DOMESTIC NATURAL RUBBER FROM GUAYULE: A MULTI-PRODUCT BIOREFINERY MODEL

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USDA-ARS-WRRC/ERRC
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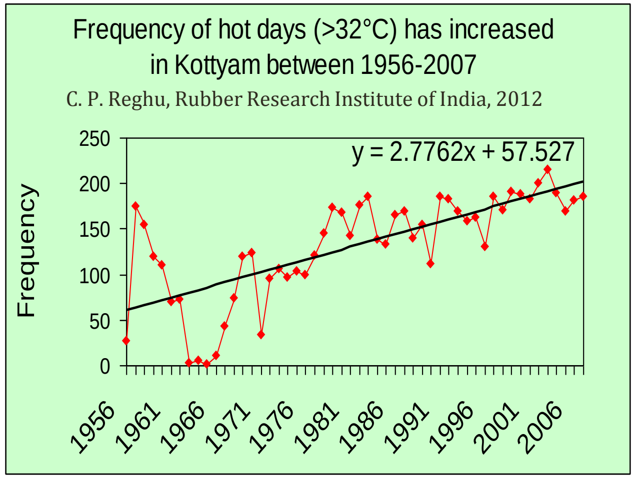
Objective

Sustainable commercial production of natural rubber by U.S. agriculture.

Matthew Busch, New York Times, August 19, 2015

Natural rubber production: sustainability

Threats:
SALB
Allergenicity
White root disease
Palm oil plantations
Deforestation
Climate change



34 Rubber & Plastics News • October 15, 2007 www.rubbernews.com

Michelin working to combat leaf blight

AGRICULTURE

The Rubber Juggernaut

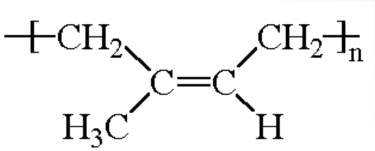
The demise of swidden cultivation in Southeast Asia may have devastating environmental consequences.

Alan D. Ziegler,[1] Jefferson M. Fox,[2] Jianchu Xu[3]

Rubber plantations are expanding rapidly throughout montane mainland Southeast Asia (1–3). More than 500,000 ha may have been converted already in the uplands of China, Laos, Thailand, Vietnam, Cambodia, and Myanmar (see the figure, panel A). By 2050, the area of land dedicated to rubber and other diversified farming systems could more than double or triple, largely by replacing lands now occupied by evergreen broadleaf trees and swidden-related secondary vegetation (2). What are the environmental consequences of this conversion of vast landscapes to rubber?

Swidden versus rubber. (A) Montane mainland Southeast Asia (green shaded areas) is defined here as the lands between 300 and 3000 m above sea level. (B) Most swidden fields and fallows on slopes near villages and roads in this area in Xishuangbanna have been converted to terraced rubber stands.

Supply security and opportunity



✓Natural rubber is a strategic biobased materials essential to medicine, defense, and industrial manufacturing in the U.S. Critical Agricultural Materials Act (2000) (PL 95-592 & 98-284).

✓The U.S. relies on imports to meet domestic needs.

✓Natural rubber was formerly produced in the U.S., but economic issues denied sustainability.

✓ Expansion of domestic rubber production can address supply security, provide rural development opportunities, and reduce the use of petroleum-based elastomers.

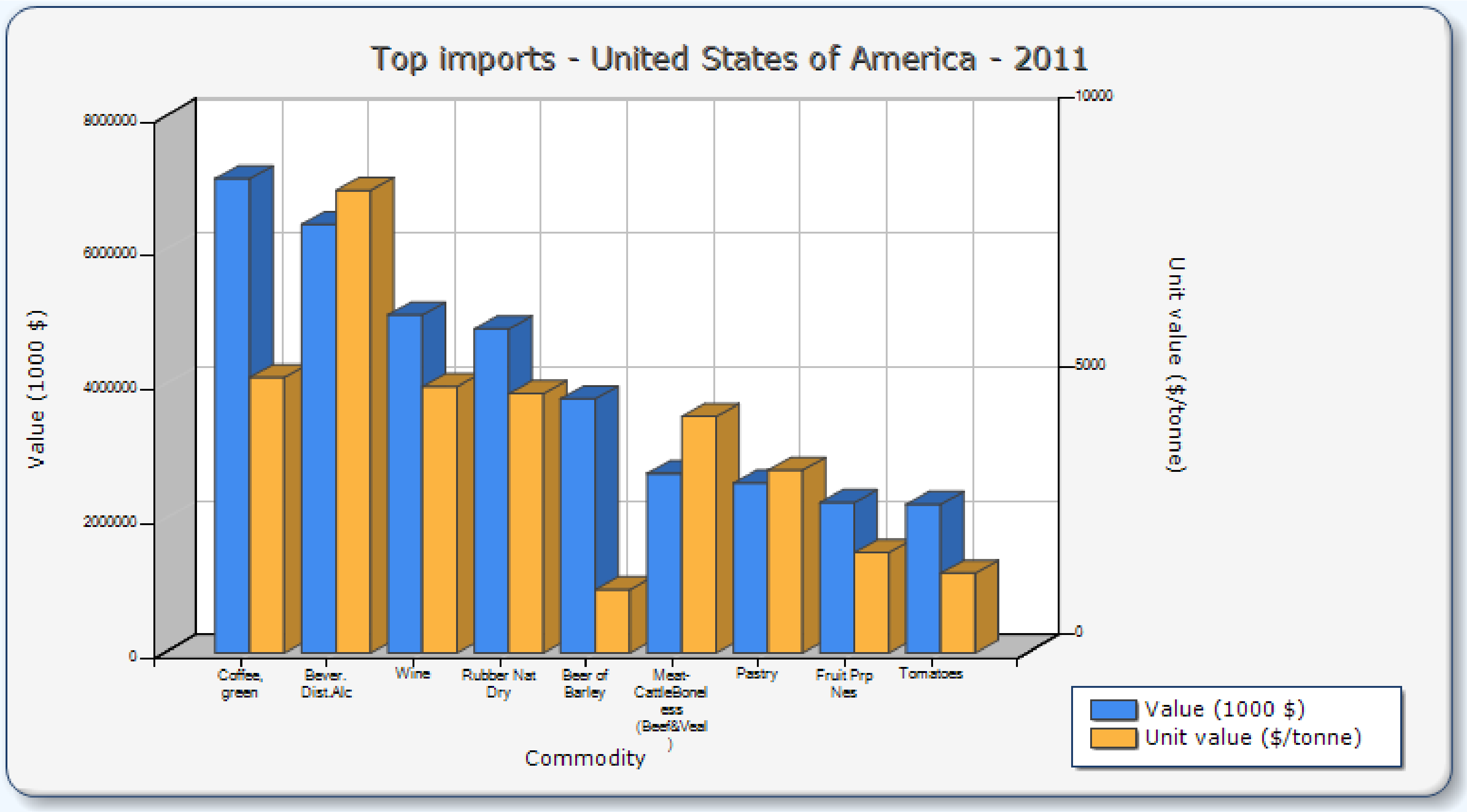
guayule (*Parthenium argentatum*)

Kazakh dandelion (*Taraxacum-kok saghyz*)

An opportunity for American farming

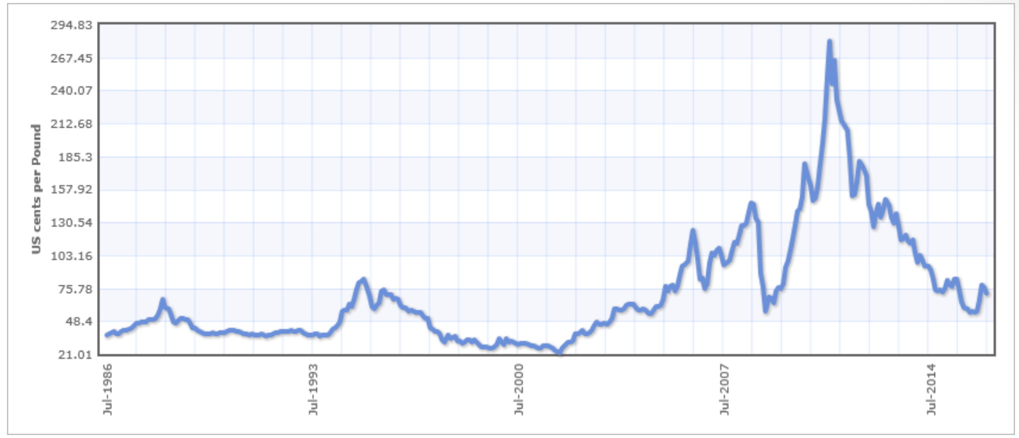
natural rubber the 4th most valuable agricultural import in the USA (1M tons, $5B)
petroleum-based rubber production over 18 million MT per annum
markets for alternative natural rubber are driving demand
US guayule growing region estimated at over 1,000,000 acres

faostat.fao.org



Why guayule now?

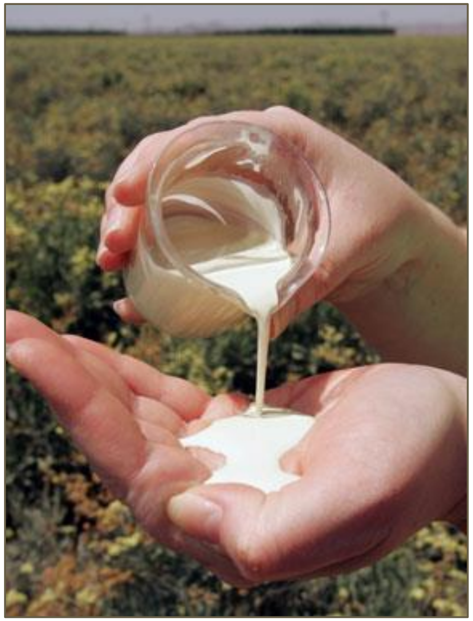
Singapore Commodity Exchange, No. 3 Rubber Smoked Sheets
US cents per Pound
Source: indexmundi.com



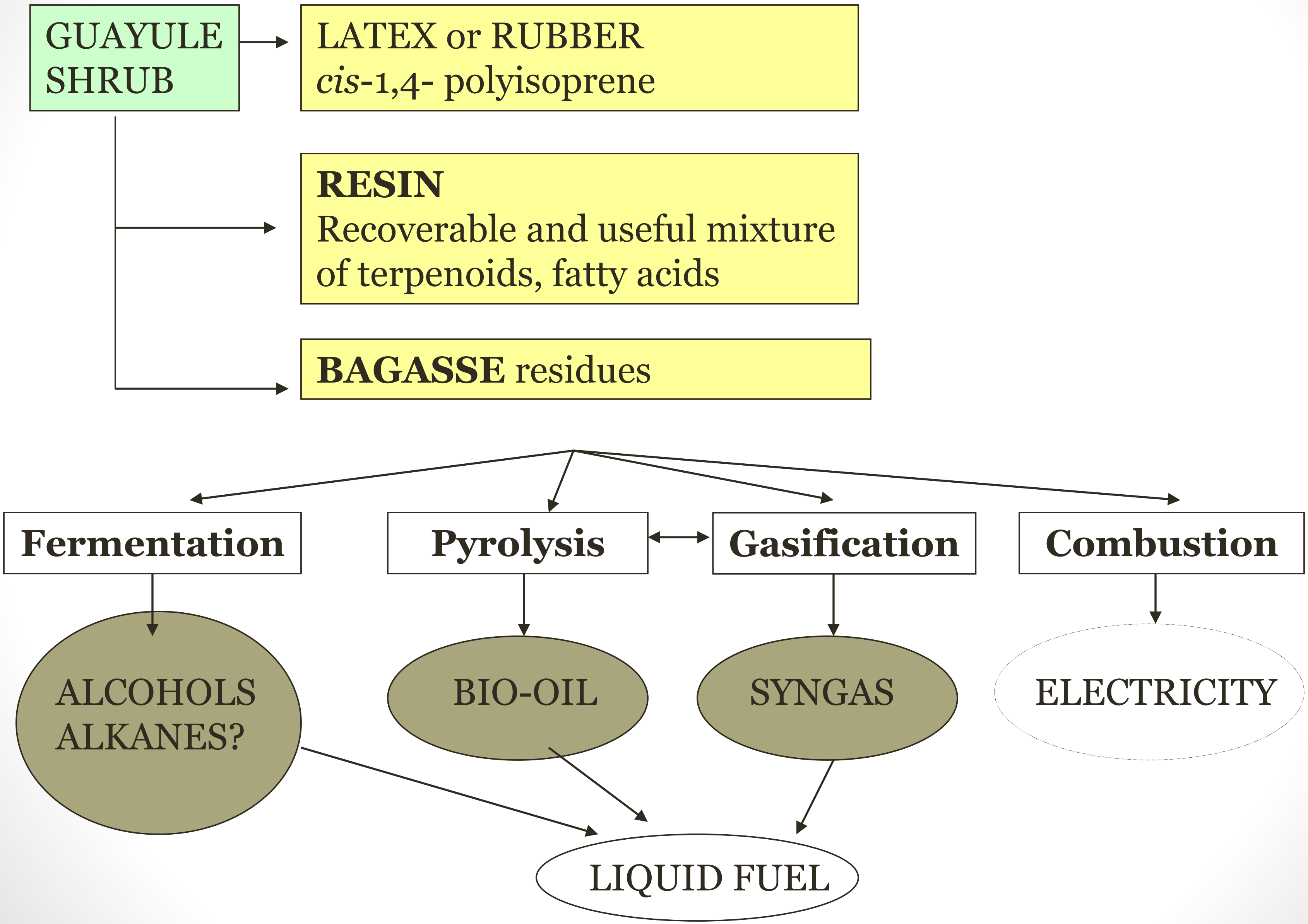
Critical Agricultural Materials Act (2000) (PL 95-592 & 98-284)

- Currently under commercial cultivation in Arizona by Yulex Corporation, PanAridus LLC, and Bridgestone Americas.
- Global demand for tires is increasing. 21 million new acres of Hevea by 2024?
- Guayule rubber quality is at least equivalent to synthetic polyisoprene.
- Volatility in *Hevea* NR prices and shortages of synthetic rubber (2008, 2011).
- Market pull for ‘green products’. Carbon credit trading is becoming an industrial reality.
- Application of the tools of modern genomics and molecular biology have tremendous potential.
- Coproducts will have to succeed this time for economic sustainability.

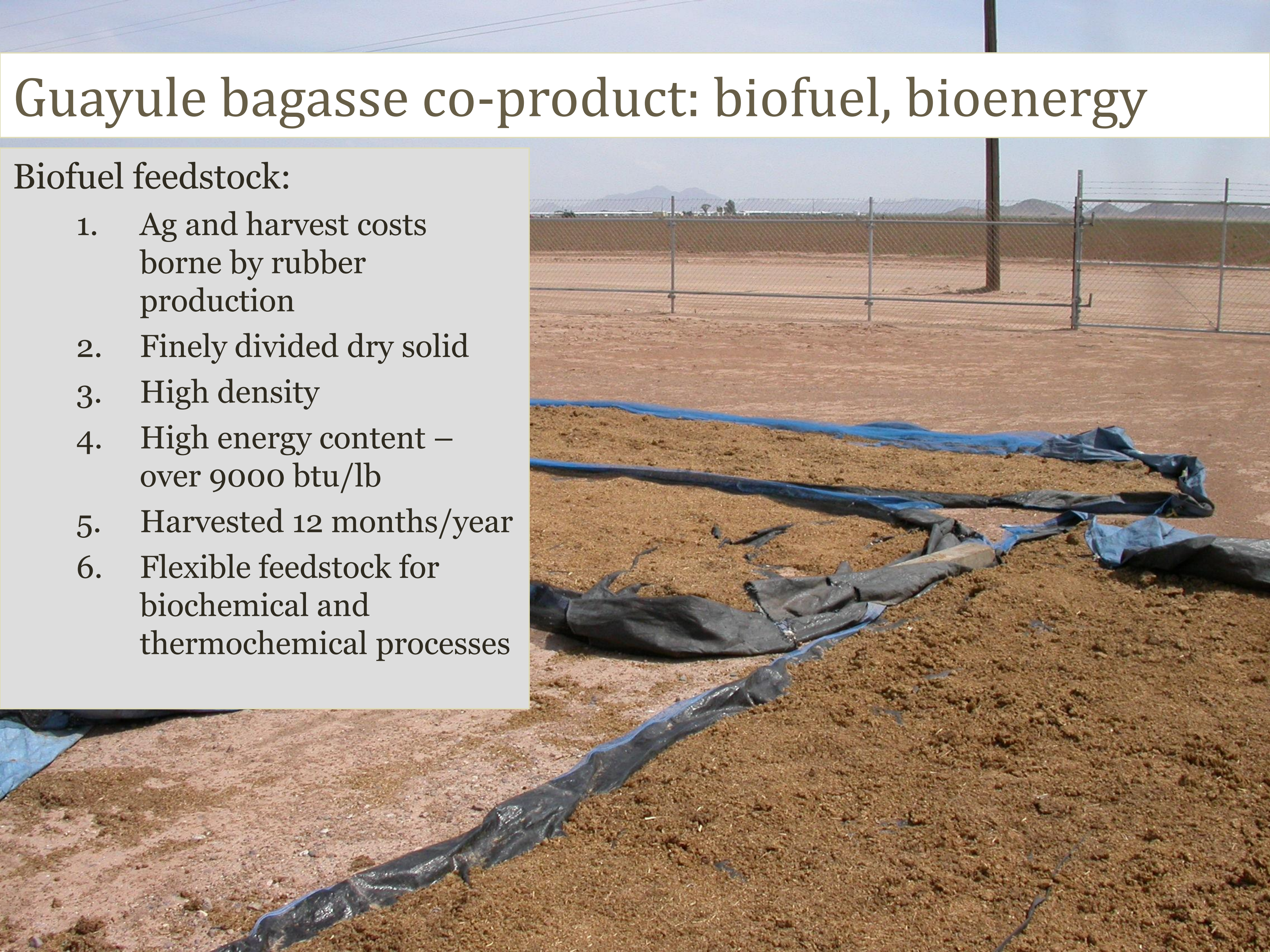
Where we are…



Guayule biorefinery: bioproducts + bioenergy



Guayule bagasse co-product: biofuel, bioenergy



Biofuel feedstock:

1. Ag and harvest costs borne by rubber production
2. Finely divided dry solid
3. High density
4. High energy content – over 9000 btu/lb
5. Harvested 12 months/year
6. Flexible feedstock for biochemical and thermochemical processes

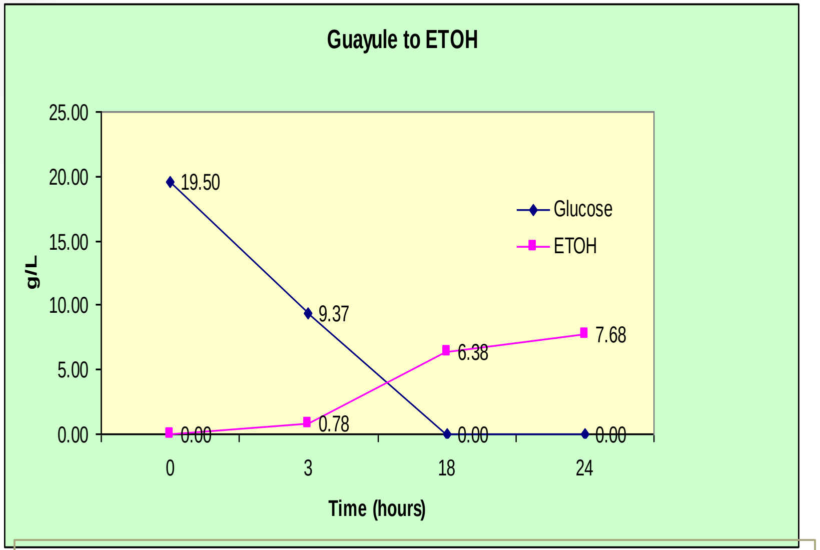
Guayule shrub and bagasse composition

Property	Method	Whole shrub	bagasse
Moisture (% as rec'd)	weight loss	2.63	3.14
Ash (%dw)	weight loss after combustion at 450 °C /16 h muffle furnace.	**12.80**	**3.15**
[1]C (%dw)	ASTM D-5291	47.09	55.19
[1]H (%dw)	ASTM D-5291	5.23	6.35
[1]N (%dw)	ASTM D-5291	1.38	0.65
[1]S (%dw)		0.62	0.20
[1]O (%dw)	ASTM D5291 (difference)	32.88	34.36
[2]Cellulose (%dw)	Cell wall glucose HPLC[1]	14.8	23.0
[2]Hemicellulose (%dw)	Σ (cell wall xylose, arabinose, mannose, uronic acids)	18.9	25.8
[2]Lignin (%dw)	acid-insoluble residue after correction for ash	**18.7**	**30.0**
[1]HHV (kJ/kg)		**18,329**	**22,385**

Boateng et al. Fuel 2009

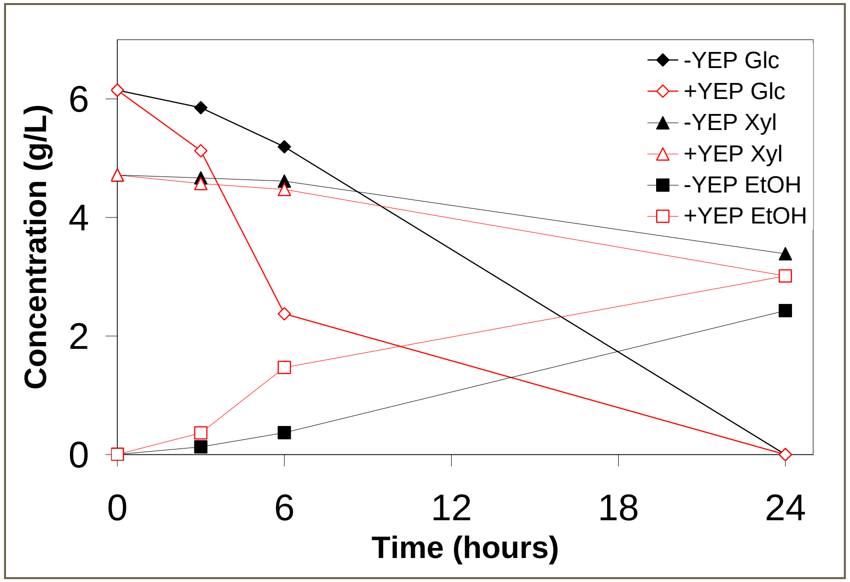
Guayule bagasse to ethanol demonstrated…

Holtman *et al*, unpublished



Organosolv Pretreatment
7:1 Liquor/Wood ratio
1:1 H2O/EtOH ratio
1 % (w/w) H2SO4 catalyst
Ramp directly to temp, 30 minutes 195°C
Enzymatic Hydrolysis
5 % solids content,
Citrate buffer, pH 4.5
50 FPU/g cellulose
1:4 cellulase:cellobiase ratio (FPU:CBU)
55 °C, 72 hours
Fermentation: standard NREL protocol

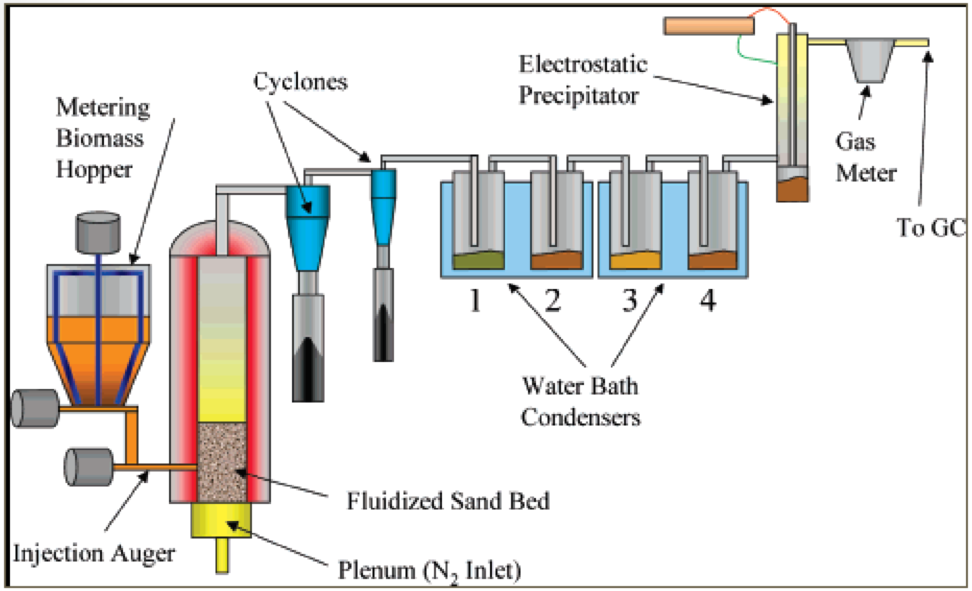
Chundawatt *et al.* 2012

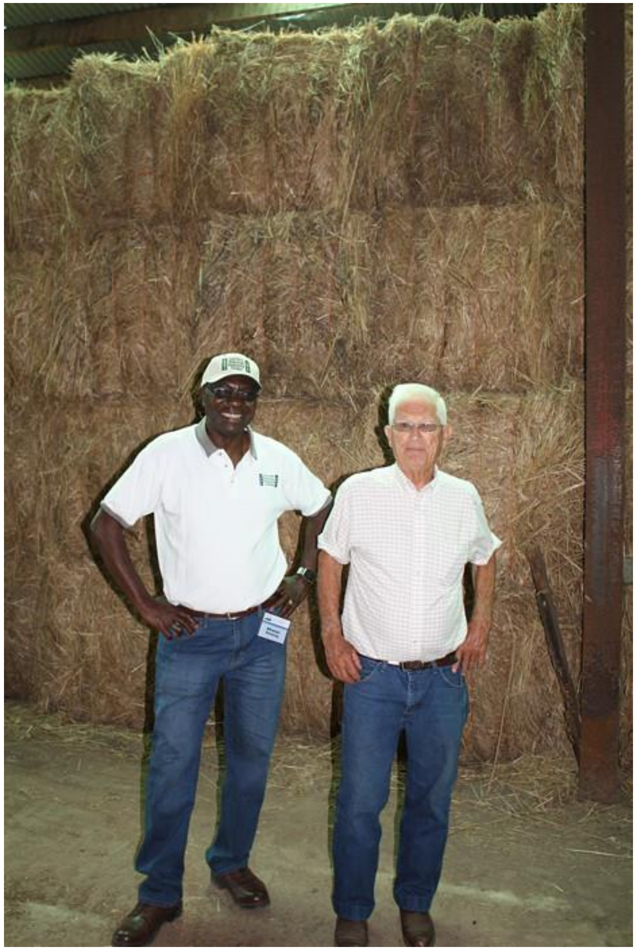


AFEX Pretreatment:1 or 2 g NH3/g dry biomass
60% moisture, dry weight basis
residence time = 30 minutes
temperatures = 150°C
Fermentation
Saccharomyces cerevisiae 424A (LNH-ST)
with and without YEP media (external nutrients)

Fast pyrolysis to bio-oil is attractive…

Boateng et al. Ind. Eng. Chem. Res. 46:1891-7 (2007)





Farm-scale fast pyrolysis: USDA-ARS-ERRC

Guayule bio-oil characteristics

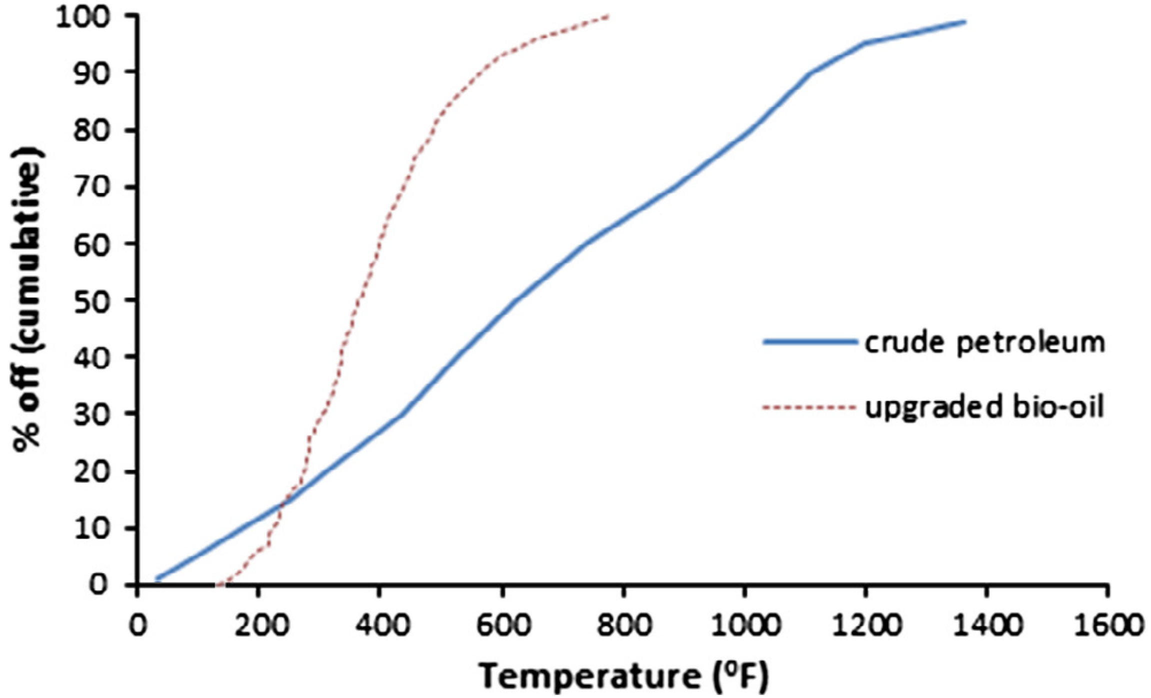
property	ASTM method	Whole shrub	Bagasse
Elemental Analysis (wt %, dry basis)		Average of the two bio-oils produced for each feedstock.	
[1]C	D5291	69.93	69.97
[1]H	D5291	8.54	7.96
[1]N	D5291	**2.92**	**0.82**
S	D4294	**0.20**	**0.07**
[1]O	D5291 (difference)	19.31	21.38
Water, %	Karl-Fisher titration	**2.11**	**1.44**
[2]Fuel Properties			
HHV (kJ/kg, wet basis)		**30,428**	**30,508**
Density (g/mL)	D4052	1.0904	1.1382
Flashpoint (°C)	D93B	>120	>120
Viscosity @ 60°C (cSt)	Kinematic viscosity ASTM D445	**2472.7**	**510.3**

Boateng et al. Fuel 2009

Guayule bagasse, converted and upgraded to hydrocarbon-compatible bio-oils

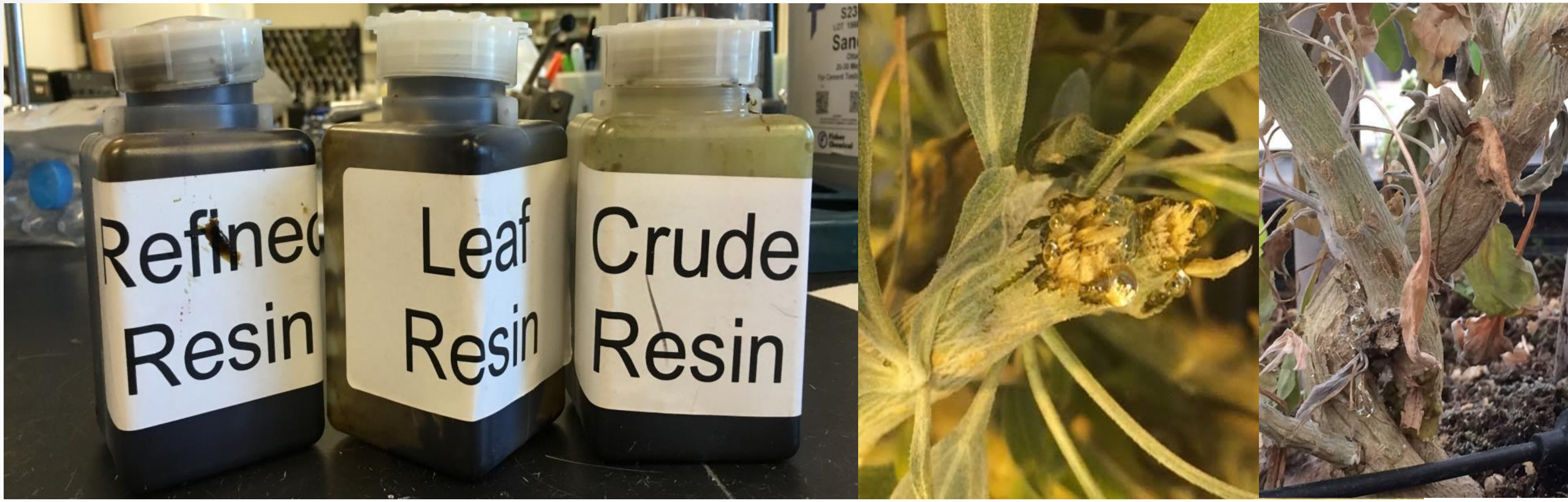
Boateng *et al.* Fuel 2015

- Tail-gas reactive pyrolysis
- Less than 0.5% oxygen following distillation and hydrotreatment
- Upgraded hydrocarbons consisted of gasoline, jet and diesel fuel cuts



Distillation curve of the upgraded guayule TGRP bio-oil, in comparison with typical crude petroleum.

Guayule resin



Natural rubber and resins are co-extracted from guayule with the solvent-based extraction process.

Guayule Solvent-extracted resin composition

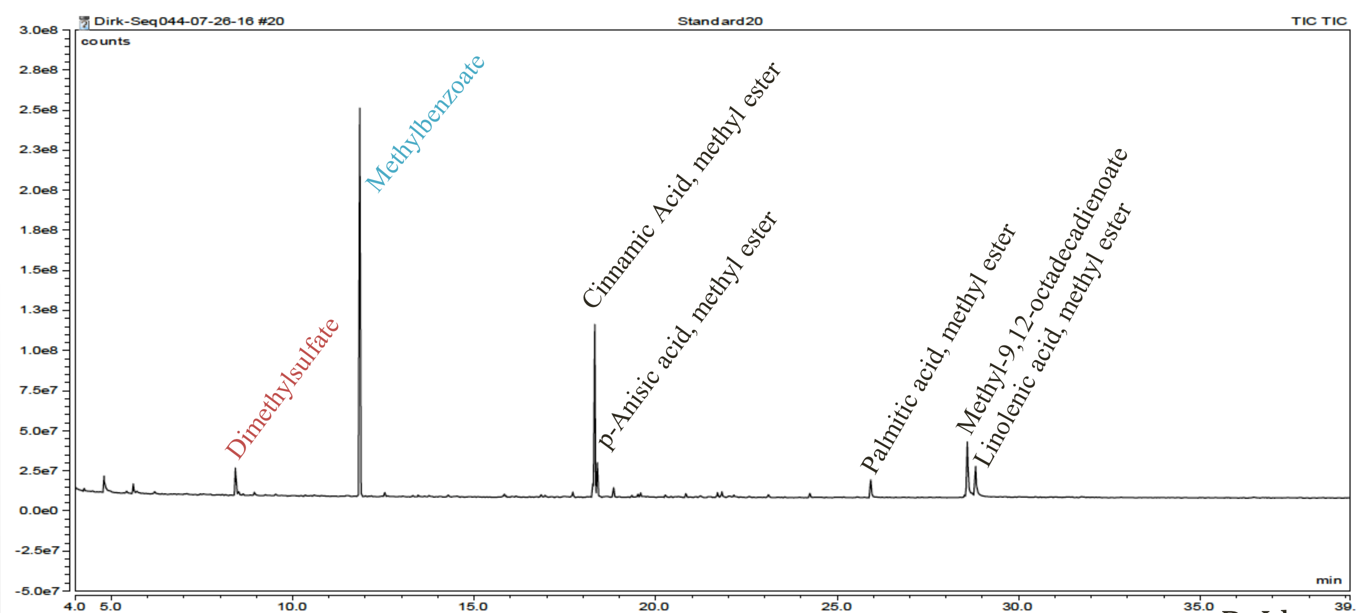
(derived from Schloman 1983, Schloman and Wagner 1991, and Scora and Kumamoto 1979)

Component	~MW	amount
Triterpenoids (argentatins)	~350-500	~27%
Sesquiterpene esters (mostly guayulin A) Sesquiterpene lactones: ambrosanolides, parthenolides, xanthanolides	~500-800	10-15%
Fatty acid triglycerides (linoleic, cinnamic, palmitic, stearic, oleic, linolenic, p-anisic)	~800-900	7-19%
Monoterpenes, diterpene keto alcohols, , etc. (α-pinene (16.7%), β-pinene (13.5%), camphene (1.2%), sabinene (6.5%), β-myrcene (2.5%), limonene (5.9%), terpinolene (9.2%), and β-ocimene (2.1%) (Scoro and Kumamoto)	~100-200	Low
Other		44-61%

SOME MAJOR COMPOUNDS IN RESINS

Retention time (min)		18.33	18.40	25.93	28.58	28.81
Resins	Organic solvent	Cinnamic acid, methyl ester	p-Anisic acid, methyl ester	Palmitic acid, methyl ester	Methyl-9,12-octadecadienoate	Linolenic acid, methyl ester
Crude	Chloroform	5.22	1.06	0.73	2.93	1.65
	Toluene	**5.63**	**0.94**	**0.75**	**2.35**	**1.46**
	Hexane	5.02	0.82	0.65	1.95	1.04
Refine	**Chloroform**	**7.12**	**1.03**	**0.98**	**3.37**	**1.94**
	Toluene	6.72	0.97	0.81	2.96	1.52
	Hexane	5.92	0.94	0.78	2.40	1.15

The refined resin concentrated sesquiterpene esters and fatty acid esters.



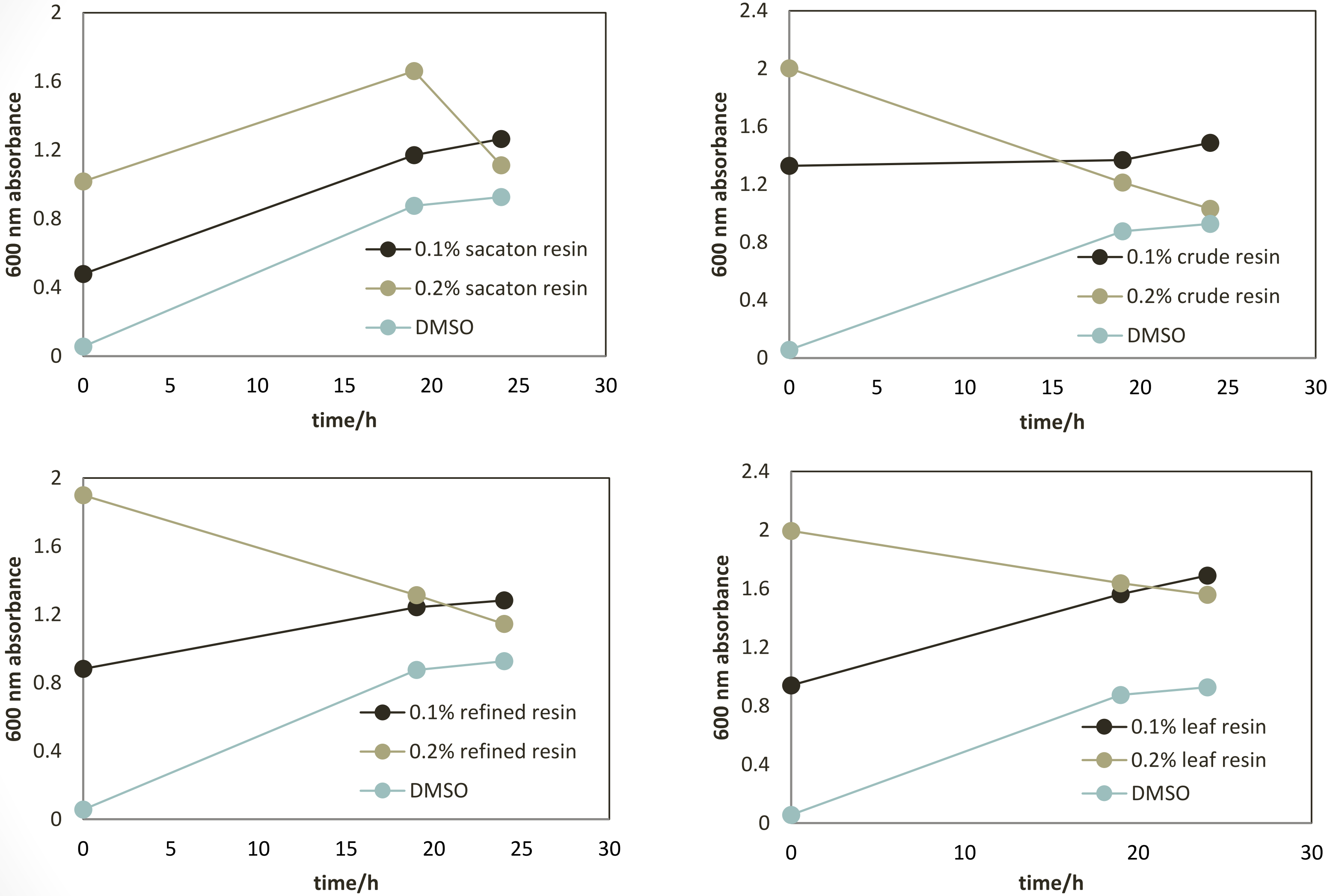
D. Lhamo, unpublished

All major and minor peaks identified - GC-MS (Crude Resin)

Compound	Common name	Molecular formula	Molecular weight	Retention time (min)	% Probability
2,4-Dimethyl-1-heptene	1-Heptene, 2,4-dimetyl	C_9H_{18}	126	4.26	42
Benzene,1,3-dimethyl-	m-Xylene	C_8H_{10}	106	5.43, 5.61	54, 27
Silanediol, dimethyl-	Dihydroxydimethylsilane	$C_2H_8O_2Si$	92	5.71	98
o-Xylene	Benzene, 1,2-dimethyl	C_8H_{10}	106	6.2	29
Sulfuric acid, dimethyl ester	Dimethyl sulfate	$C_2H_6O_4S$	126	8.42	97
Hexadecane	n-Cetane	$C_{16}H_{34}$	226	8.51	5
Benzene, 1-methyl-2-(1-methylethyl)_	o-Cymene	$C_{10}H_{14}$	134	8.94	14
Benzoic acid, methyl ester	Methyl benzoate	$C_8H_8O_2$	136	11.84	72
6-7-Dimethyl-1,2,3,5,8,8a-hexahydronaphthalene	-	$C_{12}H_{18}$	162	12.54	17
2,4,6-Trimethyldecane	Decane, 2,4,6-trimethyl-	$C_{13}H_{28}$	184	13.32	9
Methanol, oxo-,benzoate	-	$C_8H_6O_3$	150	13.45	37
Pentadecane	n-Pentadecane	$C_{15}H_{32}$	212	15.83	13
Benzenepropanoic acid, methyl ester	Hydrocinnamic acid, methyl ester	$C_{10}H_{12}O_2$	164	15.88	71
2-Cyclopenten-1-one, 3-metyhl-2-(2,4-pentadienyl)- (Z)-	Pyrethrone	$C_{11}H_{14}O$	162	16.16	66
Neoisolongifolene, 8,9-dehydro-	-	$C_{15}H_{22}$	202	16.85	36
Hexadecane	N-Cetane	$C_{16}H_{34}$	226	17.71	9
2-Propenoic acid, 3-phenyl-methyl ester	Cinnamic acid, methyl ester	$C_{10}H_{10}O_2$	162	18.32	49
Bezoic acid, 4-methoxy-, methyl ester	p-Anisic acid, methyl ester	$C_9H_{10}O_3$	166	18.4	57
4-Methl-2-phenyl-pent-3-en-1-ol	-	$C_{12}H_{16}O$	176	18.85	16
(1R,4S)-4-Isopropyl-1,6-dimethl-1,2,3,4-tetrahydronaphthalene	Trans-Calamenene	$C_{15}H_{22}$	202	19.35	37
5-Isoproyl-3-8-dimethyl-1,2-dihydronapthalene	alpha-Corocalene	$C_{15}H_{20}$	200	19.58	43
Neoisolongifolene, 8,9-dehydro-	-	$C_{15}H_{22}$	202	20.2	23
(S)-2,5,9,9-tetramethyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene	aR-Himachalene	$C_{15}H_{22}$	202	20.4	21
5-Isoproyl-3-8-dimethyl-1,2-dihydronapthalene	alpha-Corocalene	$C_{15}H_{20}$	200	20.85	42
Methyl (7E,10E, 13E)-7,10,13-hexadecatrenoate	7,10,13-Hexadecatrienoic acid, methyl ester	$C_{17}H_{28}O_2$	264	22.02	30
9-Methyl-1,2,3,4,5,6,7,8-octahydroanthracene	9-Methyl-S-octahydroantracene	$C_{15}H_{20}$	200	23.1	32
Hexadecanoic acid, methyl ester	Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	270	25.92	58
9,12-Octadecenoic acid, methyl ester	-	$C_{19}H_{32}O_2$	294	28.6	20
9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	Linolenic acid, methyl ester	$C_{19}H_{32}O_2$	292	28.82	58

D. Lhamo, unpublished

E. coli growth inhibition by guayule resins



Turbidity measurements are consistent with inhibition of *E. coli* growth at 0.2 % with refined, crude and leaf resins, not with sacaton resin.

Possible guayule resin approach:

Investigate and validate fractionation methods that can economically separate guayule resin into:

1) low molecular weight rubber
2) terpenoids and sterols
3) terpenes and sesquiterpenes
4) fatty acids
5) aromatic acids

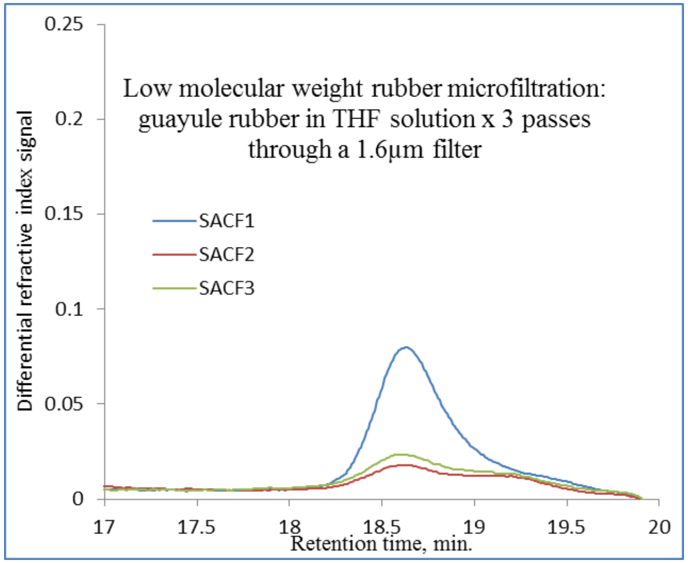
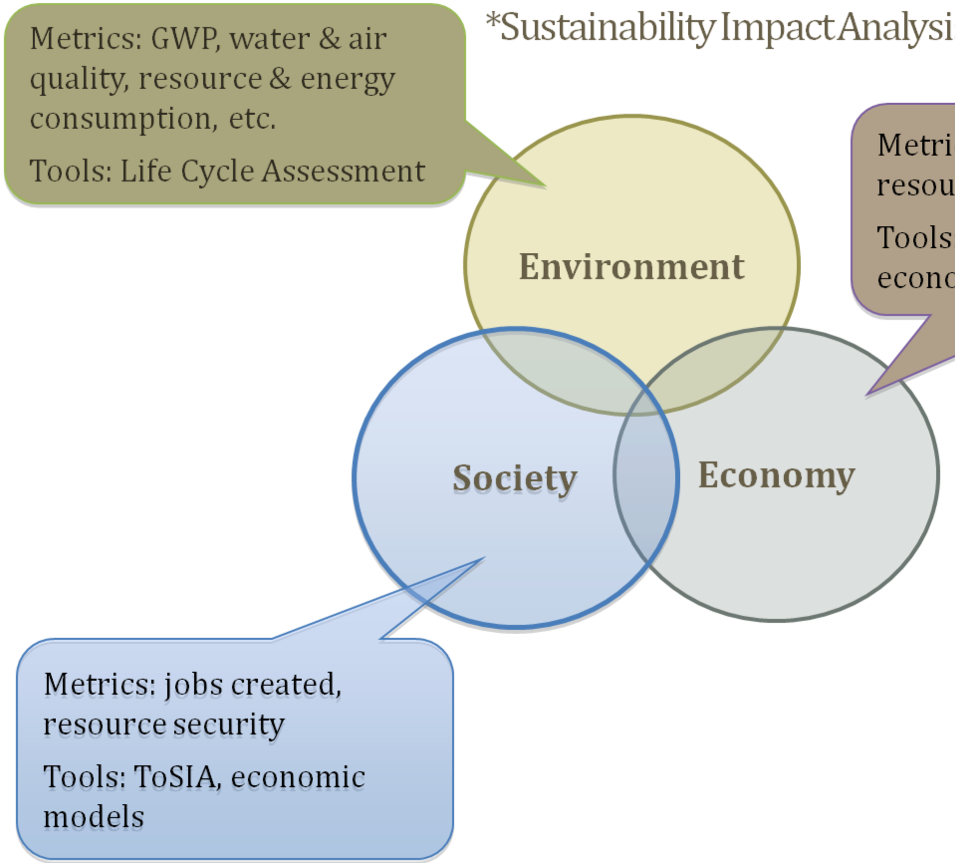


Figure 10: Gel-permeation chromatogram for guayule crude resin extract

Biofuels and Biobased Products Development Analysis

measuring sustainability

*Environmental Life Cycle Assessment (LCA)
*Sustainability Impact Analysis



Amy Landis, 2013

Rasutis, D., Soratana, K., McMahan, C., and Landis, A. 2015 A sustainability review of domestic rubber from the guayule plant. Industrial Crops and Products 70, 383-394.

Guayule resin and bagasse: informing utilization through analyses

- Sfier *et al.* (2015) concluded co-product utilization is a requirement for profitability (EU)

- Initial LCAs have been developed for irrigation water use, rubber extraction with solvent-based process.

- Preliminary analysis for bagasse conversion to ethanol ($1.60/gallon) (Lanzatech process) is not feasible without significant $ credit support.

- Preliminary analysis for bagasse to hydrocarbons exceeds $6/gallon (no RFS or other credits).

Challenges are ahead of us…..

Thank you…