



**School of Industrial and Information Engineering**  
**Course 096125 (095857)**  
**Introduction to Green and Sustainable Chemistry**

 POLITECNICO DI MILANO



# Energy Crops.

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<https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/>

<http://www.biogasmax.eu/489-handbook-on-energy-crops-for-heat-and-power.html>

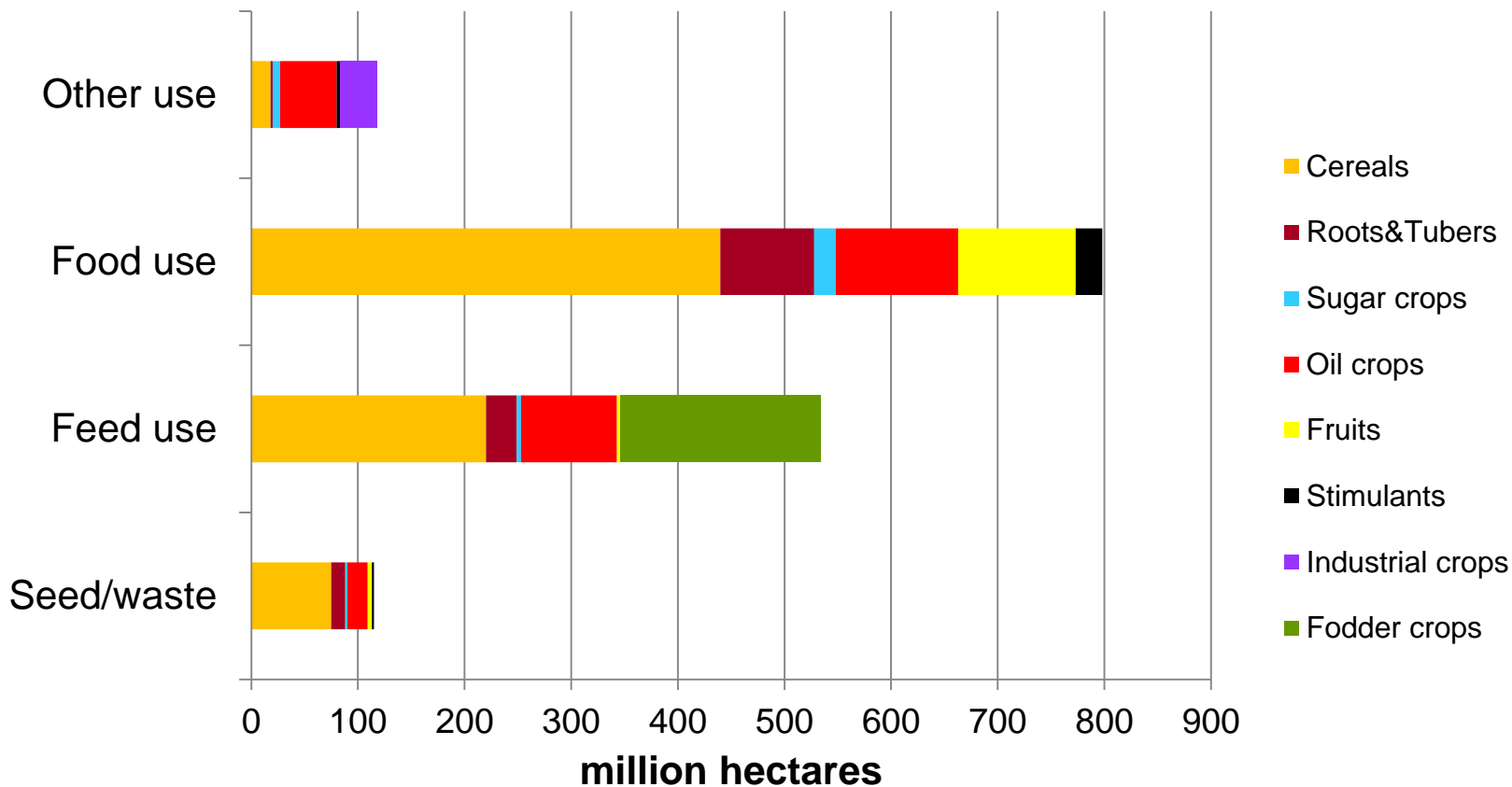


Energy from field energy crops –  
a handbook for energy producers

Intelligent Energy 

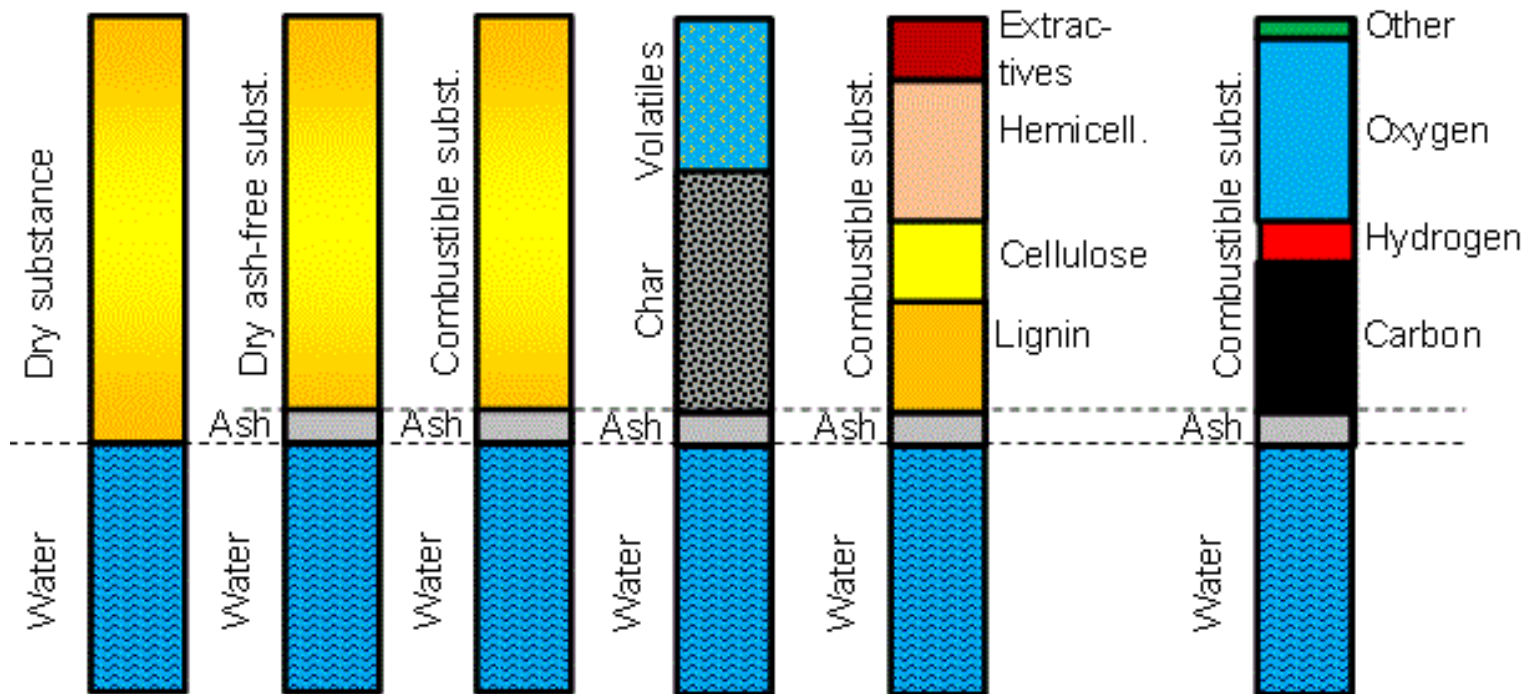


# Account of the Agricultural and Forestry Products Produced and Traded.





# Terminology in Biomass Analysis, also Applicable for Other Solid Fuels.



- The “as received” composition (ar)
- The “dry basis” composition (db)
- The “dry, ash free” basis (commonly abbreviated as “daf”)
- The elemental or ultimate analysis

[http://bisyplan.bioenarea.eu/fuel\\_appendix.html](http://bisyplan.bioenarea.eu/fuel_appendix.html)



## Trees for Bioethanol (1° generation).

A biofuel is a mixture of organic compounds derived from biological carbon fixation and whose energy content can be recovered by combustion (fuel). Biofuels include liquid fuels derived from biomass conversion, as well as solid biomass, and various biogases. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price hikes, the need for increased energy security, and concern over greenhouse gas emissions from fossil fuels.

- **Bioethanol**

- from sucrose or oligosaccharides
- from starch
- from lignocellulose materials



Biofuel of first generation

Biofuel of second generation

- **Biodiesel**

- from oil crops
- from algae



## Classification of Plants based on the Component Used to Produce the Biofuel.

Plants used for processing into Biofuels can be classified based on the main components involved in the chemical transformation :

- Plants producing sugars or starches
- Plants producing oils
- Plants whose whole biomass can be used
- Plant residuals (wastes) whose biomass can be used



## Plants Based on Starch: Wheat (genus *Triticum*).

**Wheat** - more than 10-20 species through East Mediterranean to Iran. Temperate crop.

Complex ancestry and were first domesticated in the Near East some time before 7000 BC.

Evolution through polyploidy

Diploid – *T. monococcum* (einkorn)

Tetraploid – *T. dicoccon* (emmer)

Hexaploid – *T. aestivum* (common bread wheat - *T. durum* (durum, flint, hard or macaroni))

Emmer and einkorn – high amylose and not suitable for leavened bread

Two main proteins - glutenin and gliadin which makes the dough elastic when mixed with water.







## Rice (*Oryza Sativa*).

While cooking gelatinizes and cell wall ruptures.

Two to three races

- indica type – long-grain; dry and separate
- Japonica or sativa – short grain soft and slightly gluey
- Javanica – Indochina; equatorial plane, gluey

Gelatinous temperature and amylose content.

- High amylose – dry and flaky
- Low amylose – sticky and moist

Mainly contains starch, 12% proteins

- Glutelins, albumins, prolines

Lack lysine and threonine.

Removing bran and germ removes thiamine – beriberi disease.





## Maize (*Zea mays*).

### Corn

- Domesticated in Central America; the only cereal used as vegetable; The more diffused cereal
- Ancestors – Mexican teosinte
- Flowers unisexual
- 70% endosperm and 11% embryo  
11% proteins of aleuronic layer
- The germ provides glutelin whereas aleuron layer have zein
- Zein – rich in leucine but lack of lysine and tryptophan
- Excess of leucine prevent conversion of tryptophan to niacin – pellagra.



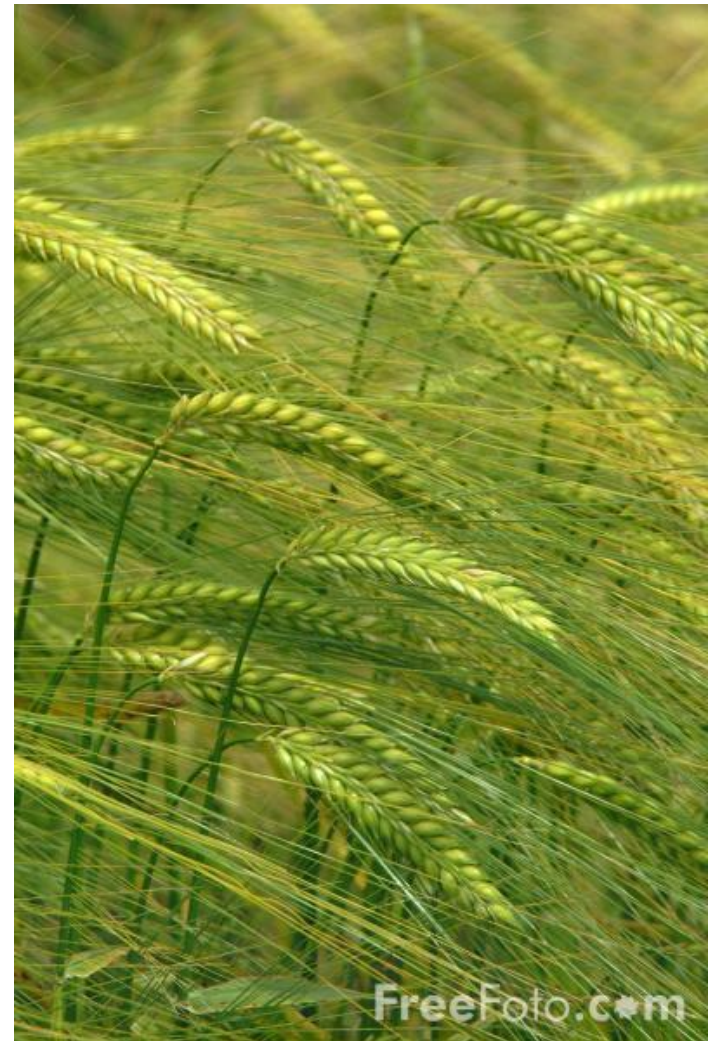




## Barley (*Hordeum vulgare*).

### *Barley:*

- A temperate plant; domesticated plant, a member of the grass family and is a major cereal grain
- A major animal feed and brewing
- Has low gluten and cannot be leavened
- Has beta glucan – lower blood cholesterol
- Reduces colon cancer
- Barley beer was probably one of the first alcoholic drinks developed by Neolithic humans.





## Oat (*Avena sativa*).

### Oat:

- Has elongated caryopsis
  - Two aleurone layers
  - 12-13% proteins; 4-5% oils; 66-77% CHO and 12-15% crude fiber (reduce blood sugar by reducing absorption)
- used more for medicinal value
- Has all essential amino acids
- is heat processed to denature enzymes





## Rye (*Secale cereale*).

### *Rye:*

- Feed cereal
- Alcoholic drinks
- Infections – **ergot**
- Has pentosans **not starch** – does not disintegrate and gelatinization – soft crumbs
- Usually mixed with wheat flour







## Soybeans (*Glycine max*).

A summer annual member of the legume family native to East Asia. The most important oil seed crop and protein crop in most countries.

The beans contain significant amounts of phytic acid,  $\alpha$ -linolenic acid, and isoflavones.

Composition: 40% proteins, 20 % oil, 35% sacc. and 5% ash.



**Soybean plants (top) and pods at harvest time (right)**



## Based on Sugars:

# Sugarcane (*Saccharum officinarum* L. (*Poaceae*)).

### Sugarcane:

- 12-15% sucrose, glucose and fructose
  - 12-20% fiber
  - 0.3-0.4% nitrogenous compounds
  - Fats, waxes, acids and pectins
- Sugarcane juice: acotinic acid, citric and malic acids; vit B, D and enzymes like invertase and oxidases.



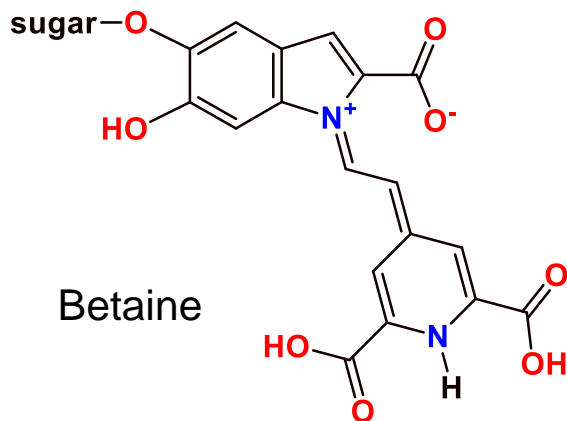




## Sugar Beet (*Beta vulgaris var. rapa*).

### *Sugar Beet:*

- Roots have up to 20% sugar.
- Betaine (red pigment) is commercially extracted.
- Waste has galacturonic acid – used to synthesize vitamin C.





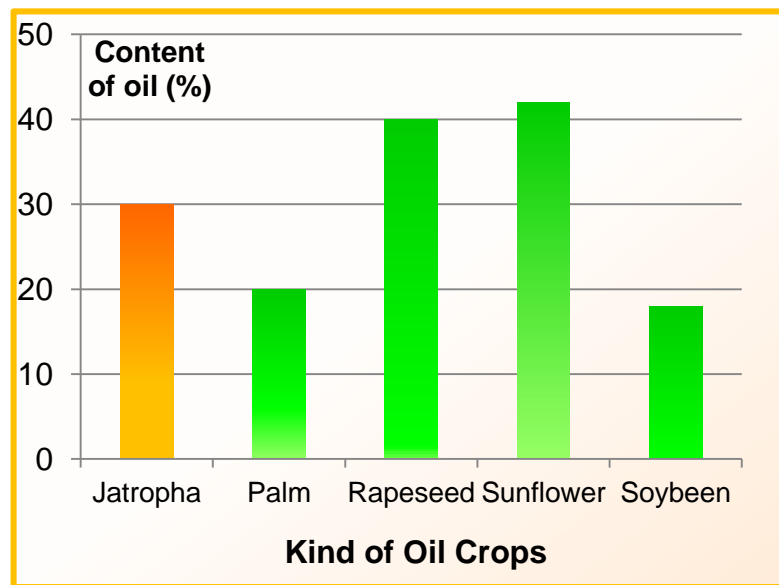
## Based on Oils: Oil Producing Trees



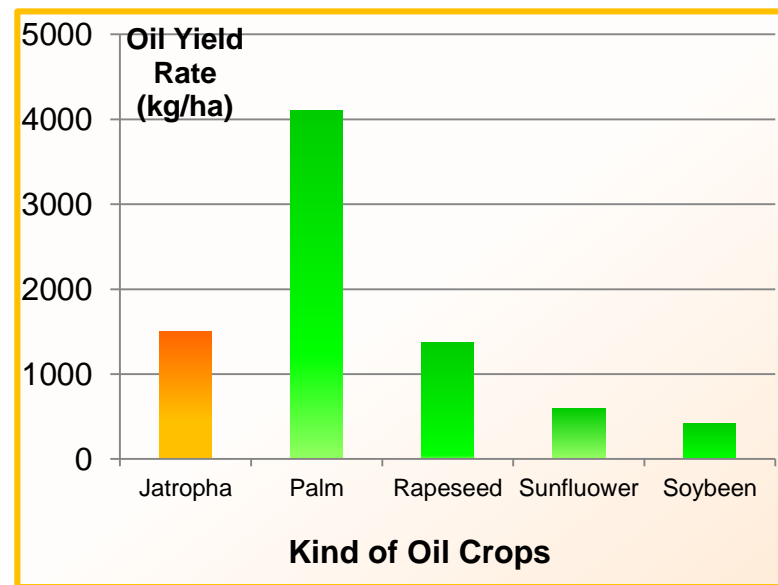


# Production, Oil-Content and Fat Yield of Oil Crops.

Kind of Oil Crops	Production Rate (kg/ha)	Oil Content (%)	Oil Yield Rate (kg/ha)
Jatropha	5,000	30	1,500
Palm	20,501	20	4,100
Rapeseed	3,440	40	1,376
Sunflower	1,434	42	602
Soybean	2,314	18	416



Oil Content of Different Oil Crops



Oil Yield Rate of Different Oil Crops



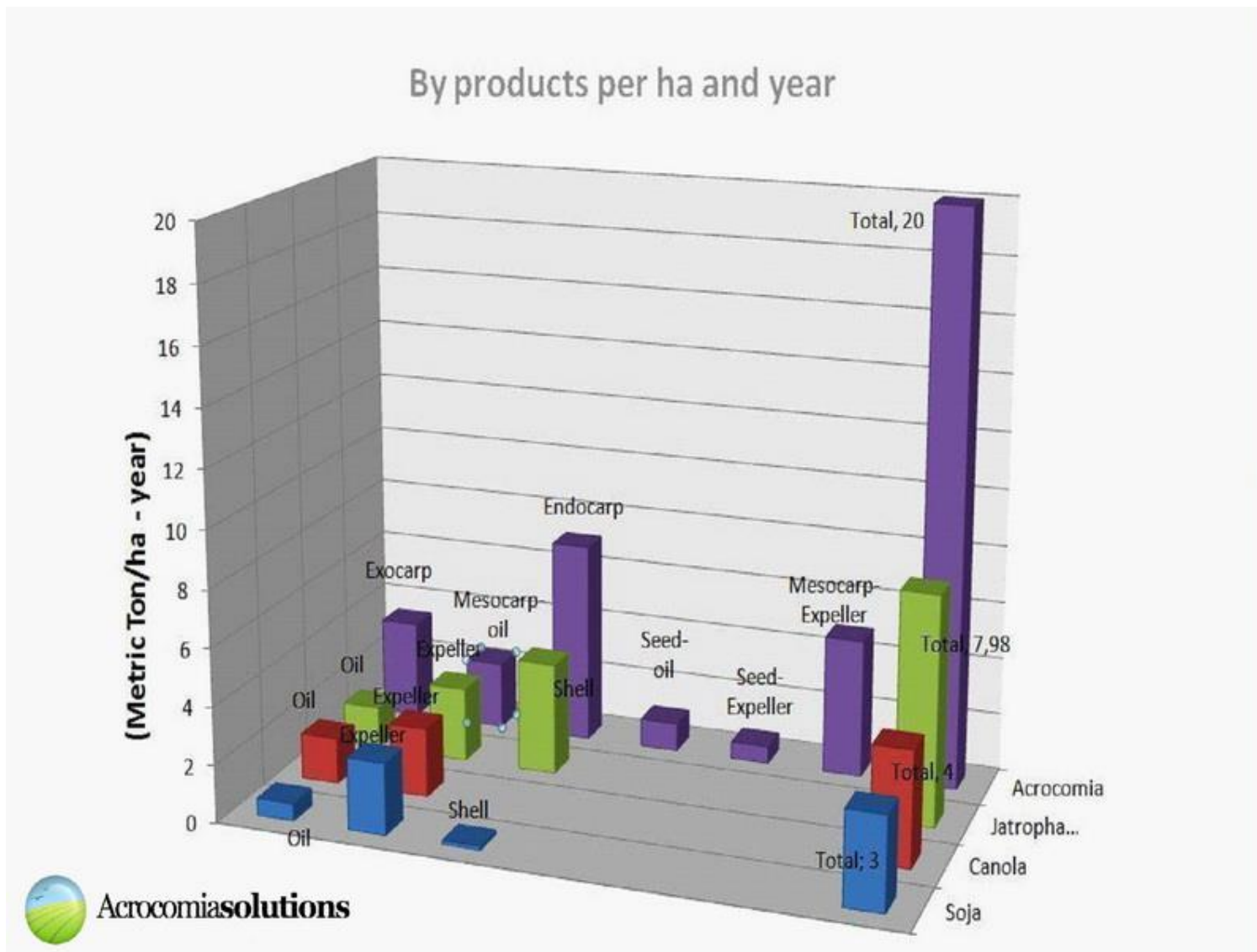
## Production of Oil by Different Crops.

Plant	Latin Name	Gal Oil /acre	Plant	Latin Name	Gal Oil /acre
Oil palm	<i>Elaeis guineensis</i>	610	Rice	<i>Ozisa sativa L.</i>	85
Macauba palm	<i>Acrocomia aculeata</i>	461	Buffalo Gourd	<i>Cucurbita foetidissima</i>	81
Pequi	<i>Caryocar brasiliense</i>	383	Safflower	<i>Carthamus tinctorius</i>	80
Buriti Palm	<i>MAuritia flexuosa</i>	335	Crambe	<i>Crambe abyssinica</i>	72
Oiticia	<i>Licania rigida</i>	307	Sesame	<i>Sesamum indicum</i>	71
Coconut	<i>Cocos nucifera</i>	276	Camelina	<i>Camelina sativa</i>	60
Avocado	<i>Persea americana</i>	270	Mustard	<i>Brassica alba</i>	59
Brazil Nut	<i>Bertholletia excelsa</i>	245	Coriander	<i>Coriandrum sativum</i>	55
Macadamia Nut	<i>Macadamia temiflora</i>	230	Pumpkin Seed	<i>Cucurbita pepo</i>	55
Jatropha	<i>Jatropha curcas</i>	194	Euphorbia	<i>Euphorbia lagascoe</i>	54
Babassu Palm	<i>Orbignya martiana</i>	188	Hazelnut	<i>Caylus avellana</i>	49
Jojoba	<i>Simmondsia chinensis</i>	186	Linseed	<i>Linus usitatissimum</i>	49
Pecan	<i>Carya illinoensis</i>	183	Coffee	<i>Coffea arabica</i>	47
Bacuri	<i>Platonia insignis</i>	146	Soybean	<i>Glycine max</i>	46
Castor bean	<i>Ricinus communis</i>	145	Hemp	<i>Cannabis sativa</i>	37
Gopher plant	<i>Euphorbia lathyris</i>	137	Cotton	<i>Gassypium hirsutum</i>	33
Piassava	<i>Attalea funifera</i>	136	Calendula	<i>Calendula officinalis</i>	31
Olive tree	<i>Olea europea</i>	124	Kenaf	<i>Hibiscus cannabinus L.</i>	28
Rapeseed	<i>Brassica napus</i>	122	Rubber seed	<i>Hevea brasiliensis</i>	26
Opium Poppy	<i>Papaver somniferum</i>	119	Lupine	<i>Lupinus albus</i>	24
Peanut	<i>Aiachis hypogea</i>	109	Palm	<i>Erythea salvadorensis</i>	23
Cocoa	<i>Theobroma cacao</i>	105	Oat	<i>Avena sativa</i>	22
Sunflower	<i>Helianthus annuus</i>	98	Cashew Nut	<i>Anacardium occidentale</i>	18
Tung oil tree	<i>Aleurites fordii</i>	96	Corn	<i>Zea mays</i>	18

da Tickell, 2000



# By-Products in Oil Crops.









## Oil Palm Tree (*Elaeis guineensis* jacq.).

- The **palm oil** tree originates from West Africa where it grows in the wild, later it was developed into an agricultural crop.
- Oil palm is a monoecious crop as it bears both male and female flowers on the same tree. Each tree produces compact bunches weighing between 10 and 25 kg with 1000 to 3000 fruitlets per bunch. Each fruitlet is almost spherical or elongated in shape. Generally, the fruitlet is dark purple, almost black and the color turns to orange red when ripe. Each fruitlet consists of a hard kernel (seed) enclosed in a shell (endocarp) which is surrounded by a fleshy mesocarp.

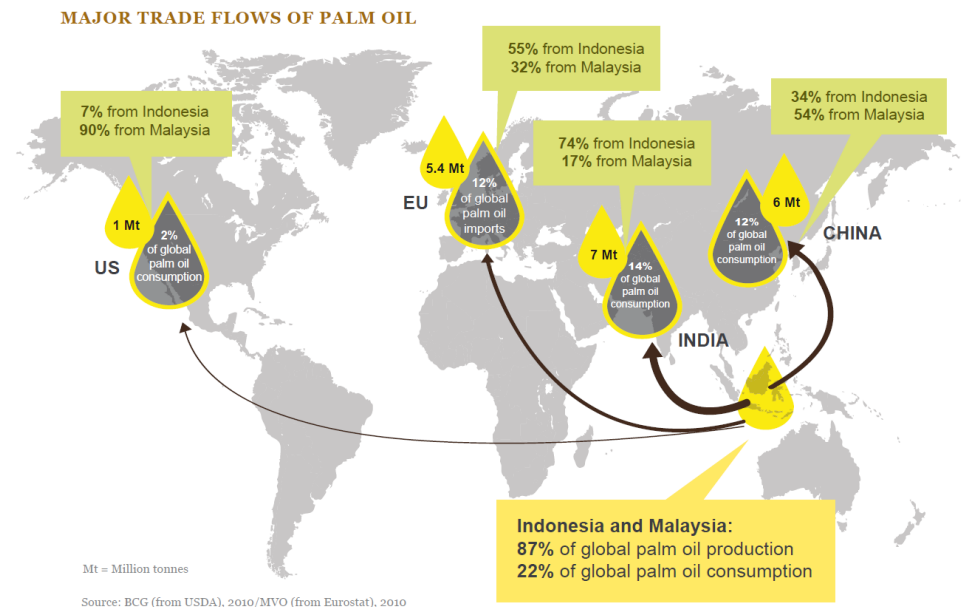




## Oil Palm Tree.

That is one of the reasons why **palm oil makes up more or less a third of the 151 million tonnes of vegetable oil produced worldwide.**<sup>1</sup> Its wide availability and low price combined with certain unique characteristics means that it is used in many packaged food and personal care products that line supermarket shelves. Ice cream, margarine, biscuits, cakes, breakfast cereals, soup stock cubes, snacks, ready meals, instant noodles, shampoos, soaps, lipsticks, candles and washing-up liquids—all of these items often contain palm oil that was produced in tropical countries such as Indonesia and Malaysia.

Demand is around 77 million tonnes to help feed the world's growing population and the increased affluence of emerging economies and its use may grow even more if demand increases for palm oil as a biofuel.

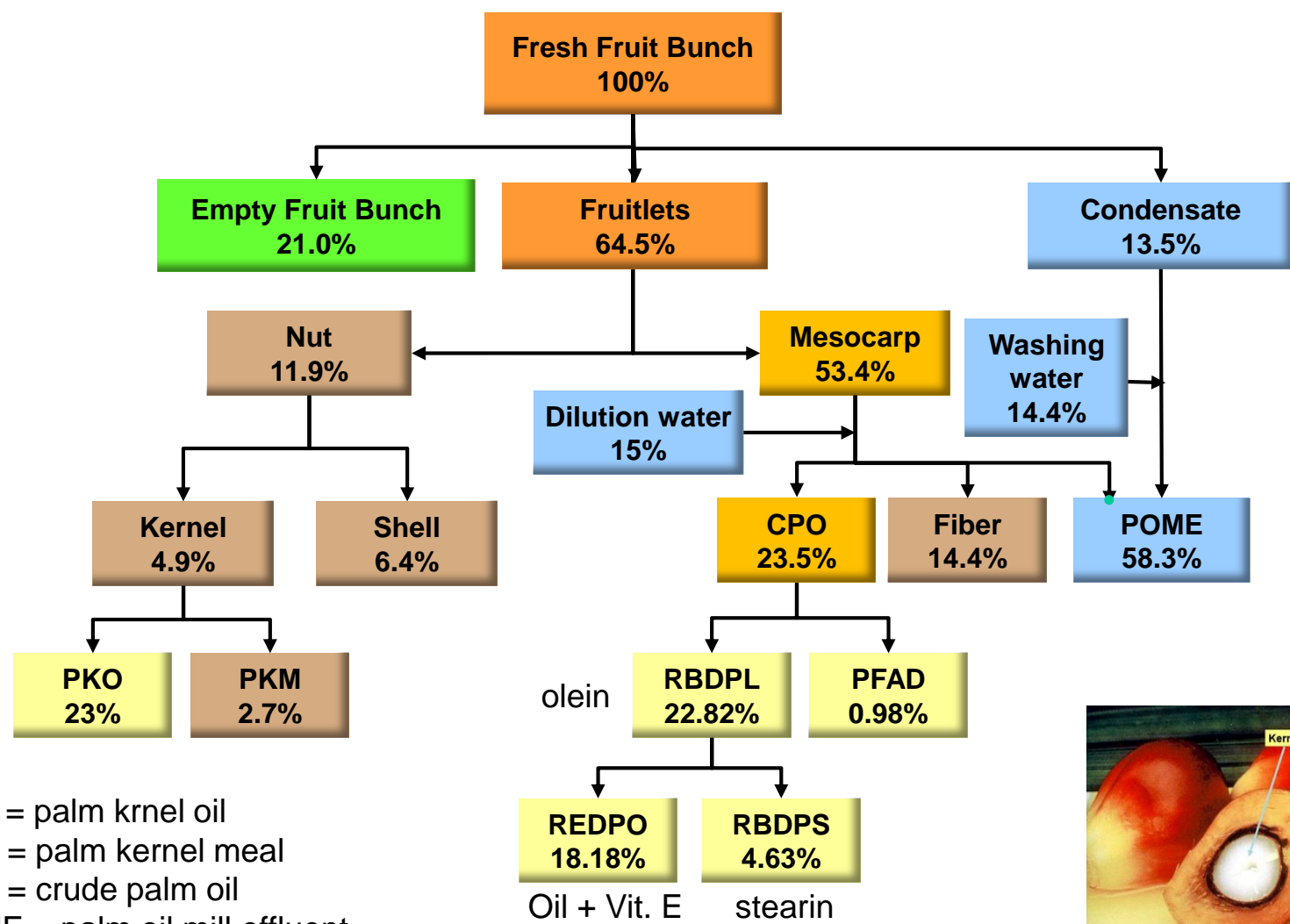


<sup>1</sup>USDA. Table 03: Major Vegetable Oils: World Supply and Distribution (Commodity View). Accessed October 22, 2011 <http://www.fas.usda.gov/oilseeds/Current/>

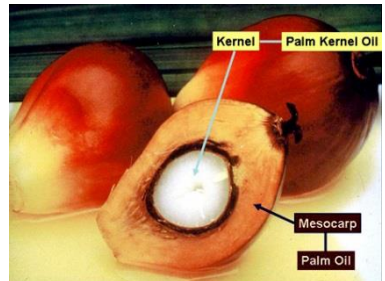
<sup>2</sup>FAO, 2006, World agriculture: towards 2030/2050. Prospects for food, nutrition, agriculture and major commodity groups. Interim report



# Mass Balance in Palm Oil Processing.



PKO = palm kernel oil  
 PKM = palm kernel meal  
 CPO = crude palm oil  
 POME = palm oil mill effluent  
 RBD = refined, bleached and deodorized  
 PFAD = palm fatty acid distillate







## Rapeseed and Canola (*Brassica spp.*).

Rapeseed is a member of the mustard family.  
Canola is a variety of rapeseed bred to have low levels of erucic acid and glucosinolates (both of which are undesirable for human consumption)

- Both spring and winter varieties grown
  - Depends on geographical location
  - Winter crop in NC
- 
- Good oil yield
  - Premium cold flow properties.
  - 70% of feedstock for EU biodiesel production.







## Camelina (*Camelina sativa*).

- Camelina is a member of mustard family
- Summer annual crop suited to grow in semi-arid climates and northern U.S.
- Research on variety development and economic feasibility are being conducted in U.S.A.
  - The cost of camelina-based biodiesel would likely be \$0.526 per *L* compared to \$0.789 per *L* for soy-based
- Variable and fixed costs are 1/3 - 1/4 the cost of canola
  - \$45 to \$68 per 4047 *m*<sup>2</sup>





## Sunflower (*Helianthus annuus*).

- Sunflower and safflower are summer annuals in the sunflower family. Sunflower and safflower seeds are excellent sources of oil. The meal can be used for animal feed.
- Safflower oil yields under irrigation range from 532 to 880 *kg/ha*. Without irrigation, safflower oil yields can drop to 112 *kg/ha*.
- Sunflower oil yields under irrigation range 840-930 *kg/ha*. Sunflower oil concentration in the seed ranges from 40-45%. \$.036-.055 per *kg* market value
- Second largest biodiesel feedstock in the EU.







## Safflower (*Carthamus tinctorius*).

Old crop (known to Egyptian and Chinese 2000 BC) is used for food and for oil. This is particularly precious for its content in unsaturated fatty acids

A source of yellow and red colors.





## Peanuts (*Arachis hypogaea*).

### Advantages:

High Oil Yield ~50-60% Soy is only ~18% oil.

Nearly 15% of peanuts are crushed for oil use in U.S.

Value range of \$ 0.23-.30 per lb. of peanut depending on state, variety, production system (higher for organic) \$ .50 per gallon of oil obtained (on average)

### Obstacles:

High Value Commodity

Shelling and sorting is costly process.





## Jatropha (*Jatropha curcas*).

**Jatropha** is a small shrub native of C. America and a member of Euphorbia family, it is a drought-resistant perennial, living up to 50 years and growing on marginal soils.

Oil content: ~35%

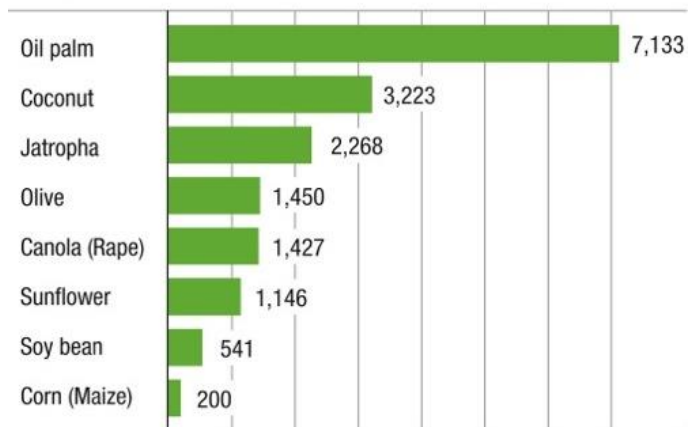
Oil: normally Not Edible.

Other oil uses: insect repellent.



### Resources for Biodiesel

Yield per hectare in liter\*



\*Under optimal conditions Quelle: Phillips McDougall, January 2008 - Copyright © Bayer CropScience







## Castor Beans (*Ricinus communis*).

**Castor bean** - drought-resistant, annual plant of tropical origin with immense spread-out. The plant can grow between 2 to 5 m.

Oil: soluble in alcohol (no heat) – fit for biodiesel..

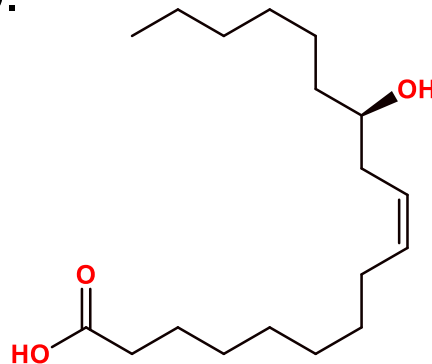
Oil content: ~55%.

Oil: Not Edible (high level of Ricinoleic Acid – 85%).

Other oil uses: Over 700.



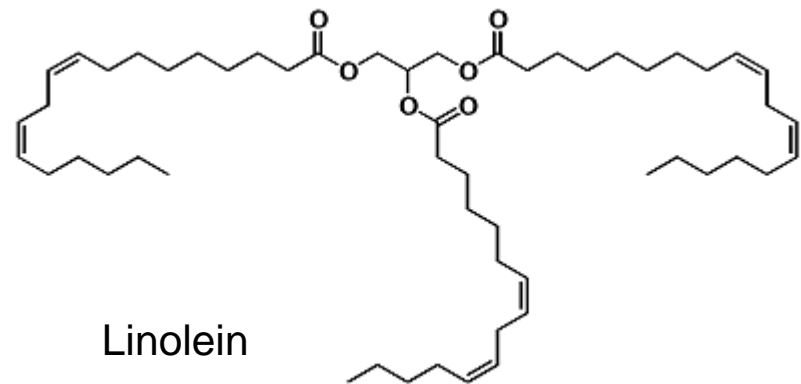
Ricinoleic Acid





## Flax (*Linum usitatissimum*).

- Flax is the source of linseed oil. Seed oil contents range from 30 to 34%.
- Both spring and winter forms are available. No specific breeding efforts are present in the Pacific Northwest.
- Used also to produce linen, also known as fiber flax.
- Flax oil contains polyunsaturated triglycerides which have a distinctive reaction toward oxygen in air.





## Crambe (*Crambe abissinica*).

Crambe is an ideal crop for production of specialised industrial oil qualities that must not be mixed with food quality oils.

Crambe is already a non-food oil crop and it does not cross fertilise with Brassicas such as rapeseed.

With regards to cultivation, Crambe is a low input oil crop compared to many others and it can be grown over large part of Europe.

Oil content in the seed: 35% with 55% erucic acid.

It is mainly used for lubricants, plastics or nylon).





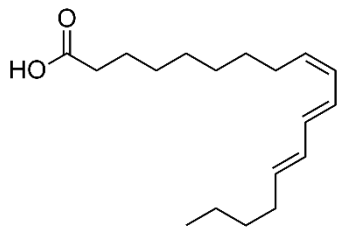


## Tung Oil Tree Plant.

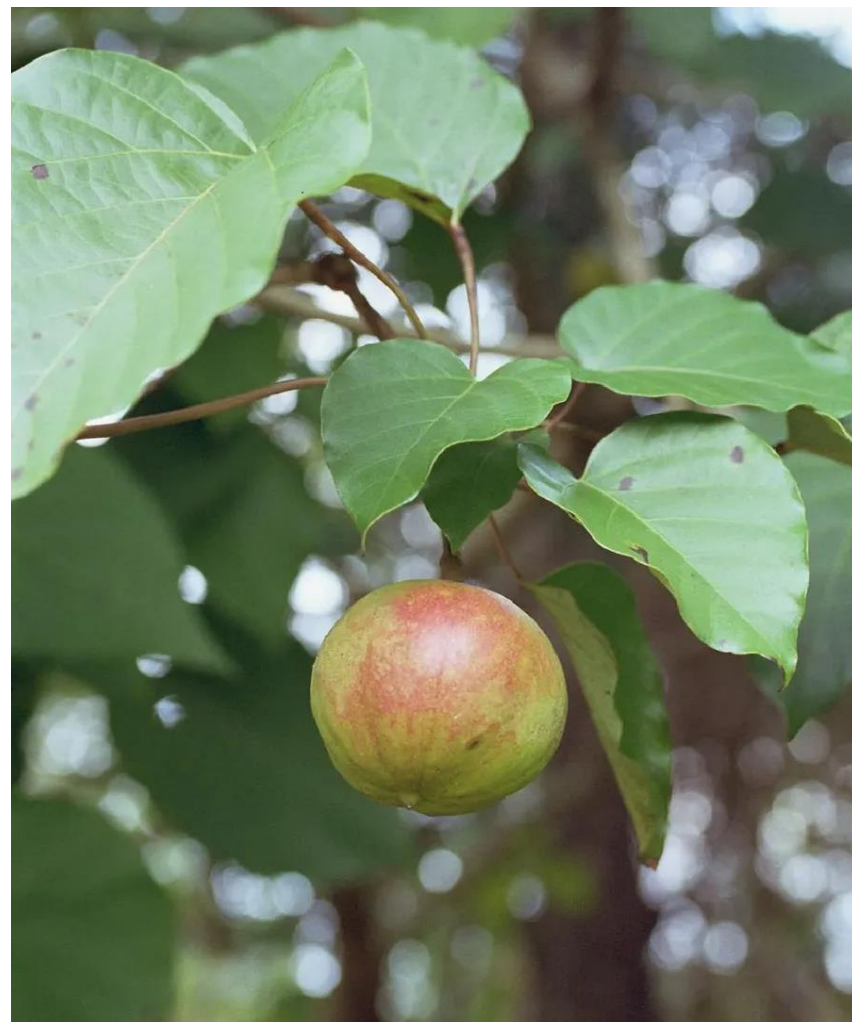
**Tung tree**, (*Aleurites fordii*) is a small Asian tree of the spurge family (*Euphorbiaceae*)

Commercially valuable for **tung oil**, which is extracted from its nutlike seeds (mainly ester of eleostearic acid).

In the Orient **tung oil** was traditionally used for lighting, but it also has important modern industrial uses (pressure sensitive adhesives, self-healed epoxy coatings, polyurethane foam, vinyl ester resins).



eleostearic acid







## Limitations of (some) 1<sup>st</sup> generation biofuels.

- Limited ability to meet fuel demands
- Compete with land for food crops
- Low net energy yield
- Limited greenhouse gas reductions
- Potentially lead to deforestation and negative impacts on biodiversity.



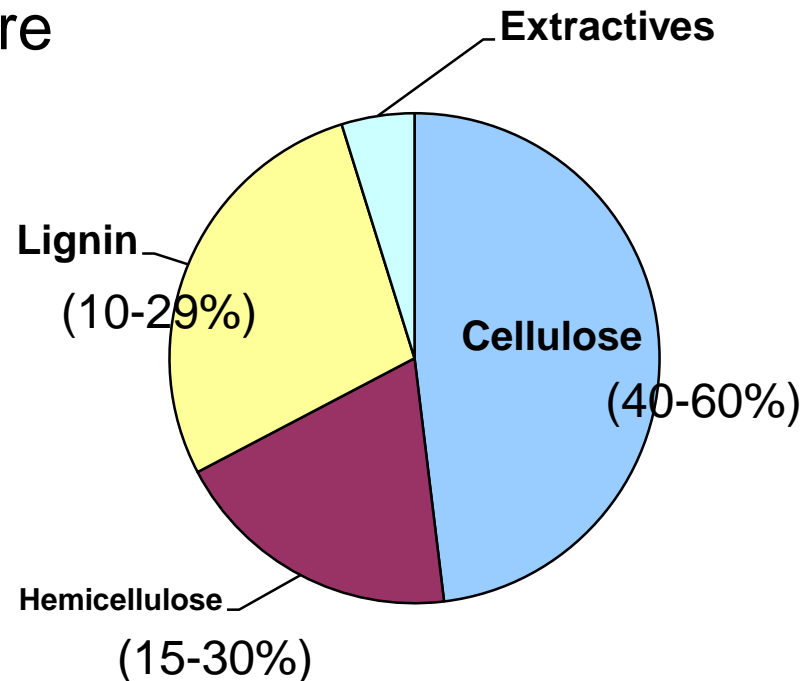


## Lignocellulose Feedstock.

- Most abundant form of biomass
- Can be grown on low-value land
- High greenhouse gas reductions
- High net energy yield
- Greater yield per hectare

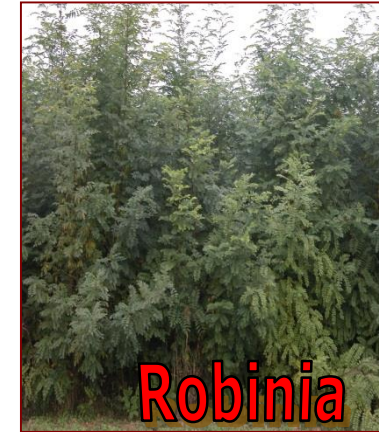
### Examples:

- woody biomass
- agricultural residues
- perennial grasses





# Based on cellulose/hemicellulose - Crops for 2<sup>nd</sup> Generation Biofuels.



Grass



Woody







## Energy Crops: Miscanthus (*Miscanthus Giganteus*).

Miscanthus is a large perennial grass (it can grow up to 13 feet in height) characterized by:

- Lower fertilizer & water needs
- Strong photosynthesis, perennial
- Stores carbon & nutrients in soil
- Great field characteristics, longer canopy season
- Economics: +\$3000vs -\$300 (10yr profit)
- 1 years growth without replanting!



20 tons/acre? ([www.bical.net](http://www.bical.net))

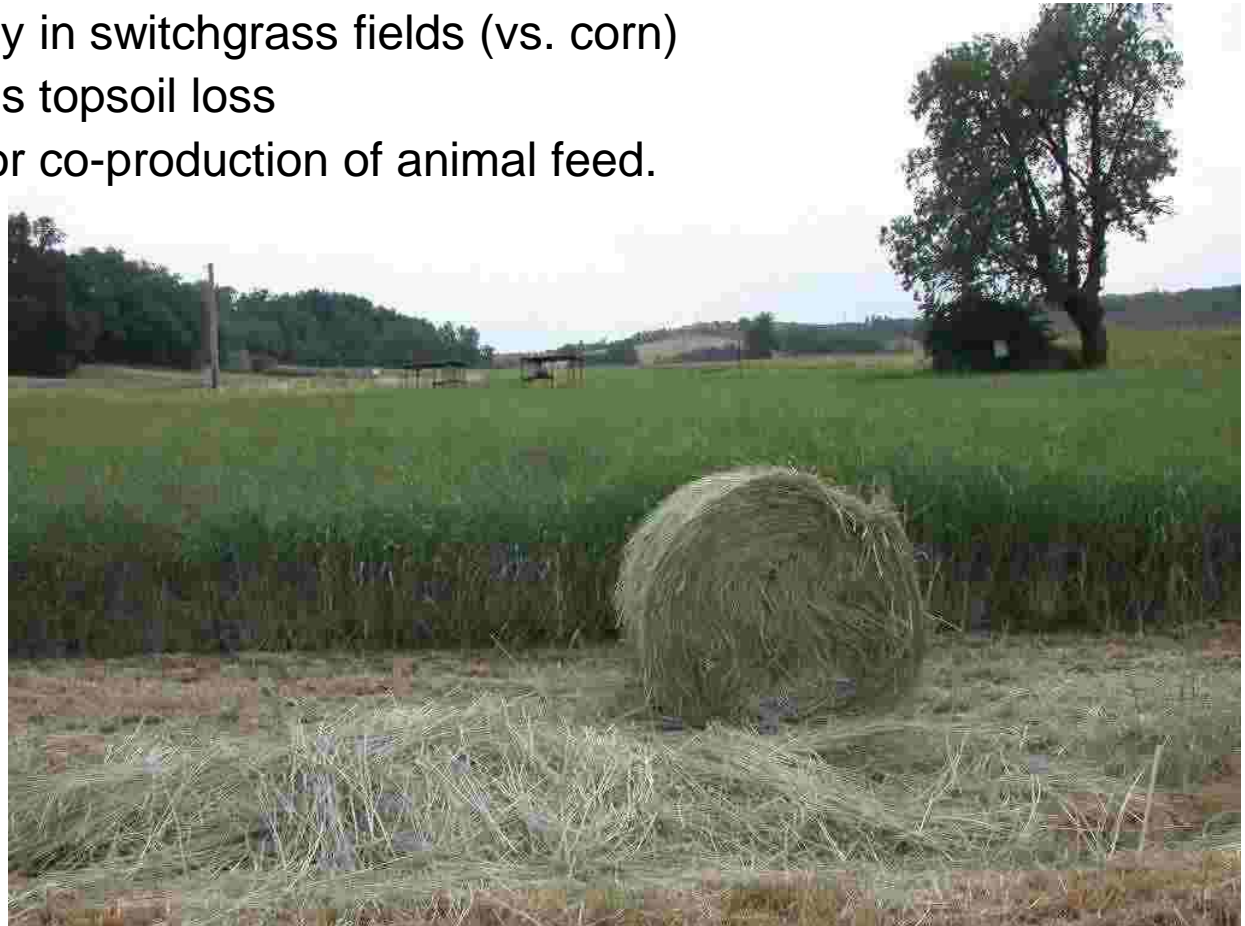
10-30 tons/acre ([www.aces.uiuc.edu/DSI/MASGC.pdf](http://www.aces.uiuc.edu/DSI/MASGC.pdf))





## Energy Crops: Switch Grass (*Panicum virgatum*).

- Natural prairie grass in the US; enriches soil
- Less water; less fertilizer; less pesticide
- Reduced green house gases
- More biodiversity in switchgrass fields (vs. corn)
- Dramatically less topsoil loss
- High potential for co-production of animal feed.





## Energy Crops: Sorghum.

Sorghum is a genus with many species and subspecies, including grain sorghums, grass sorghums (for pasture and hay), sweet sorghums (for syrups), and Broomcorn.

- Drought resistant biofuels crop
- *Sorghum bicolor* – tropical Africa.
- Major food in India, and Africa where leavened bread is not important (*Sorghum vulgare*)
- Very versatile crop
- Black and brown sorghum has polyphenol such as condensed
- Grain sorghum and maize (corn) are comparable in costs of production and in nutrition





## Energy Crops: Giant Cane (*Arundo Donax*).

Giant Cane, is a tall perennial cane growing in damp soils, either fresh or moderately saline.

is native to eastern and southern Asia, and probably also parts of Africa and southern Arabic Peninsula. It has been widely planted and naturalized in the mild temperate, subtropical and tropical regions of both hemispheres.

It forms dense stands on disturbed sites, sand dunes, in wetlands and riparian habitats.

In ideal conditions it can exceed 10 m, with hollow stems 2 to 3 cm diameter.

The maximum CO<sub>2</sub> uptake ranged between 19.8 and 37  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , depending on irradiance,







## Poplar (*genus Populus*).

Poplars are rapid-growing but relatively short-lived trees, widely distributed throughout the northern temperate regions, (North America, Eurasia, north Africa, with a few species extending even beyond the Arctic Circle). The leaves are alternate and ovate or heart-shaped in outline, with finely to coarsely toothed margins. Male and female flowers grow on separate trees and bloom in drooping catkins long before the leaves emerge. The fruits, which mature before the leaves are fully grown, are small, thick-walled capsules that contain many minute seeds clothed in cottony tufts of silky hairs, which assist in wind dispersal. The wood is soft and mostly used to make paper, cardboard boxes, crates, and veneer.







## Hemp (*Cannabis sativa*).

Hemp is a bast fiber plant similar to flax, kenaf, jute and ramie. Long slender primary fibers on the outer portion of the stalk characterize bast fiber plants. An annual fast growing plant can be grown on a range of soils, but grow best on land that produces high yields of corn. Hemp is dicotyledons, which means their stalks have an outer bast fiber and an inner core fiber. The hemp plant is harvested for its fibers, seed, seed meal and seed oil. The valued primary fibers are contained around the hollow, lignin rich woody core of the hemp stalk. **Low THC content!**

