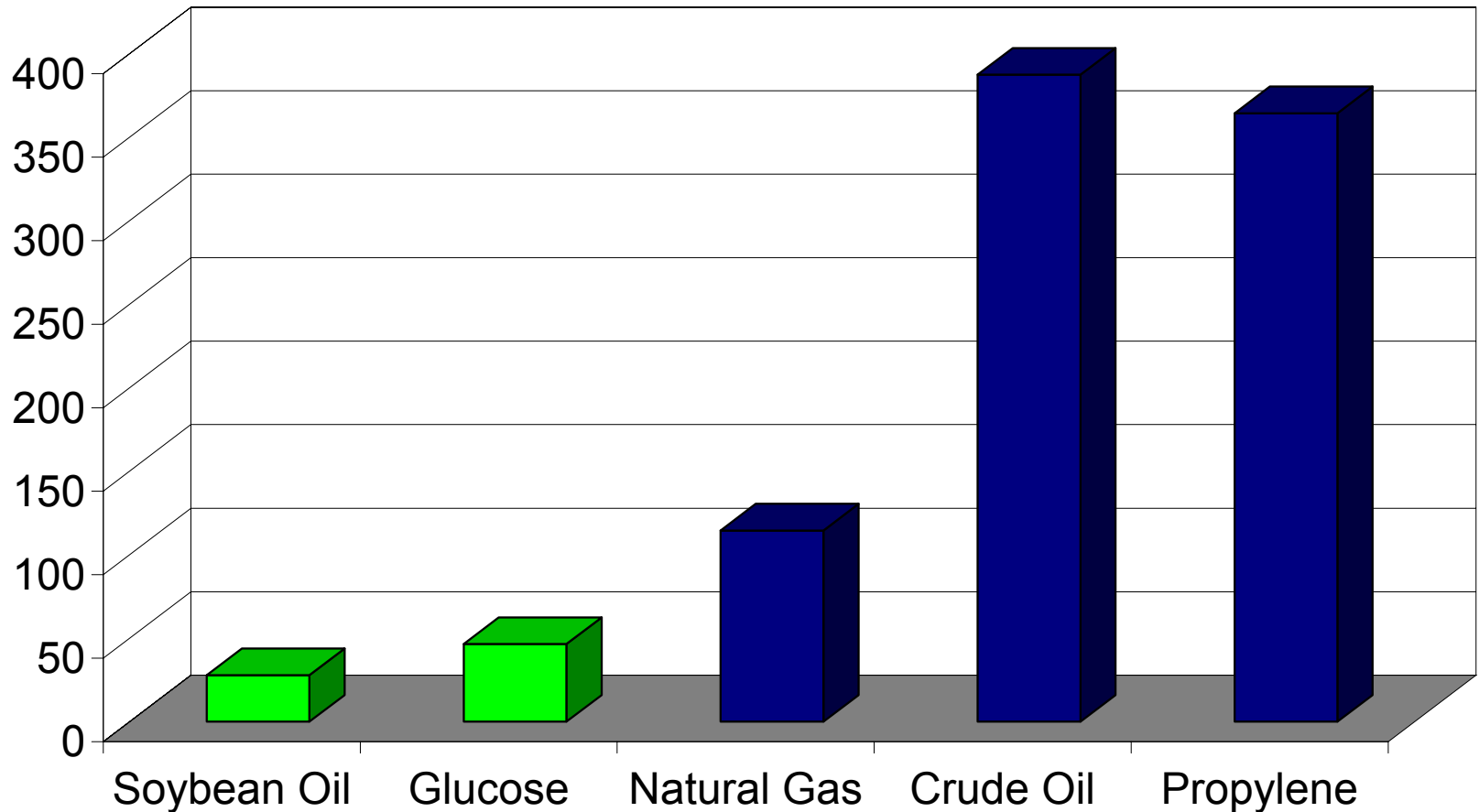
Courtesy of European Alliance for SMC/BMC

- ❖ How can we improve further?

→ **Renewable Resource-based UPRs**

Reduced Reliance on Petroleum

% Increase in Price of various Feedstocks in the last 15 years



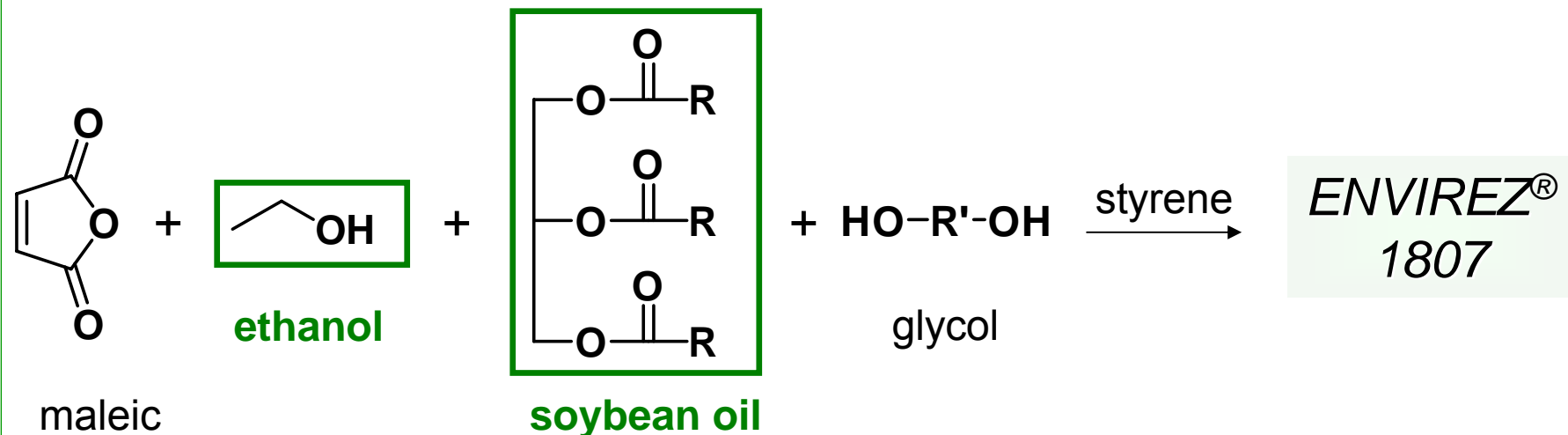
Bio-based feedstocks may offer long-term supply and cost stability.

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Development of ENVIREZ® 1807 Resin

Ashland's first renewable resource-based UPR



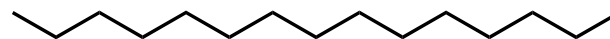
maleic anhydride

ethanol

soybean oil



Oleic acid -- 29%

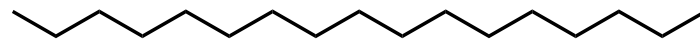


Palmitic acid -- 10%

R =



Linoleic acid -- 51%



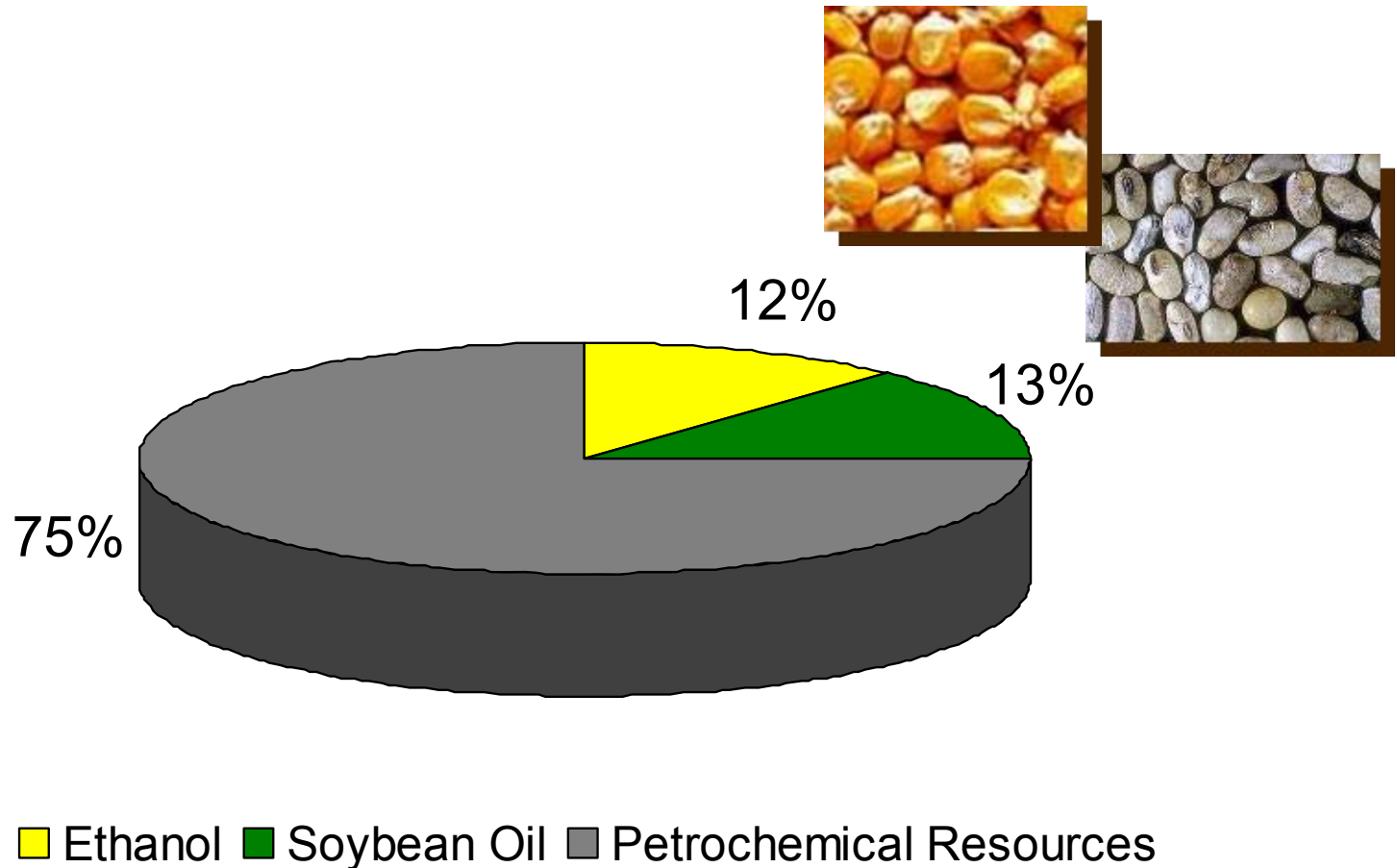
Stearic acid -- 2%



Linolenic acid -- 7%

Ashland U.S. Patent 6,222,005

ENVIREZ[®] 1807 Renewable Resource Content



Renewable resource-based materials account for up to 25% of input raw material volume.

Typical Liquid Resin Properties

Property	Bio-based Resin ENVIREZ® 1807	Standard Petrochemical Resin (control)
Viscosity (77 °F, cps)	850 – 1050	800 – 1000
Non-volatiles (%)	69.0 – 72.0	64.0 – 66.0
SPI Gel Test (180 °F, 1% BPO)		
Gel Time (min)	5.5 – 8.0	8.0 – 12.0
Peak Exotherm Time (min)	7.0 – 11.0	10.0 – 13.0
Peak Exotherm Temperature (°F)	385 – 415	420 – 460

Renewable resource-based resins are compatible with existing processes and equipment.

Typical Physical Properties (SMC panels)

Property	Bio-based SMC ENVIREZ® 1807 Resin	Standard SMC (Control) Petrochemical Resin
Tensile Strength (MPa)	102	81
Tensile Modulus (GPa)	10.8	13.0
Flexural Strength (MPa)	194	208
Flexural Modulus (GPa)	9.8	11.1
Impact, Notched (J/m)	940	1,070
Impact, Unnotched (J/m)	1,260	1,270
Glass content (%)	29	29
Shrinkage (in/in) <i>Cold -part to cold-mold</i>	-0.0005	-0.0006
Water Absorption (%)	0.480	0.490

Formulations using bio-based resins have comparable physical properties to their petroleum-based counterparts.

Paint Testing (SMC Panels)

Paint Testing Bio-based SMC	Requirements	Results	Pass / Fail
Adhesion	A	A	Pass
Initial Gloss JDM F9A – 20° Meter	≥ 80	83	Pass
Hardness	H	2H	Pass
Humidity	A	A	Pass
Chip – 1 Pint (–30 °C)	5A	9A	Pass
Chip – 3 Pint (–30 °C)	---	8A	Pass
Chemical Resistance – Cure (MEK)	No Removal	No Change	Pass
Chemical Resistance – Water Immersion	A	---	Pass
Environmental Cycling	---	---	Pass

Bio-based resins can display improved paint yield.

Implementation of Bio-based SMC

Combine Styling Panels, 2001-02



Tractor Hood & Side Panels, 2004



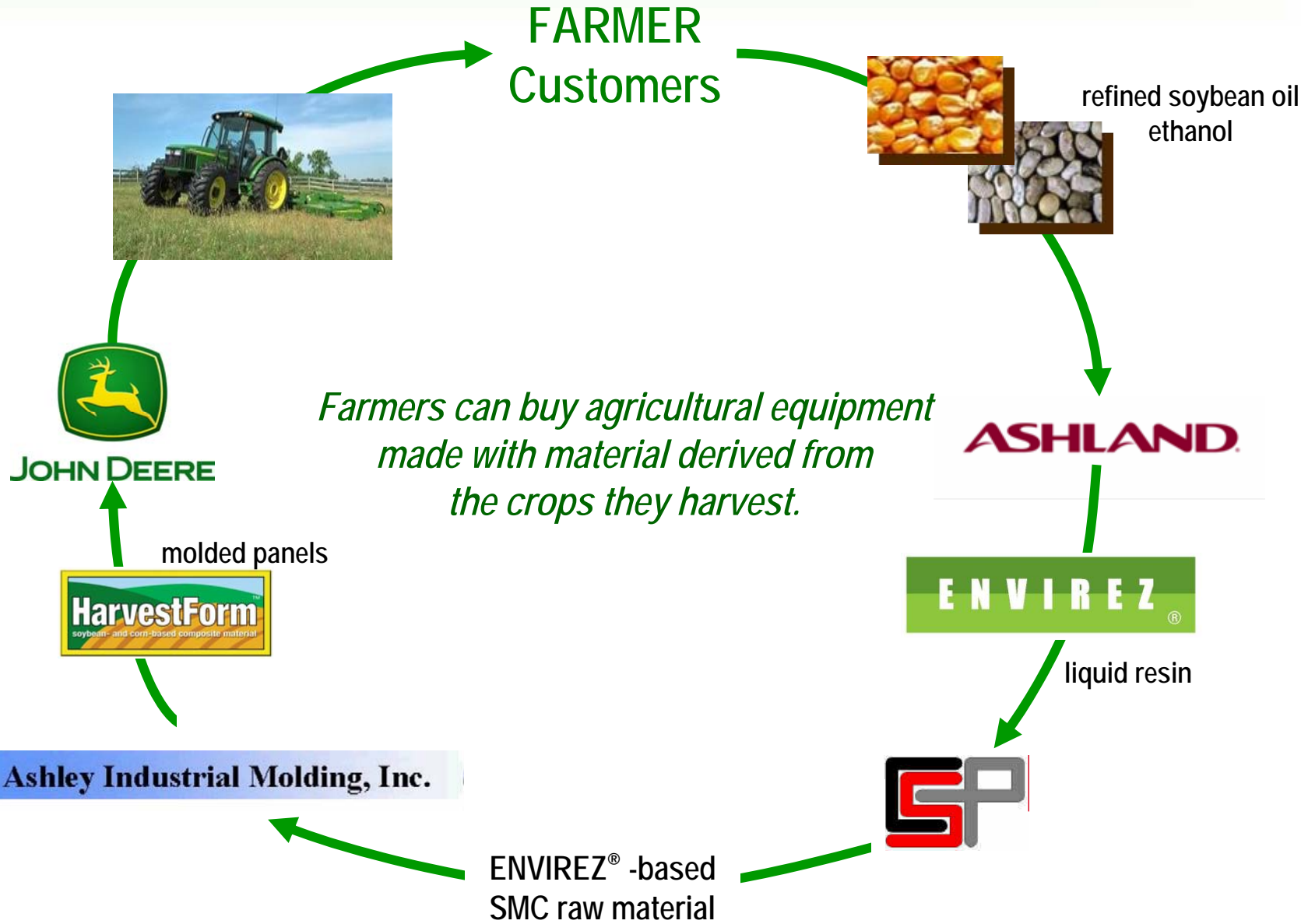
Backhoe Hood Components, 2003



JOHN DEERE

photos courtesy of John Deere

From Corn & Beans to Machines



Example 2: Structural SMC

Property*	Bio-based Resin	Petrochemical Resin (control)
Tensile Strength (MPa)	103	95
Tensile Modulus (GPa)	12.0	13.6
Flexural Strength (MPa)	250	260
Flexural Modulus (GPa)	12.3	14.7
Toughness (psi)	156	151
Orange Peel (>7)	8.2	7.7
ALSA Index (<60)	55-65	55-65
DOI (>80, max 100)	90	85

DOI = Distinctness of Image



Formulations using bio-based resins have comparable physical and surface properties to their petroleum-based counterparts.

**Properties are typical values and may vary from sample to sample.*

Example 3: Class A Surface SMC

Property*	Bio-based Class A SMC	Petrochemical Class A SMC (control)
Tensile Strength (MPa)	80	86
Tensile Modulus (GPa)	10.6	9.4
Flexural Strength (MPa)	170	170
Flexural Modulus (GPa)	11.2	10.0
Orange Peel (>7)	9.0	9.0
ALSA Index (<60)	40-55	45-50
DOI (>80, max 100) <small>DOI = Distinctness of Image</small>	98	99



Formulations using bio-based resins can provide Class A surfaces with comparable physical properties to their petroleum-based counterparts.

**Properties are typical values and may vary from sample to sample.*

Example 4: Infusion

Property <i>(low temperature post cure)</i>	Bio-based Low Profile Resin	Standard Petrochemical Low Profile Resin (control)	
		“Low”	“High”
Tensile Strength (MPa)	32	17	40
Tensile Modulus (MPa)	1775	1224	2275
Elongation at Break (%)	3.2	2.8	3.0
Flexural Strength (MPa)	41.6	27.5	56
Flexural Modulus (MPa)	1438	1365	1875
Heat Distortion Temperature (°C)	78	70	76



Bio-based Low Profile resins have equivalent properties to their petroleum-based counterparts.

**Properties are typical values and may vary from sample to sample.*

Example 4: Infusion

Property* <i>(after final postcure)</i>	Bio-based Low Profile Resin	Standard Petrochemical Low Profile Resin (control)	
		"Low"	"High"
Orange Peel	8.2	7.0	9.9
ALSA Index	60	90	40
DOI <small>DOI = Distinctness of Image</small>	83	70	100

For automotive Class A surfaces: Target = DOI > 80; AI < 60; OP > 7



*Surface quality (distinctness of image)
for gel coated infusion panel*

Class A surfaces can be achieved with bio-based Low Profile infusion resins.

**Properties are typical values and may vary from sample to sample.*

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Environmental Benefits

Example:

One Batch (38,000 lb.) of ENVIREZ® 1807 Resin

- Saves 10 Barrels of Crude Petroleum*
- Removes an Estimated 34,000 lbs of CO₂**

Compared to Similar Petroleum-based Resins

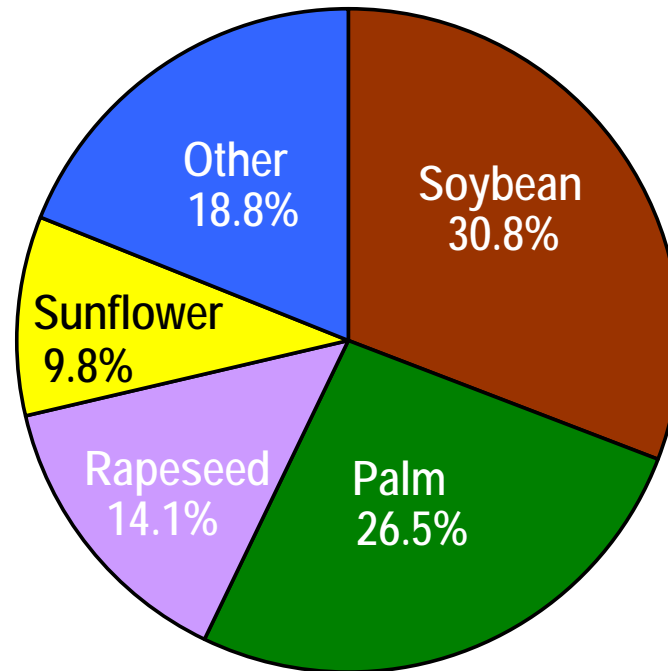
**This calculation is the net of the energy consumed in manufacturing as well as by farming and processing soy and corn into oil and ethanol, respectively.*

***For each pound of soy oil produced, 2.67 pounds of CO₂ are removed from the air. For each pound of ethanol produced, 1.5 – 2.0 pounds of CO₂ are removed from the air.*



Local Sources for Renewable Materials

World Oil Crops Production (marketing years 1998/99 – 2002/2003)



Gallons per Acre

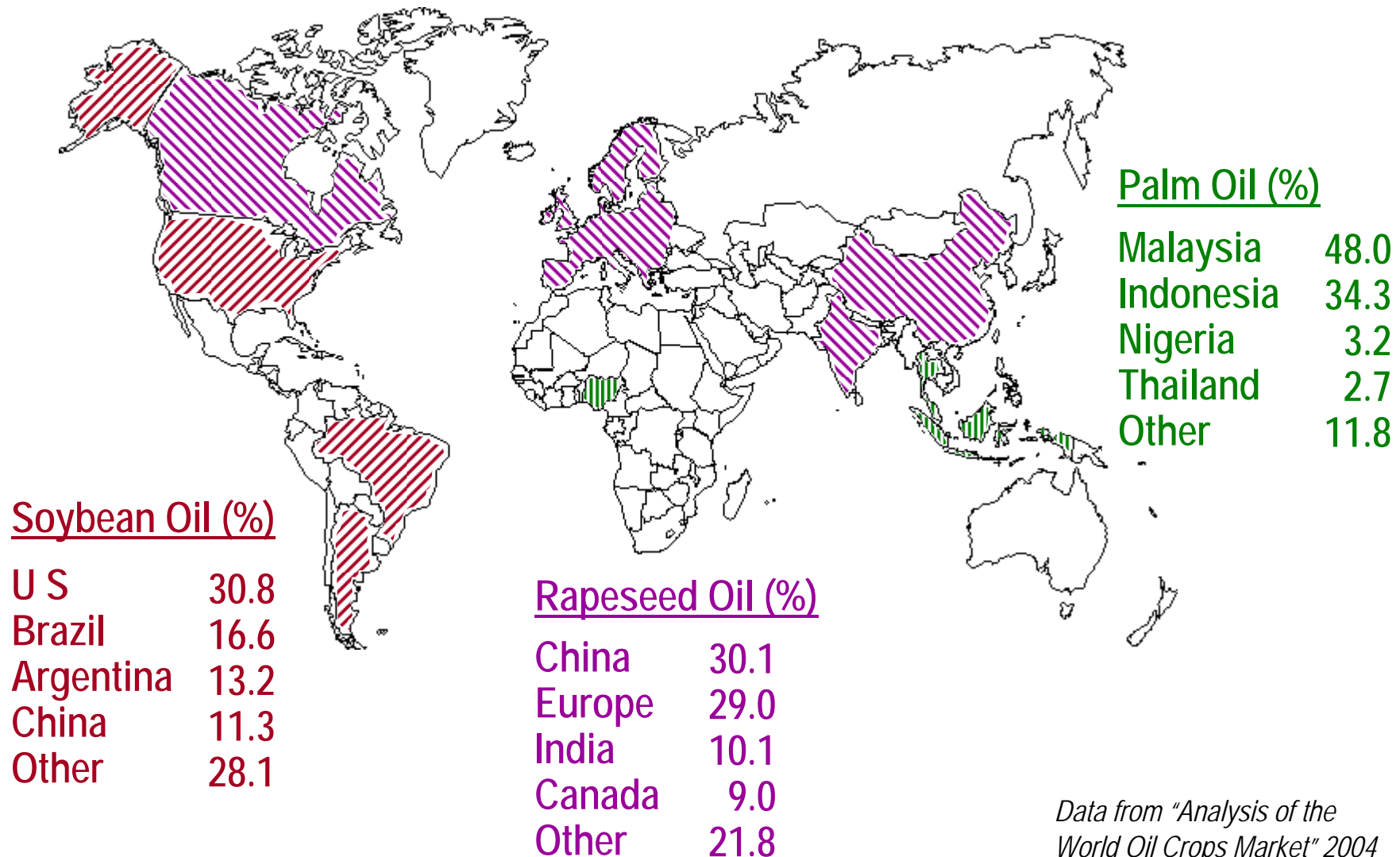
Soybean 48

Palm 635

Rapeseed 127

Local Sources for Renewable Materials

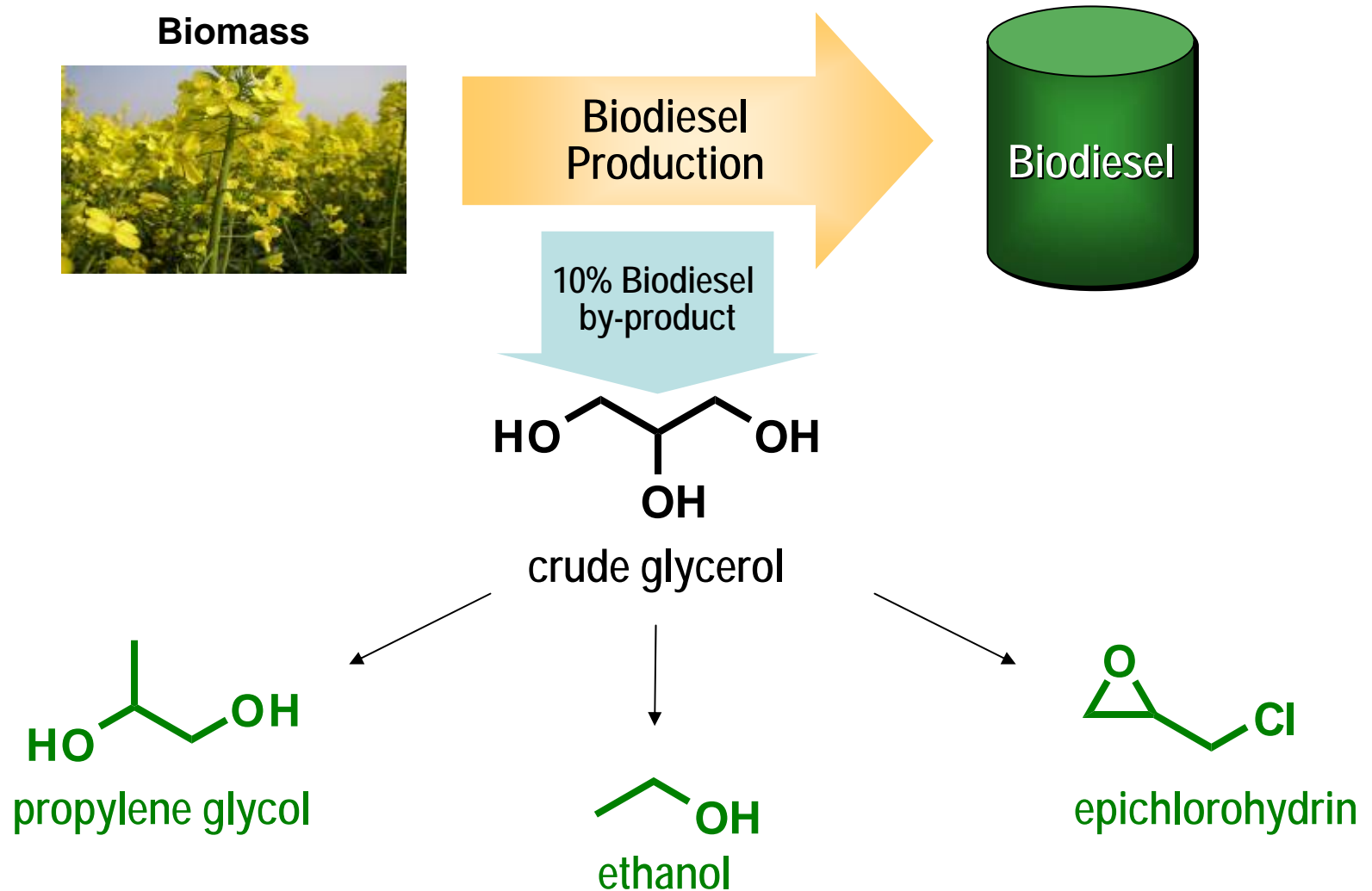
World Oil Crops Production by Country (1998 – 2003)



Data from "Analysis of the World Oil Crops Market" 2004 by J. Mattson, C. Sun, W. Koo

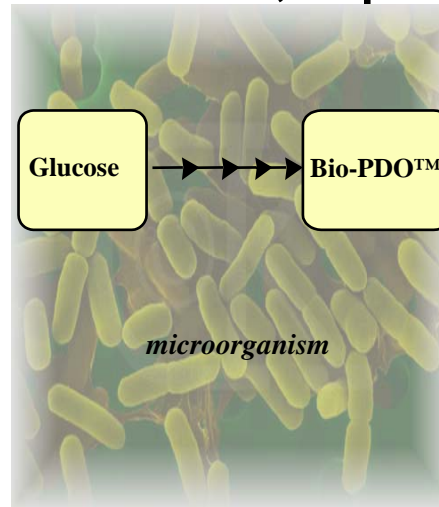
Availability of New Renewable Raw Materials

Opportunities from growth in bio-based fuels



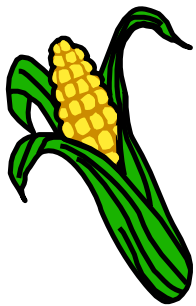
Availability of New Renewable Raw Materials

Conversion of glucose to 1,3-propanediol

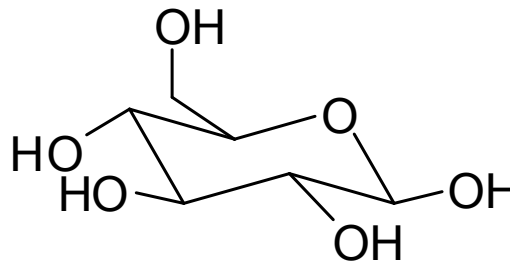
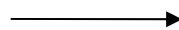


Ferment glucose to PDO
using patented microorganism

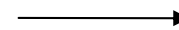
Refine to 99.7% purity



Corn



Dextrose



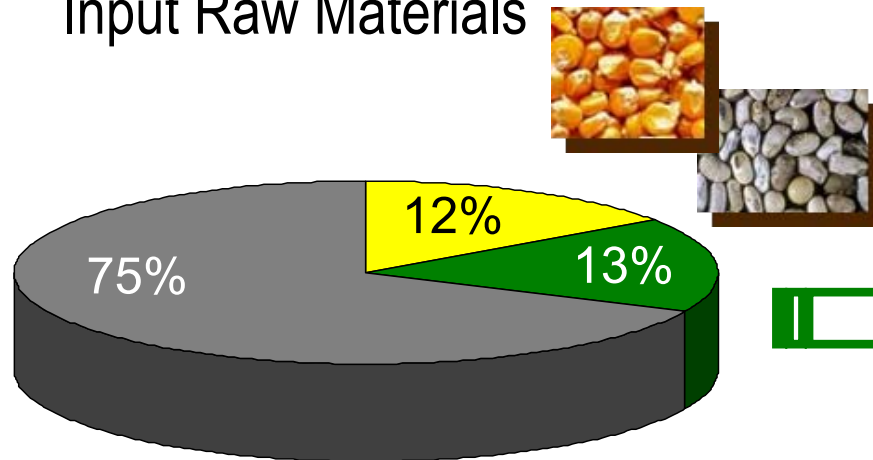
1,3 Propanediol

Courtesy of DuPont Tate & Lyle BioProducts LLC

¹Susterra is a trademark of DuPont Tate & Lyle BioProducts LLC

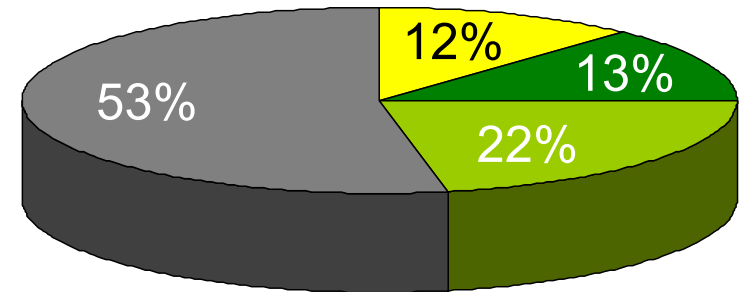
Availability of New Renewable Raw Materials

Current Bio-based Resin
Input Raw Materials



- Ethanol
- Soybean Oil
- Petrochemical Resources

Bio-based Resin
Input Raw Materials
with Renewable Glycol



- Ethanol
- Soybean Oil
- Renewable Glycol
- Petrochemical Resources

Government and Corporate Sustainability Initiatives

USDA BioPreferred¹ Program (formerly FB4P)

(FB4P: Federal Biobased Products Preferred Procurement Program)

- Preference program that serves to increase the procurement and use of biobased products by Federal agencies.
- Propelled by a provision of the 2002 Farm Security and Rural Investment Act.



United States Department of Agriculture
BioPreferred¹

for more information, see: www.biobased.oce.usda.gov

¹ BioPreferred is a service mark of the U.S. Department of Agriculture



Photos by Michael Crane for the
DOE Idaho National Laboratory

Government and Corporate Sustainability Initiatives

LEED¹ for sustainable construction

**LEADERSHIP in
ENERGY and
ENVIRONMENTAL
DESIGN**

A leading-edge system for certifying
**DESIGN,
CONSTRUCTION,
& OPERATIONS**
of the greenest buildings in the world

for more information see: www.usgbc.org/LEED/

Other NGO Influences:

- Architecture 2030 Challenge
- Clinton Initiative

¹ LEED is a registered trademark of the U.S. Green Building Council



7 World Trade Center
Officially Certified as NYC's
First "Green" Office Tower

*photo by David Shankbone

Conclusions and Outlook

Renewable resource-based resins have:

- ❖ Performance equivalent to petrochemical-based resins
- ❖ Various applications
- ❖ Unique environmental assets
- ❖ Opportunities for growth

Thank you for your attention!

