Biodiesel Fuel from Connecticut Oilseed

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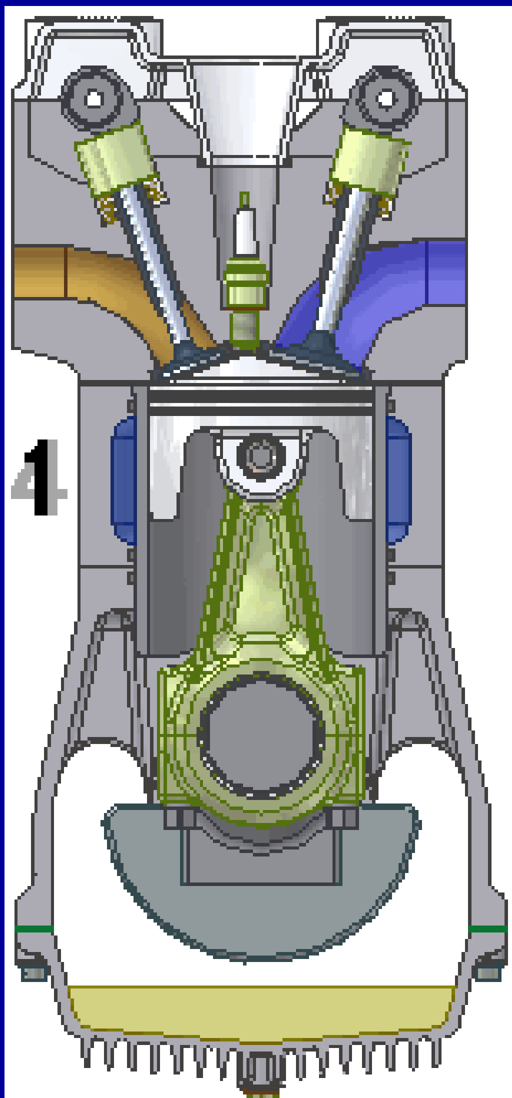
Department of Analytical Chemistry

The Connecticut Agricultural Experiment Station

Ottomobile (Spark) Engine



- In 1864 invented the "Atmospheric Gas Power Machine"
- In 1872 with Gottlieb Daimler and Wilhem Maybach produced 4-stroke cycle, Otto cycle, engine described in 1876

Nikolaus August Otto
(1832 – 1891)

- The Otto cycle is characterized by four *strokes*, *Or* straight movements; alternately, back and forth, of a piston inside a cylinder

1. Intake
2. Compression
3. Power
4. Exhaust

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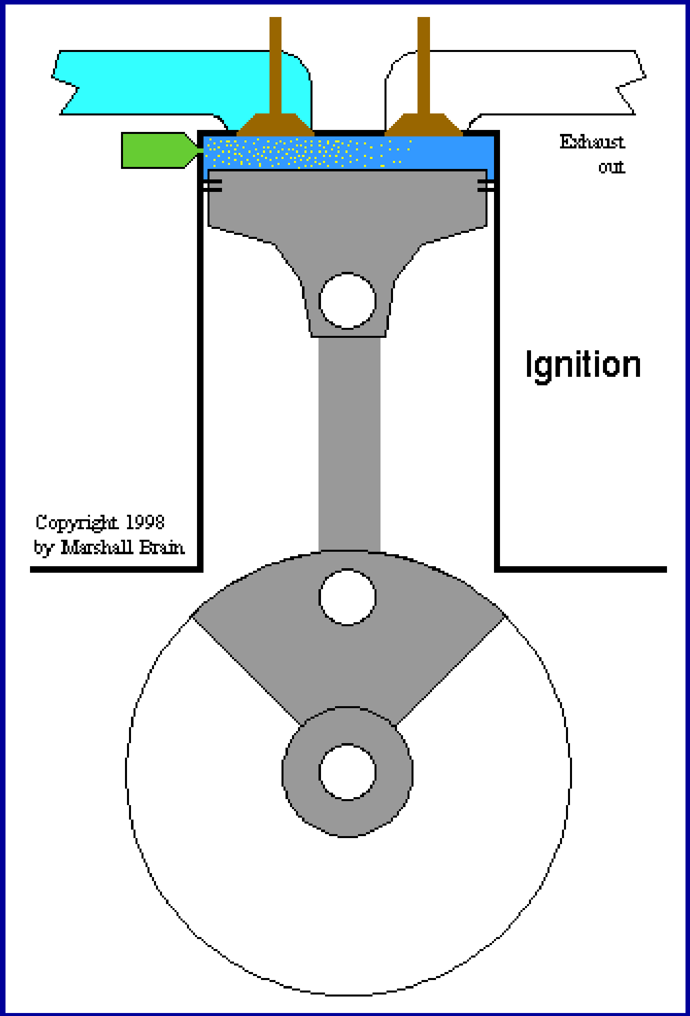
Diesel (Compression) Engine



- 1897 – Engine that does not require a spark ignition
- Engine originally designed to run on peanut oil or coal dust
- Compression ratio typically between 15 and 20 to ignite fuel longer, slower burning fuel

Rudolf Christian Karl Diesel (1859 – 1913)

adiabatic compression followed by a constant pressure combustion process, then an **adiabatic expansion** as a power stroke and an isovolumetric exhaust.

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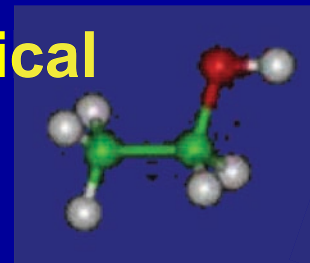
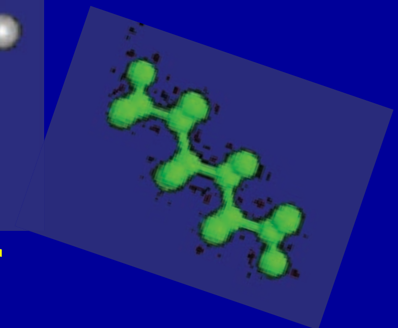
Fuel Characteristics

- **Ethanol – Defined Chemical makeup C_2H_5OH**



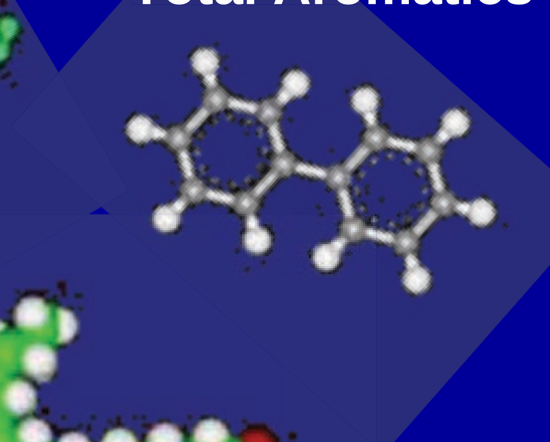


- **The average chemical formula for Gasoline is C_6H_{14} ranging from C_4H_{10} to $C_{13}H_{28}$**

50 – 80 %
Mixed Alkanes

20 – 50 %
Total Aromatics

Flammable Class / Division III Liquid



- **The average chemical formula for Diesel fuel is $C_{12}H_{26}$ ranging from $C_{10}H_{22}$ to $C_{15}H_{32}$**

- **Fatty Acid Methyl Ester's – FAME's**

Combustible Class II Liquid

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American Petroleum Institute

Comparative Fuel Characteristics

	Gasoline	Ethanol	Diesel	Biodiesel
Formula	C4-C12	C_2H_5OH	C8-C20	C12-C22
Avg MW	100-105	46.07	200	292
%C,H,O	86,13,0	52,13,35	87,13,0	77,12,11
BP ºF	100 – 400[1]	172[1]	370 – 650[1]	360 – 640[1]
FP CC ºF	- 49	16	140 – 176	260 – 300
AI Temp ºF	495	685	254 – 285	–
BTU / lb	18,676	11,583	18,394	16,131
BTU / gal 60 ºC	116,090	76,330	129,050	118,170

1. Tyson, K. Shaine, Biodiesel Handling and Use Guidelines. National Renewable Laboratory, Colorado, 2001. Provisional Standards
2. http://www.eere.energy.gov/afdc/pdfs/fueltable.pdf

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Ethanol – Corn Fermentation

Male Flowers

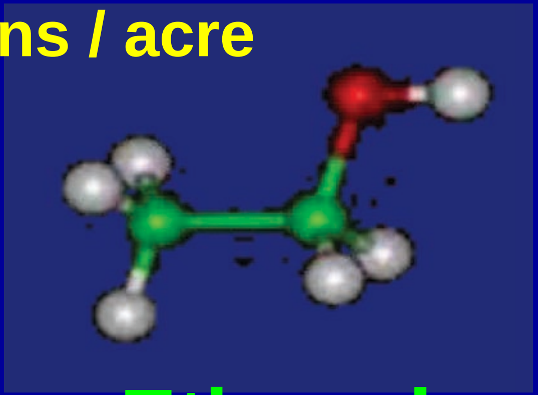
Female Flowers

- **The *Pimentel* Energy Debate**
  Ethanol Energy (im)Balance
- **32.5 Ears of Corn ≈ 1 Gallon**
  344 Gallons / acre

Corn Kernels

Fermentation

Distillation



Ethanol

C_2H_6O

- **In 2006 Kansas harvested 3.14 M acres which could have provided 1.08 B gallons of ethanol**

Biodiesel – Oilseed Crops

Canola Flowers

Soybean Flowers

Sunflower

Male Oil Palm

Female Oil Palm

Canola Oil

Vegetable Oil

Canola Seed

Soybean Seed

Sunflower Seed

Oil Palm Seed

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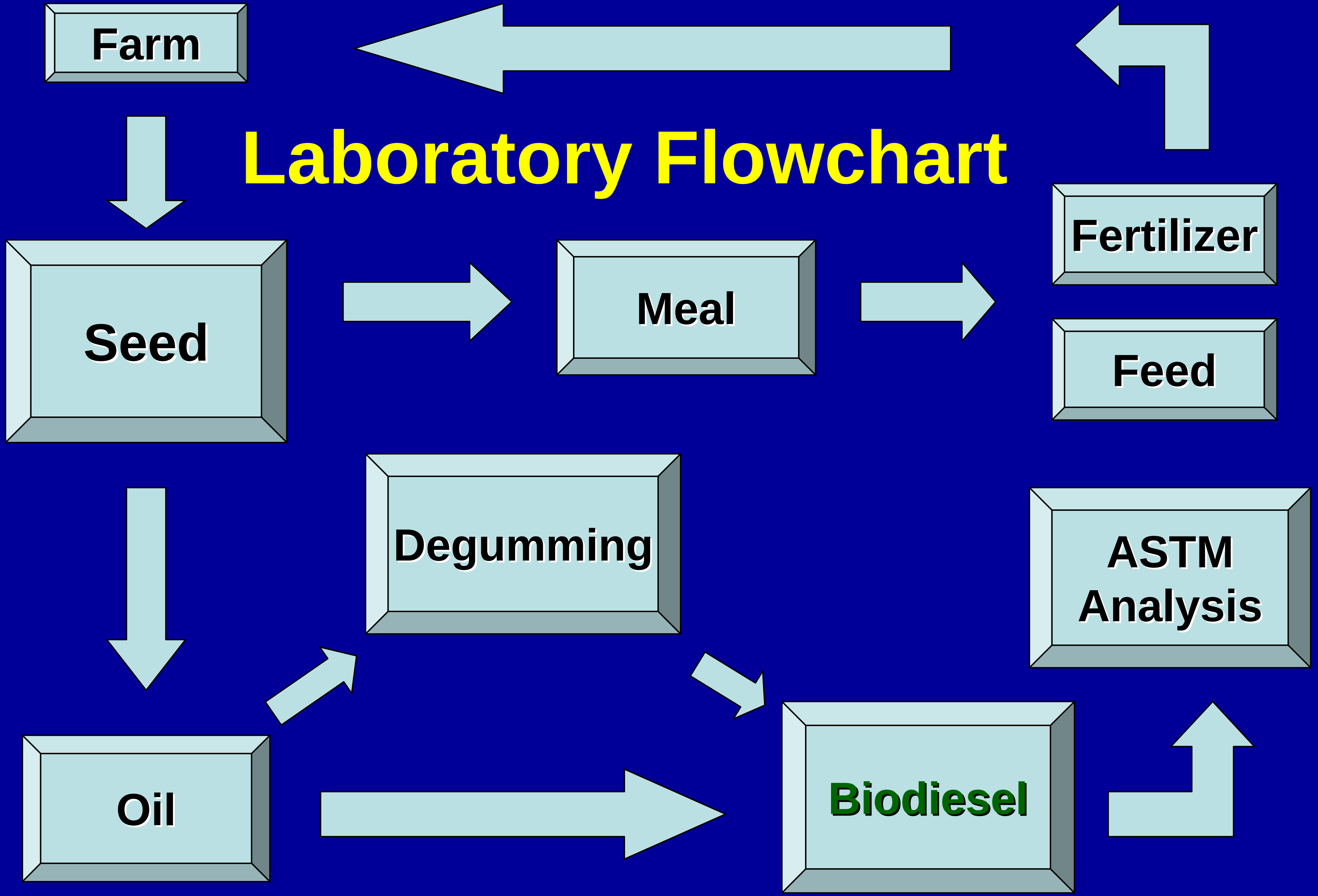
Current Work in Connecticut

1. Farming Component (Dr. James LaMondia)
   - Win over Connecticut farmers with IPM aspect
   - Evaluate oil seed crop rotation
   - Evaluate cultivars and time of planting/ harvest
   - Study agricultural value of meal produced

2. Laboratory Component
   - Work out details of oil extraction
   - Study the seed / oils / meals:
     nutritional value; metals; pesticides; glucosinolates
   - Study the conversion to biodiesel

3. Regulatory Component
   - Ensure biodiesel meets ASTM criterion
   - Establish Connecticut Biodiesel testing program
   - UCONN collaboration

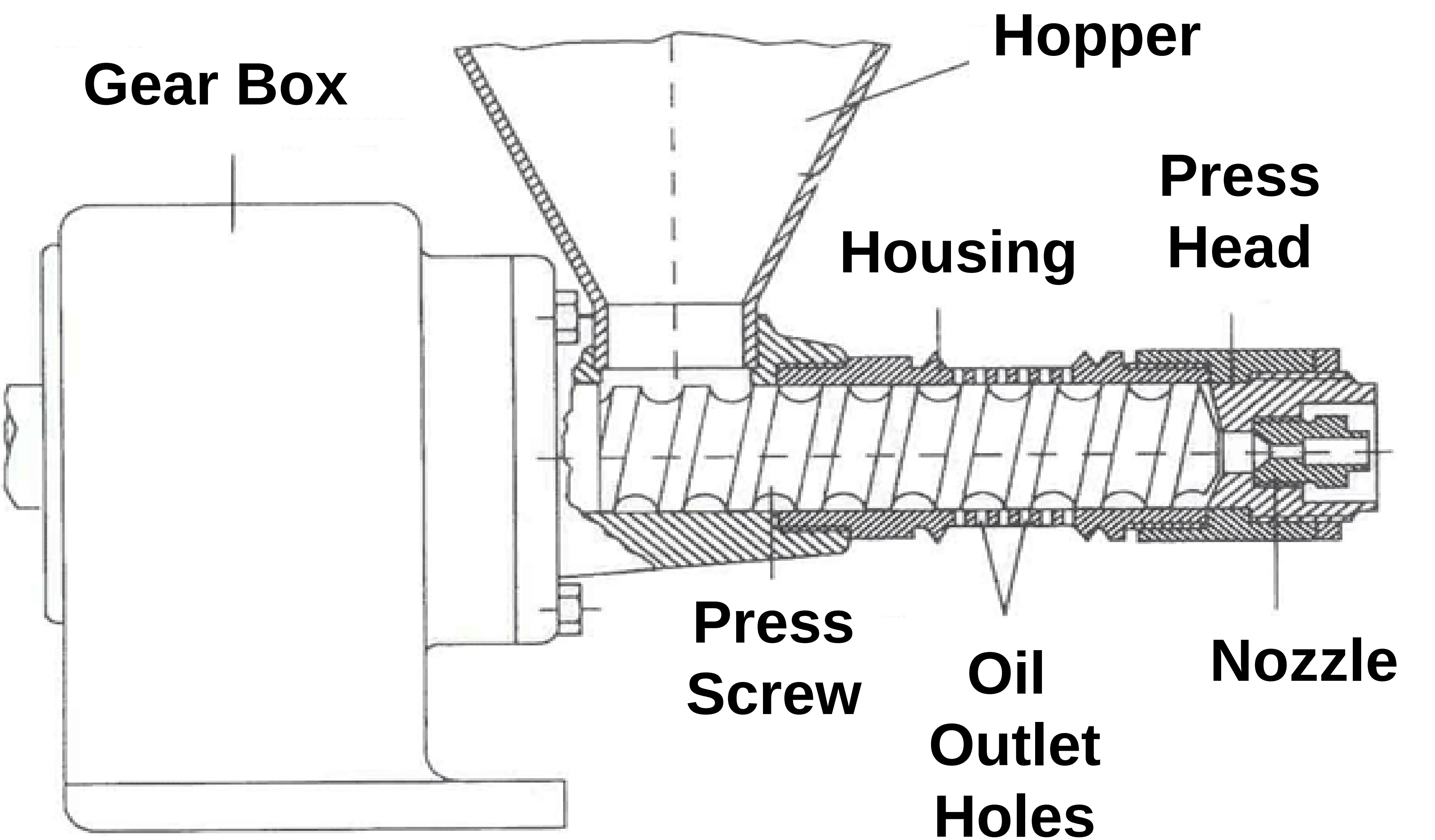
Laboratory Flowchart



Whole Seed Characterization

	Canola				Soybean
	Lockwood		Windsor		Windsor
	Dekalb	Hyola	Dekalb	Hyola	6193 RR
% Oil	**29.5**	**28.7**	**28.4**	**25.5**	**10.2**
% Nitrogen	**4.4**	**3.7**	**4.4**	**4.7**	**6.6**
% Protein	**19.4**	**18.7**	**21.2**	**21.6**	**41.5**
% Fiber	**30**	**24**	**24**	**27**	**8.3**
% Moisture	**6.8**	**6.2**	**9.2**	**8.3**	**7.6**

Schematic View of Oil Press



Oil (Feedstock) Extraction

Täby Type 20 oilseed press (Electrolux®)

Canola	Wt % Oil
Hyola 357 Magnum	28.7
Dekalb 38-25	28.4
Soybean	
6193 RR 1-9 Maturity	10.2

Hyola 357 Magnum (1356 * 0.287) / 7.7 lb/gal = 50.6 gal/acre
Dekalb 38-25 (1319 * 0.284) / 7.7 lb/gal = 47.0 gal/acre

(Seed Yield lb / acre * Oil Yield)

6193 RR 1-9 Maturity (3695 * 0.102) / 7.7 lb/gal = 49.0 gal/acre

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Seed Oil Pressing Components

Meal Byproduct

	Canola				Soybean
	Lockwood		Windsor		Windsor
Fertilizer value:	Dekalb	Hyola	Dekalb	Hyola	6193 RR
% Nitrogen	**4.4**	**3.7**	**4.4**	**4.7**	**6.8**
% Phosphorous	**1.2**	**0.9**	**2.2**	**1.3**	**0.7**
% K, Potassium	**1.8**	**1.2**	**1.8**	**1.5**	**2.3**
Feed value:					
% Protein	**27.4**	**23.4**	**27.2**	**29.3**	**48.1**
% Fat	**14**	**17**	**16**	**15**	**1.4**
% Fiber	**13**	**18**	**12**	**12**	**3.8**

- **High Protein / Low Fat & Fiber Desirable**

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Vegetable Oil Characterization

- Six metals with ASTM Biodiesel specifications

All values in mg/kg (ppm)

		Canola				Soybean
		Lockwood		Windsor		Windsor
		Dekalb	Hyola	Dekalb	Hyola	6193 RR
Na	Sodium	<2	<2	<2	<2	<2
K	Potassium	<40	125	265	<40	26
P	Phosphorous	51	300	601	30	182
S	Sulfur	9	7	8	6	<6
Mg	Magnesium	13	57	180	9	26
Ca	Calcium	47	95	316	27	30

ASTM – American Society for Testing and Materials

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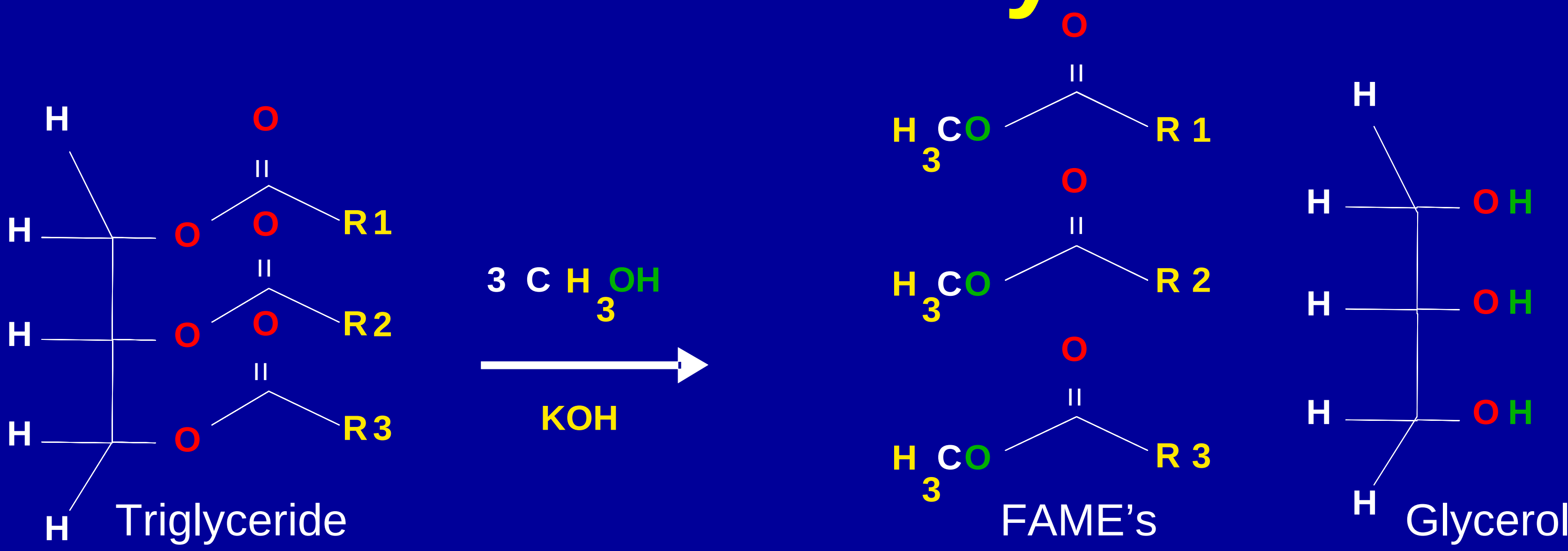
Oil Chemistry



	R=	Canola	Soybean	Sunflower
Unsaturated				
Palmitic	C16:0	4	11	7
Stearic	C18:0	2	4	5
Monounsaturated				
Oleic	C18:1	62	24	19
Polyunsaturated				
Linoleic ω6	C18:2	22	54	68
alpha Linoleic ω3	C18:3	10	7	1

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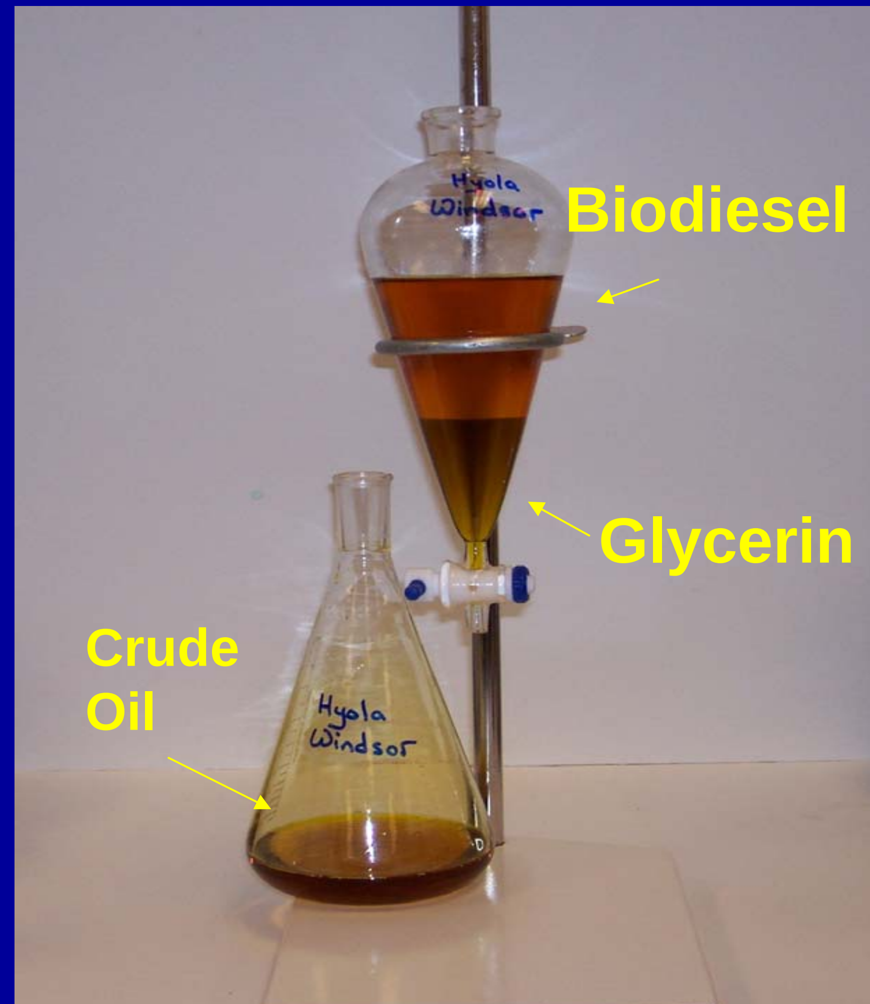
Laboratory Hydrolysis



ASTM Standard 6751- 06b

Property	Test Method	Limits	Units
CAES			
Ca / Mg, combined	EN 14538	5 max	ppm (ug/g)*
Phosphorous	D 4951	10 max	ppm (ug/g)*
Na / K, combined	EN 14538	5 max	ppm (ug/g)
Sulfur S500	D 5453	500 max (500)	ppm (ug/g)
S15	D 5453	15 max (15)	ppm (ug/g)
UCONN			
Flash Point	D 93	130 min	ºC
Kin. Viscosity, 40 ºC	D 445	1.9 - 6.0	mm^2/sec
Free Glycerin	D 6854	0.020	% mass
Total Glycerin	D 6854	0.240	% mass
Other			
Water & Sediment	D 2709 (4176)	0.05 max	% volume
Sulfated Ash	D 874	0.02 max	% mass
Copper Corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud Point	D 2500	Report	ºC
Carbon Residue	D 4530	0.05 max	% mass
Acid Number	D 664	0.50 max	mg KOH/g
Distillation, T90 AET	D 1160	360 max	ºC
Oxidation Stability	EN 14112	3 min	hours**
Visual Appearance	D 4176	Free of water, sediment, etc	

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*changed in 06a; ** changed in 06b

ASTM Critical Metals (mg/kg)

	Na	K	Mg	Ca	P	S
Limit	Combined Na / K = 5		Combined Mg / Ca = 5		10	15
Lockwood Soil		516	2589	1977	1164	146
Windsor Soil		412	1783	1458	989	87
Canola						
Harvested Seed	<4	11832	4627	4535	8737	
Seed Cake		15698	5792	4838	12203	
Oil	<2	19	18	69	72	<40
Biodiesel	<2	25	9	54	<3	<40
Soybean						
Harvested Seed	<4	18720	3539	3119	6189	3161
Seed Cake	<4	21261	3918	3319	7702	3775
Oil	<2	62	17	38	137	<40
Biodiesel	<2	6	<2	16	<3	<40

Blank spaces denote NDA

Degumming Work

- Does degumming affect the quality of Biodiesel

Oil

CT Canola
CT Soy
GA Soy

Wash → 1*N* HCl Or Water

1*N* Oil

Or

H_2O Oil

Dry → Heat Or N_2

1*N* Heat Oil

Or

1*N* N_2 Oil

N_2 = Centrifugation; decant H_2O; remove remaining H_20 with N_2 stream

Canola
Canola H_20 Heat
Canola H_20 N_2
Canola 1*N* HCl Heat
Canola 1*N* HCl N_2

MeOH → KOH

COOB
CHBB
CHNB
CABB
CANB

Biodiesel

Biodiesel Metal Values

Sample:		Na	K	Mg	Ca	P	S
ID		ppm	ppm	ppm	ppm	ppm	ppm
	Limits	Combined Na / K = 5		Combined Mg / Ca = 5		10	15
CT Canola Biodiesel							
COOB		<2	25	9	54	<3	<40
CHBB		<2	33	8	56	<3	<40
CHNB		<2	10	6	33	<3	<40
CABB		<2	9	<2	17	<3	<40
CANB		<2	7	<2	23	<3	<40
CT Soybean Biodiesel							
SOOB		<2	6	<2	16	<3	<40
SHBB		3	18	<2	16	<3	<40
SHNB		<2	55	<2	18	<3	<40
SABB*		<2	323	<2	17	<3	<40
SANB		<2	9	<2	17	<3	<40
GA Soybean Biodiesel							
GOOB		<2	14	7	24	<3	<40
GHBB		<2	21	9	29	<3	<40
GHNB		<2	37	3	20	<3	<40
GABB		<2	5	<2	15	<3	<40
GANB		<2	13	<2	17	<3	<40

ppm = mg/kg

SABB* -- Did not hydrolyze

ICP AES (ASTM D4951)

- Current ASTM method is used only for Phosphorous analysis

- We intend to analyze:
  - Phosphorous P
  - Magnesium Mg
  - Calcium Ca
  - Sodium Na
  - Potassium K
  - Sulfur S

  and study other metals

- Corrosive to engine parts; detrimental to environment

2005 – Connecticut Planting Statistics:

- 4,200 Farms Averaging 86 Acres
- 360,000 *Total* Acres in Farms (*Incl. Livestock Farms*)
- Planted 271,430 Acres

Commodity	Harvested Acres	Yield/ Acre	Production Totals	Price	Value ($)
Hay All (*dry*)	63,000	1.9 t	118,000 t	162 $/t	19,153,000
Hay Other (*dry*)	55,000	1.8 t	99,000 t	157 $/t	15,543,000
Tobacco (*All*)	2,430	1,674 t	4,067,000 lb	5.85 $/lb	15,356,000
Binder	1,500	1,750 lb	2,625,000 lb		
Wrapper	930	1,550 lb	1,442,000 lb		
Hay Alfalfa (*dry*)	8,000	2.4 t	19,000 t	190 $/t	3,610,000
Silage Corn	26,000	20 t	52,000 t		

117,000 All Purpose Acres (Grain Corn – 28,000)
(Alfalfa and Mixture – 2,000) (Field Crops/ Misc. – 87,000)

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Source: USDA National Agricultural Statistics Survey

Connecticut Fuel Consumption

Total Energy 888,663 billion BTU 0.9% (2003)

	Barrels	US%	Period
➢ Total Petroleum	86,141,000	1.1	2004
Gasoline	43,740,000	1.3	2004
Distillate Fuel	28,850,000	1.9	2004
Jet Fuel	2,382,000	0.4	2004
LPG	3,057,000	0.4	2004
Other	8,112,000		

1 barrel = 42 gallons

➢ Ethanol in Gasohol	20,478,000 gal	0.7	2003
➢ Natural Gas	162,642,000,000 cf	0.7	2004
➢ Coal	2,076,000 st	0.2	2005

Energy Information Administration
http://www.eia.doe.gov

Economics

- Assume we plant *ALL* 360,000 acres of CT farmland with oilseed crop; 100% crop yield; 50 gallons oil / acre

	Gallons	Barrels
Theoretical CT Yield	18,000,000	428,572
2004 CT Distillate Fuel use	1,211,700,000	28,850,000
	1.5% of CT Oil / Diesel Needs	

- In 2005 US: Planted 1,153,000 acres Canola / Rapeseed
  Harvested 1,125,000 acres Canola / Rapeseed
  Yield 1,333 lb / acre (CT 1337.5)

2005 Theoretical US *Canola* Biodiesel Yield	56,250,000	1,339,286
	4.6% CT Requirement	

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Source: Montana State University AMPC, Nov 2005 Briefing 60.

Today's Problems with Palm Oil

- "Well meaning efforts to limit carbon emissions may backfire….by destroying Asian rainforests to develop lucrative plantations."
- 600 Mt CO_2 / yr drained swamps; 1.4 Bt CO_2 from burning rainforest. 2 Bt = 8% fossil fuel emmissions[1]
- "Astonishing" – "This undermines the whole project"[2]
- Major power companies are divided on whether to continue or pursue palm oil generation
- Deforestation is the No. 2 cause of greenhouse gas emission after fossil fuels

Arthur Max, AP, 04/02/07

[1]Based on data from Wetlands International, Deft Hydraulics, Alterra Research Center

[2]Anne van Schaik – Friends of the Earth

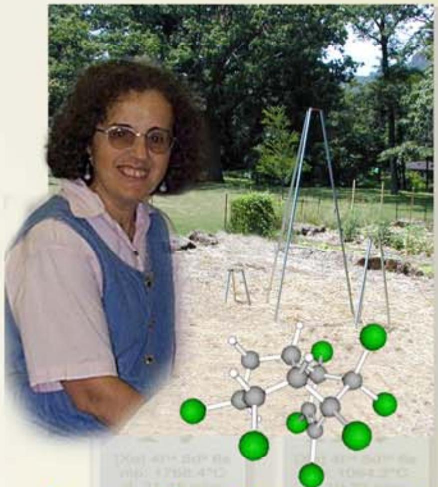
Summary

- Biodiesel is an alternative oil for use in diesel engines and home heating and is not the same as ethanol
- It is a renewable oil derived from plant material
- In 2006 many details of planting, harvesting, extracting, producing and analyzing Biodiesel have been examined in Connecticut
- Science needs to drive this work
- Future work in progress:
    - Over Wintering canola; increased oil seed yield
    - Better methods of determining metals in oils
    - Reducing metal content in Biodiesel

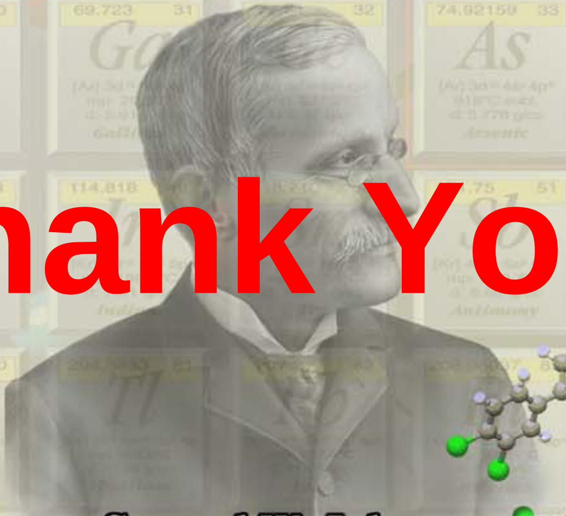
Department of Analytical Chemistry

Extracting biodiesel fuel from soybeans and canola

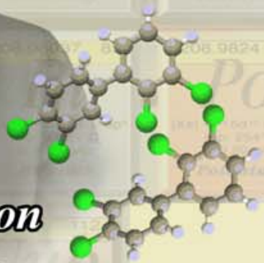
Thank You!



Investigating persistence of chlordane in soil, plants, and air



Samuel W. Johnson

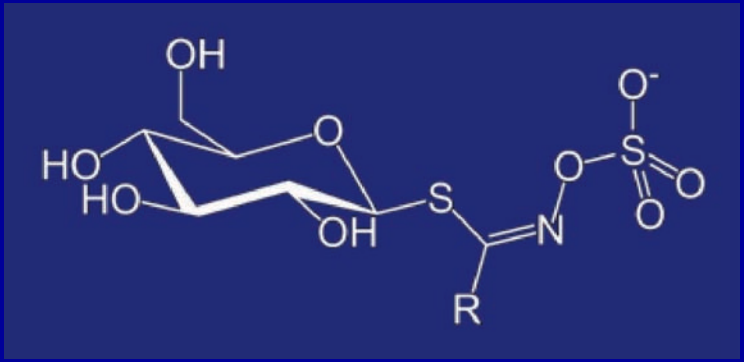


Detecting polychlorinated biphenyls (PCBs) in the environment

Analyzing nitrogen levels in feeds and fertilizers

Determining sources of lead contamination in maple syrup

Glucosinolates (*Brassica*)



R = varied

Required stabilized cation for thiocyanates

Myrosinase

Glucose

R–N=C=S
Isothiocyanates

R–S–CN
Thiocyanates

R–CN
Nitriles

- Glucosinolates are sulfur-rich, anionic natural products
- Amino acid derived *via* amino acid aldoximes
- Hydrolysis by myrosinases yield different products
- Products are defense compounds & attractants
- Humans take advantage of cancer-preventing agents, biopesticides, flavor compounds
- Each species produces 30 – 40 different

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2005 CT Electric Power Emissions

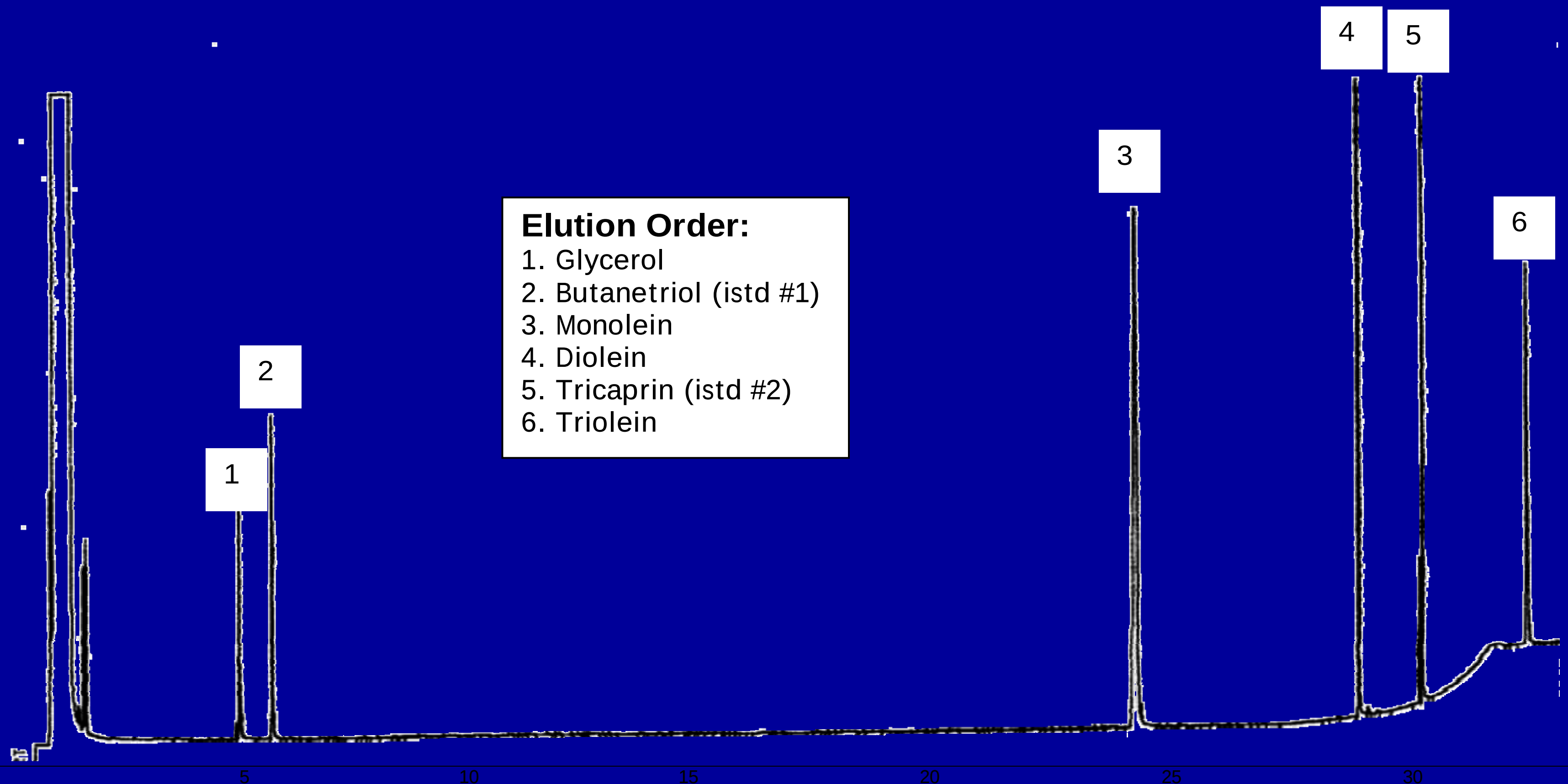
		Metric Tons	US %	Period
CO_2	Carbon Dioxide	11,541,609	0.5	2005
SO_2	Sulfur Dioxide	7,758	0.1	2005
NO	Nitrous Oxide	10,518	0.3	2005

- The average household CO_2 emissions from electricity are approximately 7.4 metric tons per year (about 16,290 lbs)

Energy Information Administration
http://www.eia.doe.gov

BIODIESEL STANDARD BY HIGH TEMPERATURE GC

ASTM Method D6584-00 (2000): Test Method for the Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography



COLUMN: #400-5HT-10-0.1F, 5% Phenyl Methyl Silicone, 10M. x 0.23mm I.D. x 0.1 um film, AL-CLAD fused silica capillary column
Temperature: 50°C (1.0 min. hold) - 15°C/min. to 180°C – 7°C/min. to 230°C - 30°C/min. to 380°C, hold 10 min.
Injector: cool on column injection, 1 microliter sample
Detector: FID, 380°C
Carrier Gas: Helium at 1.8 mL/min measured at 50°C column temp.
Carrier Make-up 23.4 ml/min, Hydrogen flow 28 mL/min, air flow about 350 mL/min.

QUADREX CORPORATION
PO Box 3881, Woodbridge, CT 06525
sales@quadrexcorp.com www.quadrexcorp.com

Chromatogram courtesy of James D. Stuart, Emeritus Professor, Analytical and Environmental Chemistry, University of Connecticut, Storrs, CT 06269-3060

Summary

- Oilseed crops should be viewed as a supplement to our foreign energy deficit – NOT A REPLACEMENT
- US Energy goals needs to focus on combining many such resources:
  - Ethanol, Oilseed, Willow, Sawgrass, Hybrid Trees
  - Solar, Wind, Water & Nuclear Power
- Currently collaborating with Industry, Farmers and Institutions of Higher learning promoting Green Agriculture
- Working to ensure CT has ability to analyze Biodiesel to ensure its proper use in CT

DO YOUR PART BY REDUCING YOUR PERSONAL ENERGY CONSUMPTION & GREENHOUSE EMMISSIONS

Alternative Energy Resources

Willow Biomass	Dr Larry Smart	SUNY, Syracuse
Switchgrass	Dr Albert Kausch	URI, West Kingston
Hybrid Poplar	Dr Yi Li	UCONN, Storrs

2006 Field Studies (Feedstock)

- 2006 Crops grown at Lockwood and Windsor farms

Canola

	lb/acre	bu/acre
Hyola 357 Magnum	1356	22.6
Dekalb 38-25	1319	22.0

Soybean

	lb/acre	bu/acre
6193 RR 1-9 Maturity	3695	61.6

Valley Labs
Windsor, CT
Crop Yields

Ethanol – Corn Fermentation

- 2006 Kansas Corn Kansas harvested 3.15 M acres
- Average yield of 123 bushels / acre

2.8 Gallons of Ethanol

plus

-- 13.5 pounds of Gluten Feed
-- 2.6 pounds of Gluten Meal
-- 1.5 pounds of Corn Oil

In 2006 KS alone could theoretically have provided:

344 Gallons / acre
1.08 B Gallons

- One Bushel of Corn (56 pounds) provides:

~ = 1 Gallon of Ethanol

www.caes.state.ct.us

1. Kansas State University Research and Extension Service, Manhattan, KS

Biodiesel Fuel

- Recycling of used waste vegetable oils
  UCONN – Dorm Fryers to Transportation
  - Renewable resource from oilseed crops such as canola, soybean, sunflower, castor bean and flax
  - Triglyceride oils converted to fatty acid methyl esters

Environmentally Friendly

Reduce CO_2, CO, S, N and soot emissions

- High temperature / pressure catalytic de-polymerization of waste plastics and oils

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Terminology

- The Flash Point (FP) is the lowest temperature at which a substance can form an ignitable mixture with oxygen

Gasoline = Spark

- The Autoignition (AI) temperature or kindling point of a substance is the lowest temperature at which a chemical will spontaneously ignite in a normal atmosphere *without* an external source of ignition (flame or spark)

Diesel = Compression

  - Gasoline has a low FP and high AI temperature
    FP > - 45 ºC (- 49 ºF); AI 246 ºC (475 ºF)

  - Diesel has a high FP and low AI temperature
    FP > 62 ºC (144 ºF); AI 210 ºC (410 ºF)