Biodiesel Production

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ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

- ✓ Introduction
- ✓ Feed stocks (vegetable oils)
- ✓ Oil extraction
- ✓ Biodiesel process
- ✓ Biodiesel process for WCO

Introduction

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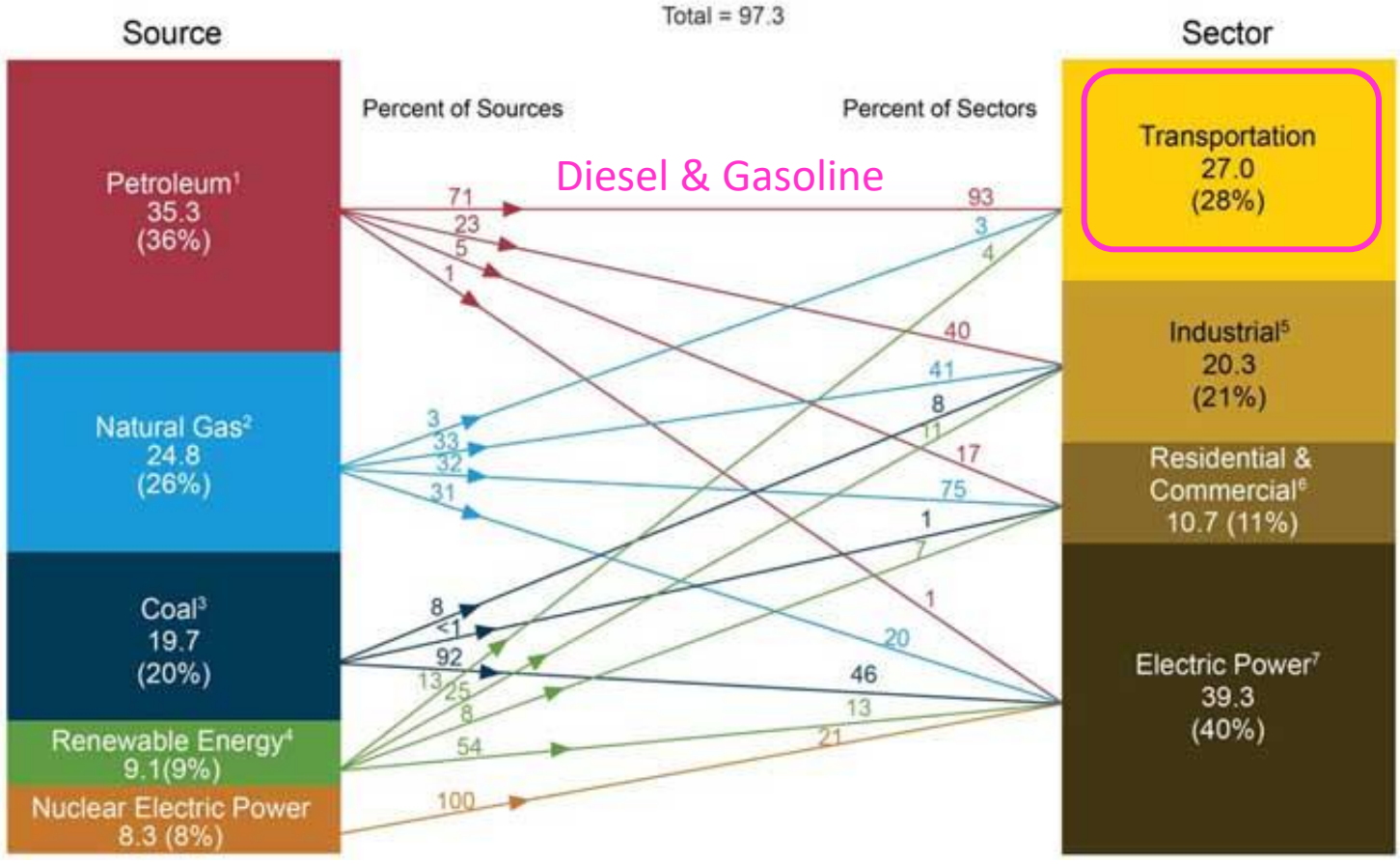
❖ Primary energy consumption by source and sector in USA (2011)



✓ Well developed refining and transportation infrastructures.

✓ Well developed engines.

Introduction - Growth

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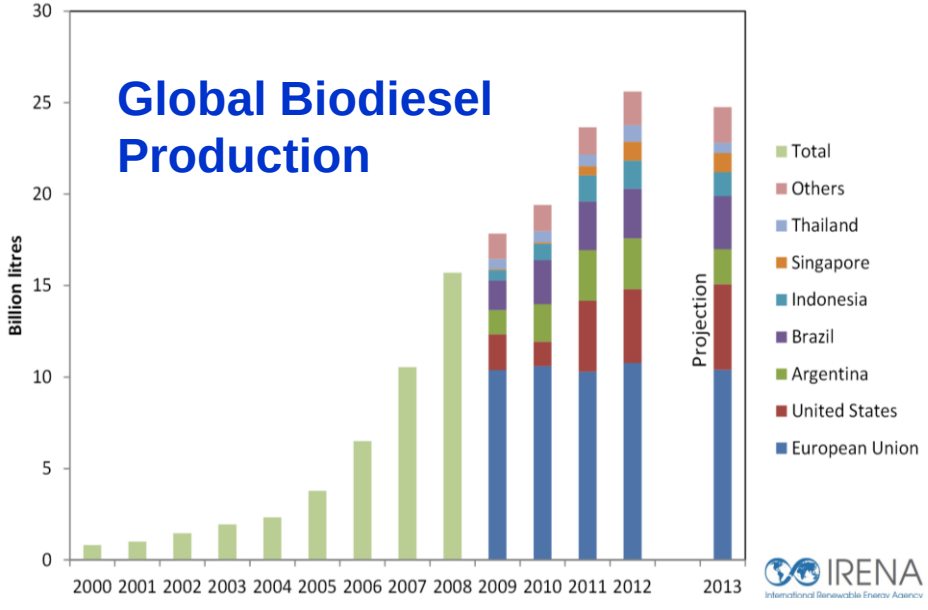
- Bio-fuels have potential to replace fossil fuels.
- Biodiesel and bioethanol are two most common liquid bio-fuels.
- Biodiesel can be blended with diesel & bioethanol can be blended with gasoline.



World Ethanol Fuel Production in Million Litres						
	2006	2007	2008	2009	2010	2011
Europe	1,627	1,882	2,814	3,683	4,615	5,467
Africa	0	49	72	108	165	170
Americas	35,625	45,467	60,393	66,368	77,800	79,005
Asia/Pacific	1,940	2,142	2,743	2,888	3,183	4,077
World	39,192	49,540	66,022	73,047	85,763	88,719

Surec: Global Renewable Fuels Alliance

Introduction – Energy Content

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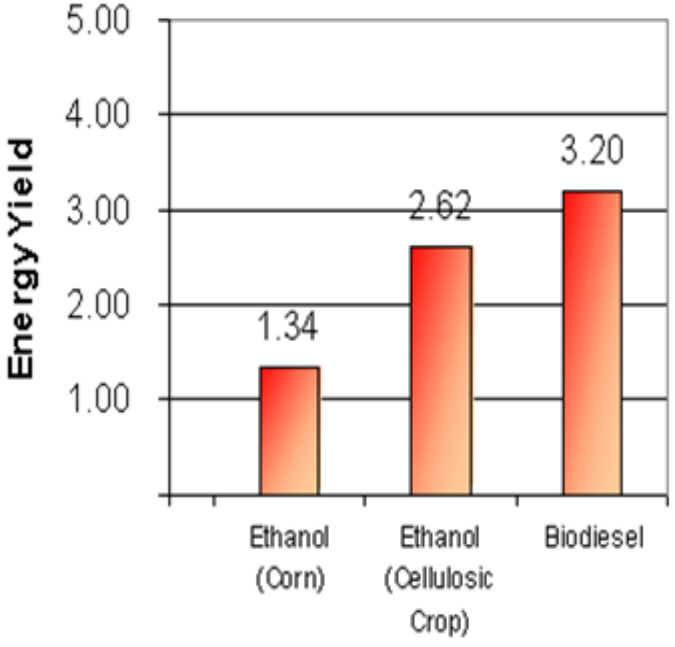
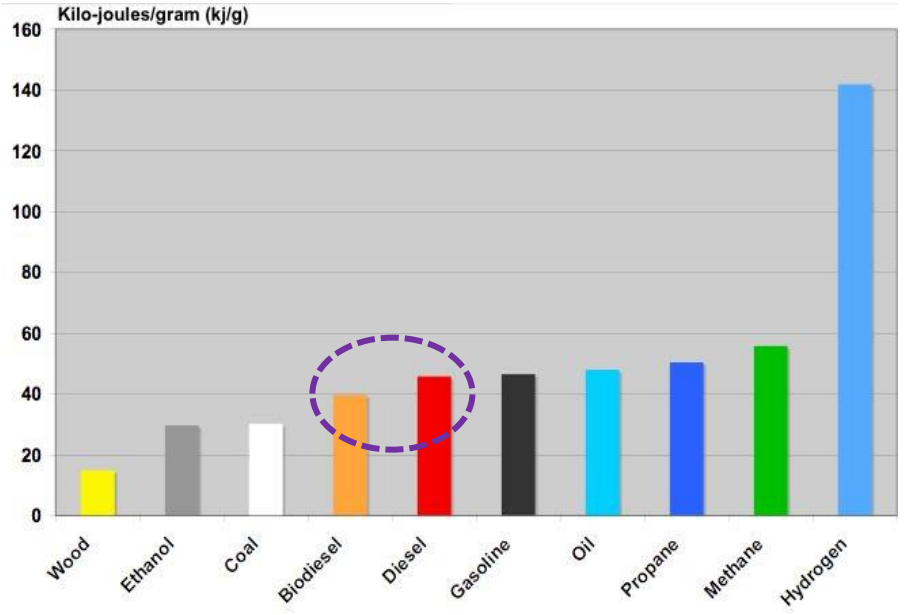
What is biodiesel?

Fuel produced from vegetable oil or animal fat.

It can be blended in diesel, and then can be used in traditional engines.





Energy yield = amount of energy gained versus the amount of energy required to produce.

Specific energy = energy content per kg of fuel.

Introduction - Emissions

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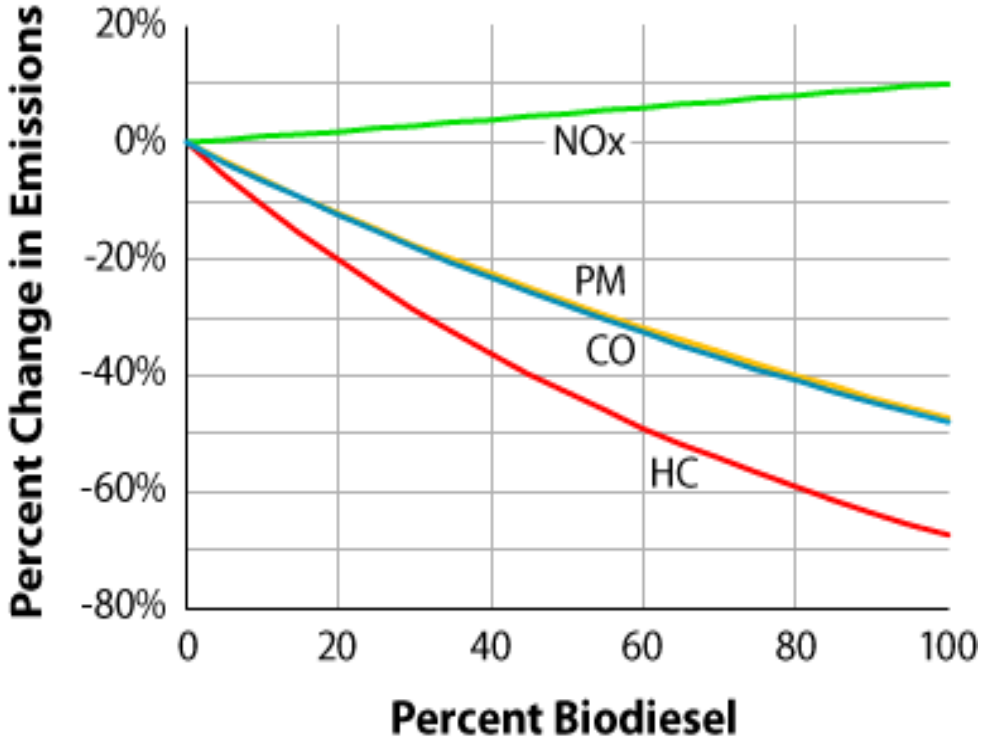
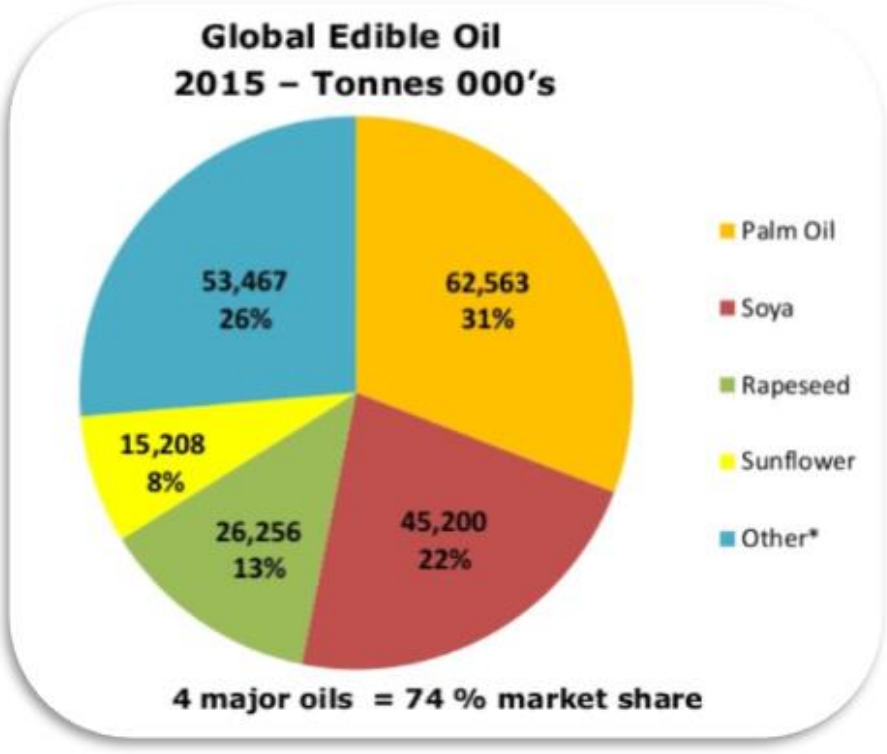
- ✓ Biodiesel is a cleaner burning replacement fuel made from renewable sources like new and used vegetable oils and animal fats.
- ✓ Low level blends (≤ 20%) can be used in almost any existing diesel engine.
- ✓ High level blends (> 20%) can be used in most new diesel engines → cold start (preheating).
- ✓ NOx emissions → fuel injection timing.

Average emission impacts of biodiesel for heavy duty vehicle



Fuel bound oxygen → NOx

Feed Stocks

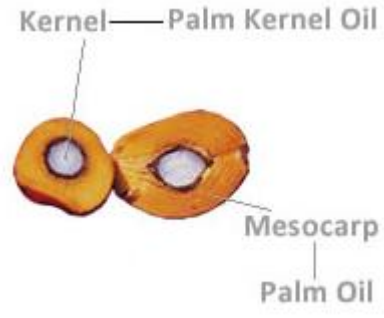


Soya bean

Rapeseed

Sunflower

Groundnut (Peanut)



Productivity of Various Major Oil Crops (2006/2007)

Oil Crop	Oilseeds yield ($t\ ha^{-1}\ yr^{-1}$)	Oil Content (%)	Calculated oil yield ($t\ ha^{-1}\ yr^{-1}$)
Palm Oil (mesocarp)	19.03	20.1	3.82
Palm Kernel	0.999	45.4	0.45
Cottonseed	1.28	14.7	0.19
Groundnut	1.04	43.2	0.45
Sunflower	1.25	41.2	0.52
Rapeseed	1.75	39.7	0.69
Coconut	0.52	66.1	0.34

Feed Stocks

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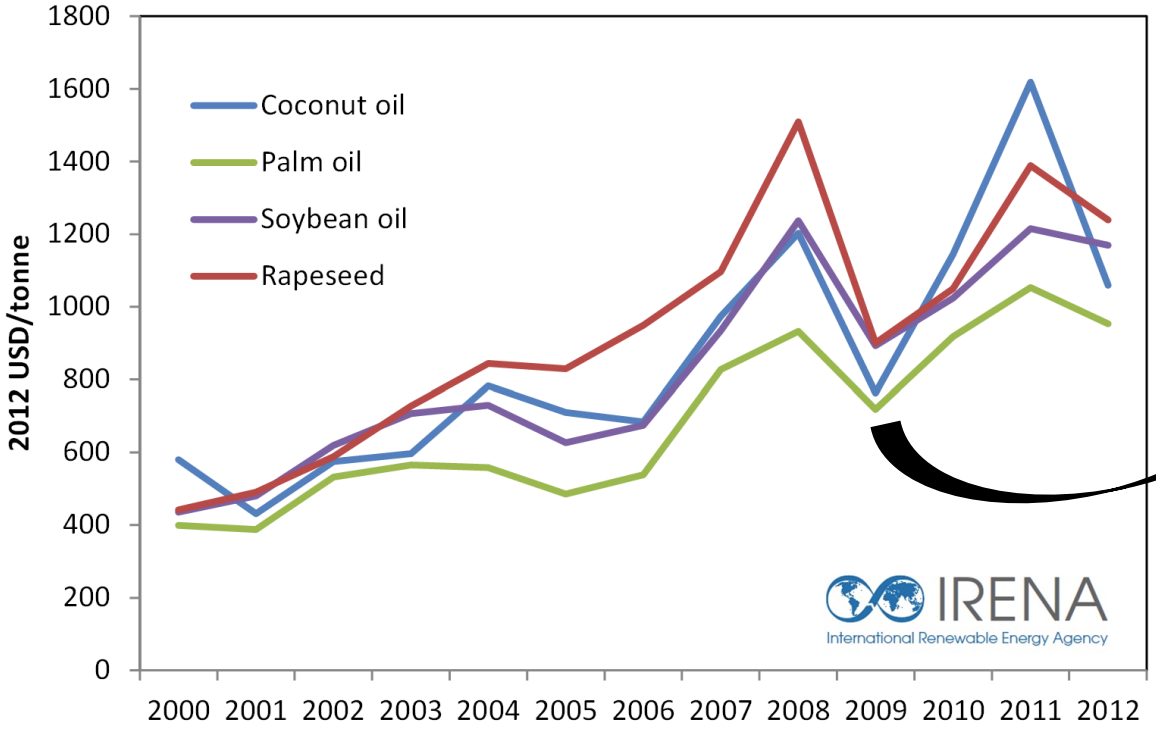
- Feed stock cost contributes about 60-70% to biodiesel production cost.
- Soybean and other plant oils have long term price issues.



Crude petroleum price crisis

✓ What type of oil is used for biodiesel production?

Soybean oil in the USA

Rapeseed oil in Europe

Feed Stocks

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- ✓ **Can we use vegetable oils in diesel engines?**

Vegetable oil	Kinematic viscosity at 38 °C (mm^2/s)	Cetane no. (°C)	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Corn	34.9	37.6	39.5	−1.1	−40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	−15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	−12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	−15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	−6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133
Soya bean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161
Palm	39.6	42.0	–	31.0	–	267	0.9180
Babassu	30.3	38.0	–	20.0	–	150	0.9460
Diesel	3.06	50	43.8	–	−16	76	0.855

- ✓ Kinematic viscosity
- ✓ Flash point

- ✓ Preheat the oil
- ✓ Process the oil

Feed Stocks

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➢ Oil Compositions

Typical fatty acid composition (wt%) of selected vegetable oils and fats

	16:0	18:0	18:1	18:2	18:3
Cocoa butter	26	34	35	–	–
Corn	13	3	31	52	1
Cottonseed	23	2	17	56	–
Groundnut[a]	7–12	3	46–71	14–35	–
Linseed	6	3	17	14	60
Linola[b]			16	72	2
Olive	10	2	78	7	1
Palm	44	4	39	11	–
Palm olein	41	4	31	12	–
Palm stearin	47–74	4–6	16–37	3–10	–
Palm mid-fraction	41–55	5–7	32–41	4–11	–
Rape (high erucic)[c]	3	1	16	14	10
Rape (low erucic)	4	2	62	22	10
Rice bran oil	20	2	42	32	–
Safflower (regular)	7	3	14	75	–
Safflower (high oleic)	6	2	74	16	–
Sesame	9	6	41	43	–
Soybean	11	4	23	53	8
Sunflower (regular)	6	5	20	60	–
Sunflower (Sunola)	4	5	81	8	–
Sunflower (NuSun)	4	5	65	26	–

– indicates values of 0–1.
[a] also C_{20}–C_{24} saturated and unsaturated acids 4–7%.
[b] also saturated acids 10%.
[c] also 20:1 6% and 22:1 50%.

$CH_2OOC(CH_2)_{14}CH_3$
|
$CHOOC(CH_2)_{14}CH_3$
|
$CH_2OOC(CH_2)_{14}CH_3$

Palmitic Acid (16:0) - $CH_3(CH_2)_{14}COOH$

Saturated Fatty Acids

16:0	Palmitic acid
18:0	Stearic acid

Unsaturated Fatty Acids

18:1	Oleic acid
18:2	Linoleic acid
18:3	Linolenic acid

Number of "C"

Number of "= bond"

Oil Extraction

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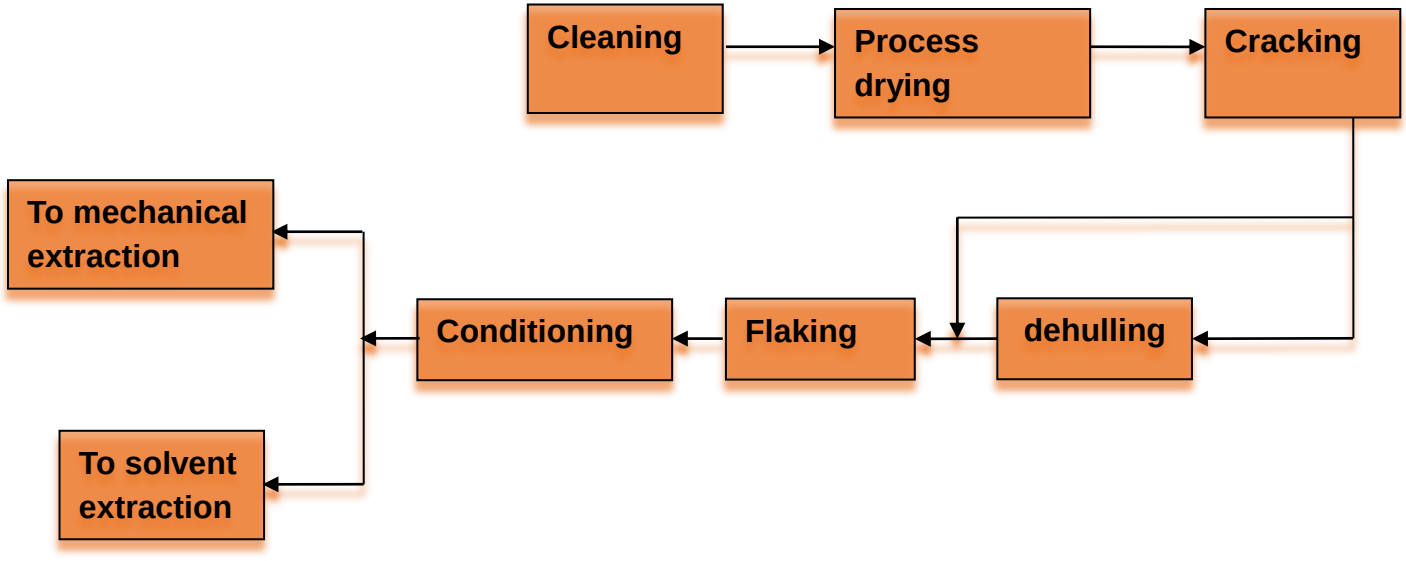
Mechanical Extraction:

Typically used for facilities with daily capacities of less than 150 tons.

Solvent Extraction:

Typically used for facilities with daily capacities of greater than 300 tons.

Commonly used after some type of mechanical extraction.



Oil Extraction

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- **Seed Preparation**

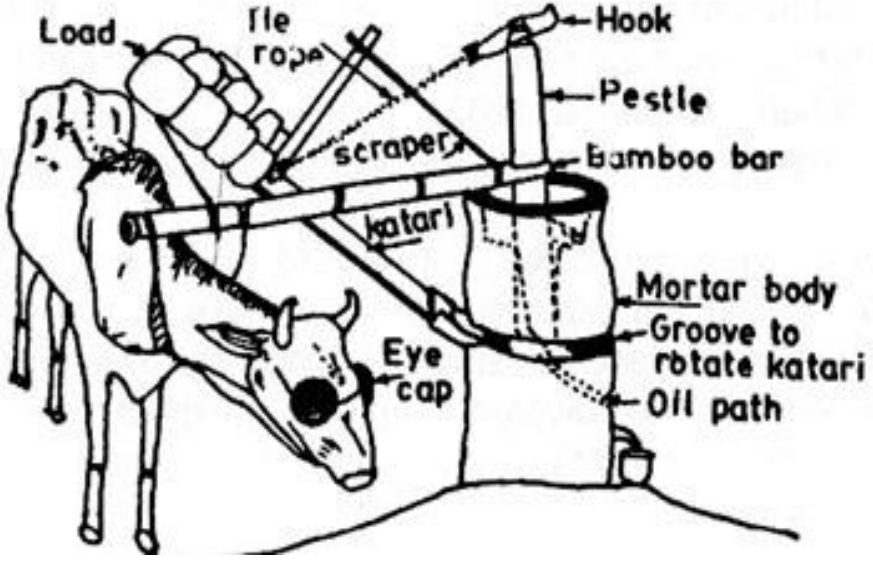
  Removal of foreign objects.

  Removal of seed hulls or shells for some seeds.

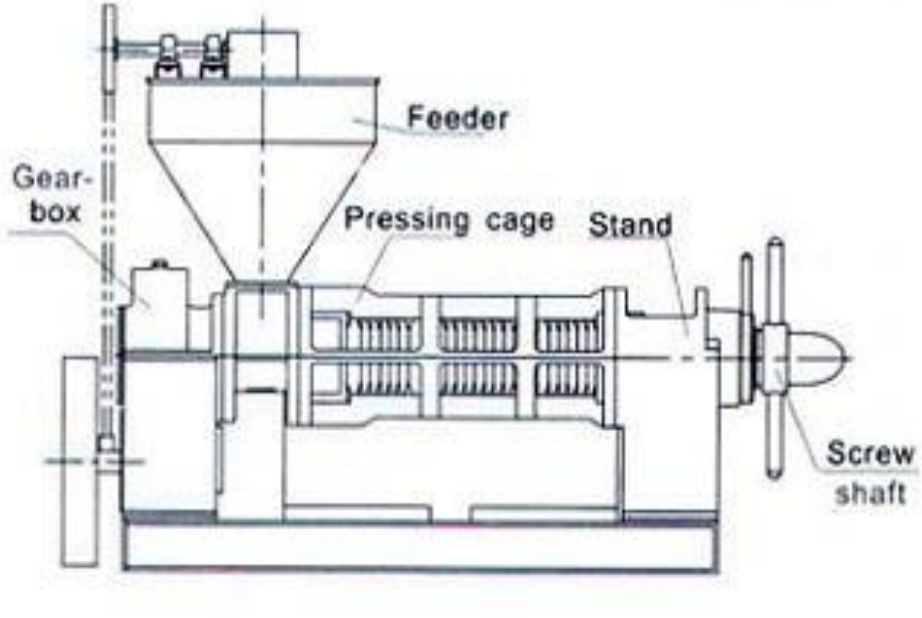
- **Mechanical Extraction**

  Seed is processed by a mechanical press.

  Removes 65-80% of oil contained in the seed.



Animal driven oil expeller



Screw Press

Oil Extraction

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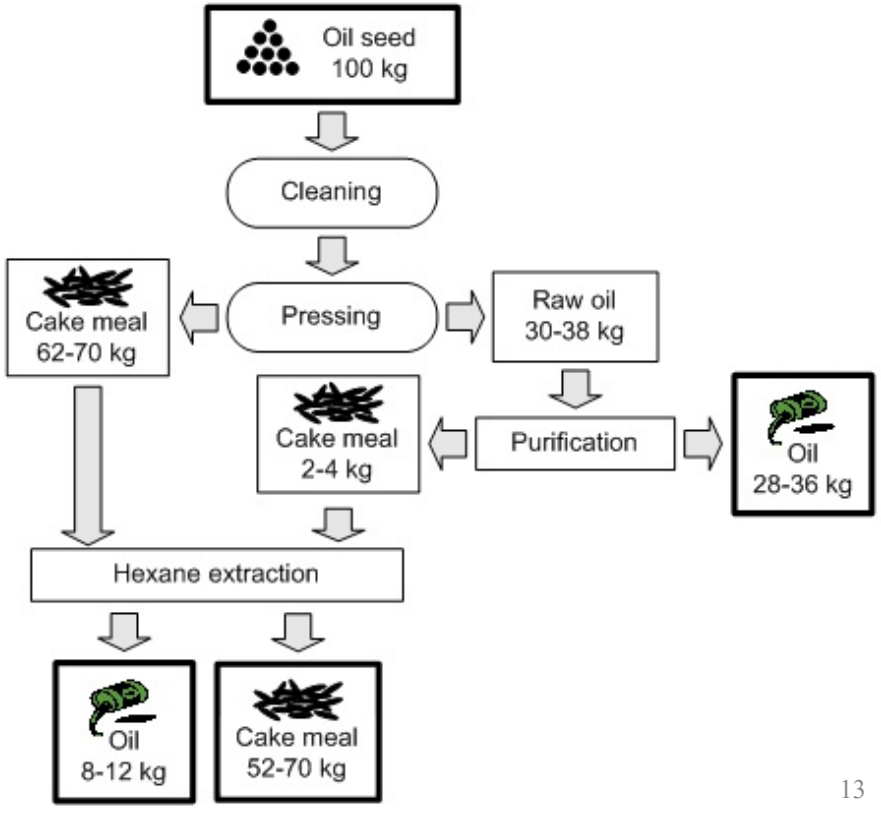
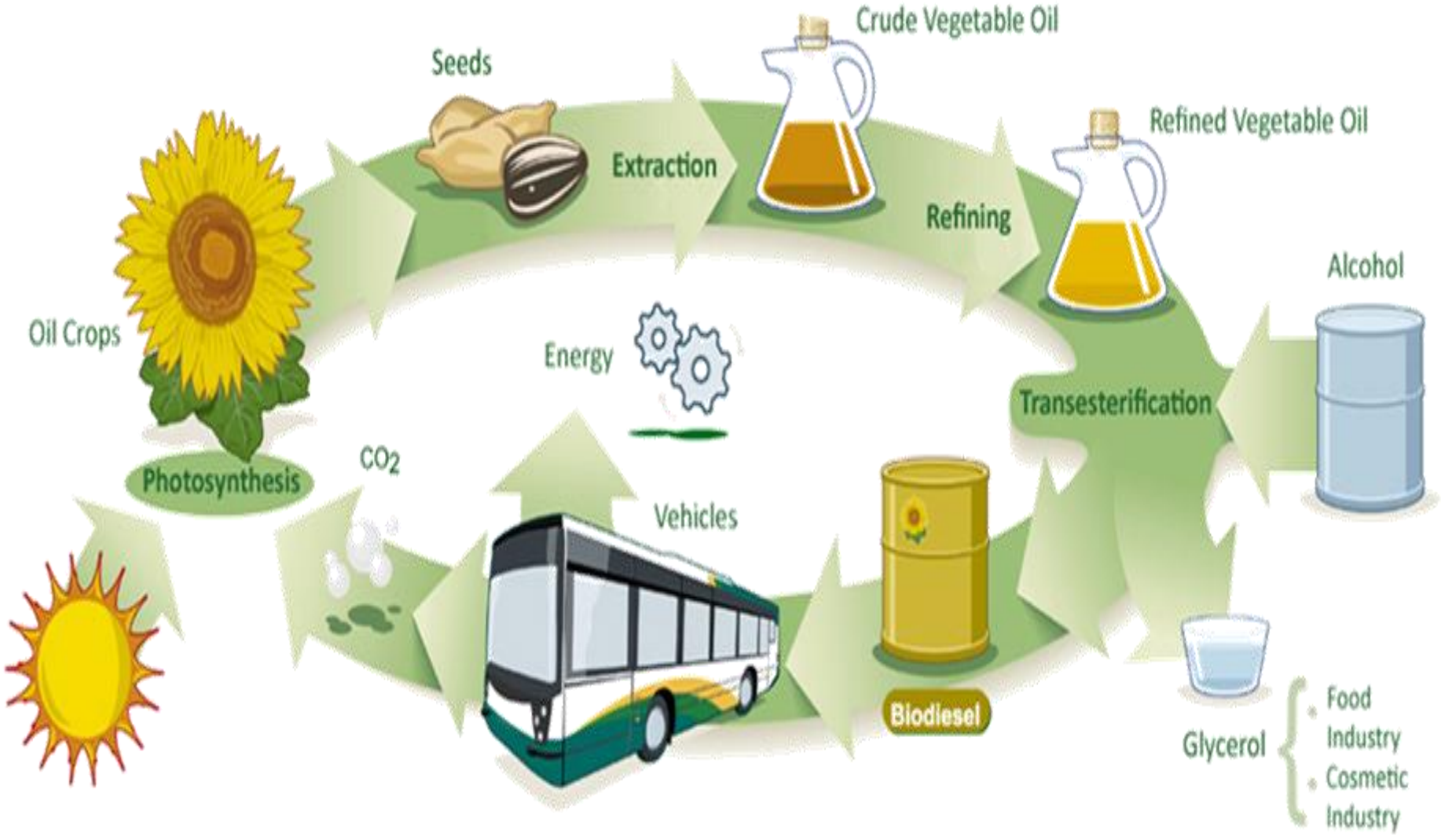
Solvent extraction

- ✓ Solvent (hexane) is applied to the pre-pressed material.
- ✓ The solvent bonds to the oil.
- ✓ Solvent and oil mixture is removed.
- ✓ The oil is then separated from the solvent which is reused in the process.
- ✓ Solvent extraction is capable of recovering ~99% of total oil content.
- ✓ Require large capital investment.




Crude Vegetable Oil
Seeds
Extraction
Refined Vegetable Oil
Refining
Alcohol
Oil Crops
Energy
Transesterification
Photosynthesis
CO_2
Vehicles
Biodiesel
Glycerol
Food Industry
Cosmetic Industry

Biodiesel Process: Reactions

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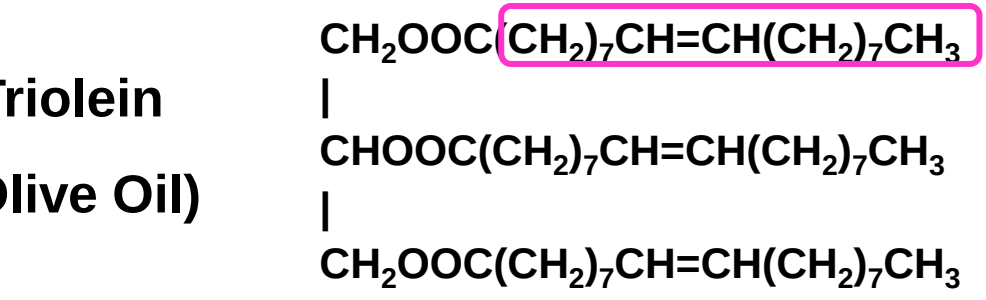
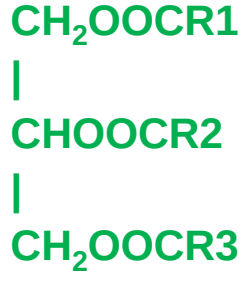
Oleic Acid (18:1): $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

Glycerol

Triolein

(Olive Oil)





- ✓ R1, R2, and R3 are **fatty acid alkyl** groups.
- ✓ R1, R2 and R3 could be same or different.
- ✓ The fatty acids in oil determine the final properties of the biodiesel.

Biodiesel Process: Reactions

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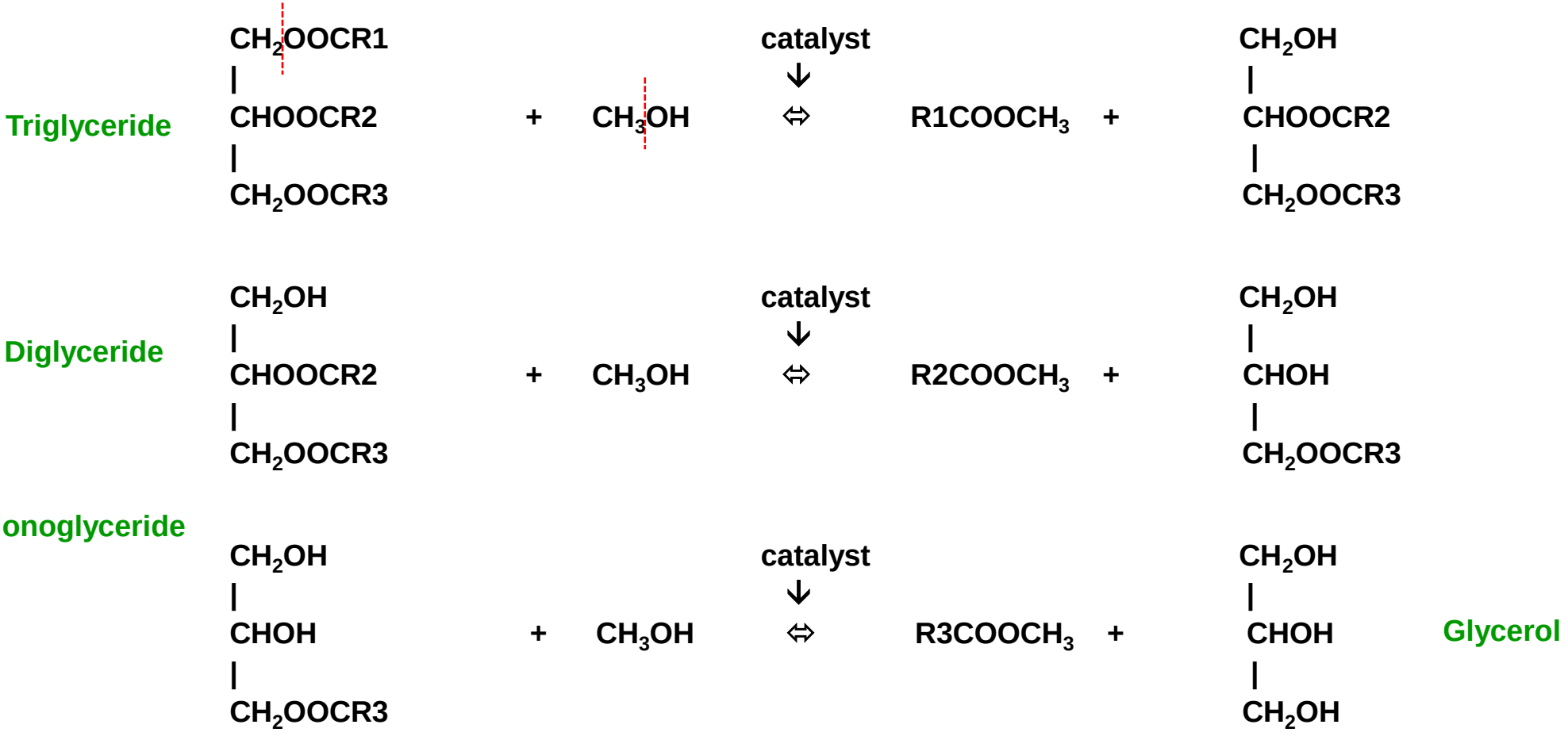
Transesterification of Oils



$R1COOCH_3$ = Fatty Acid Methyl Esters (FAME) or biodiesel

Biodiesel Process: Vegetable Oils

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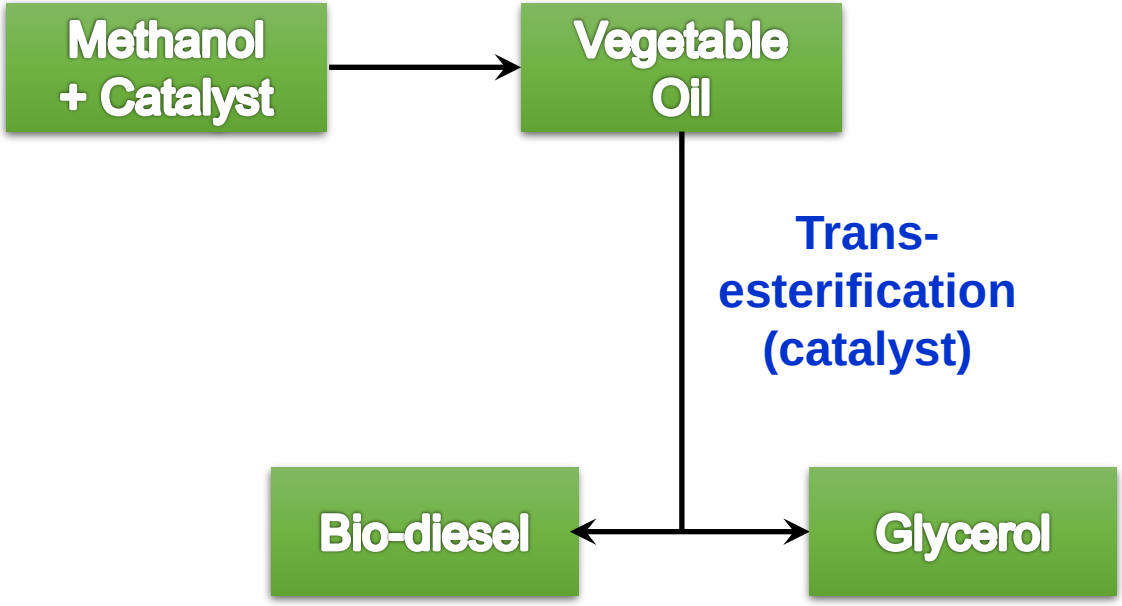
1. Acid catalyzed process (H_2SO_4)
2. Alkali catalyzed process (NaOH)
3. Heterogeneous acid catalyzed process (SnO)
4. Supercritical process

	Pre-treated alkali-catalyzed	Acid-catalyzed	Heterogeneous acid-catalyzed	Supercritical process
Transesterification				
Catalyst	H_2SO_4[a]/NaOH	H_2SO_4	SnO	N/A
Reactor type	CSTR[a]/CSTR	CSTR	Multiphase	CSTR
Temperature (°C)	70[a]/60	80	60	350
Pressure (kPa)	400[a]/400	400	101.3	20×10^3
Alcohol-to-oil ratio	6:1[a]/6:1	50:1	4.5:1	42:1
Residence time (h)	1[a]/4	4	3	0.333
Conversion (%)	100[a]/95	97	94	98

Biodiesel Process: Vegetable Oils



- Free fatty acid (i.e., fatty acid not attached to glycerol) content < 1 wt%.
- Both acid or alkali catalysts can be used.
- Alkali catalyzed process is efficient for producing bio-diesel using pure vegetable oils.
- Industrial processes are using alkali catalyst.

Biodiesel Process: WCO

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- ✓ Waste cooking oil is cheaper than pure vegetable oils.
- ✓ Significant impact on the environment if they are disposed without re-use.
- ✓ Their use to produce bio-diesel is attractive for both economic and environmental reasons.

  - ❖ Waste cooking oils have higher content **(> 5%)** of free fatty acid (FFA).
  - ❖ FFA produces soap and water by reacting with alkali catalyst.
  - ❖ The waste cooking oils require pretreatment with acid catalyst .
  - ❖ FFA < 1 wt% → alkali catalyzed process.

Oleic Acid (18:1): $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

Biodiesel Process: WCO

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Esterification of Free Fatty Acid

Oleic Acid (18:1): $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
: R1COOH

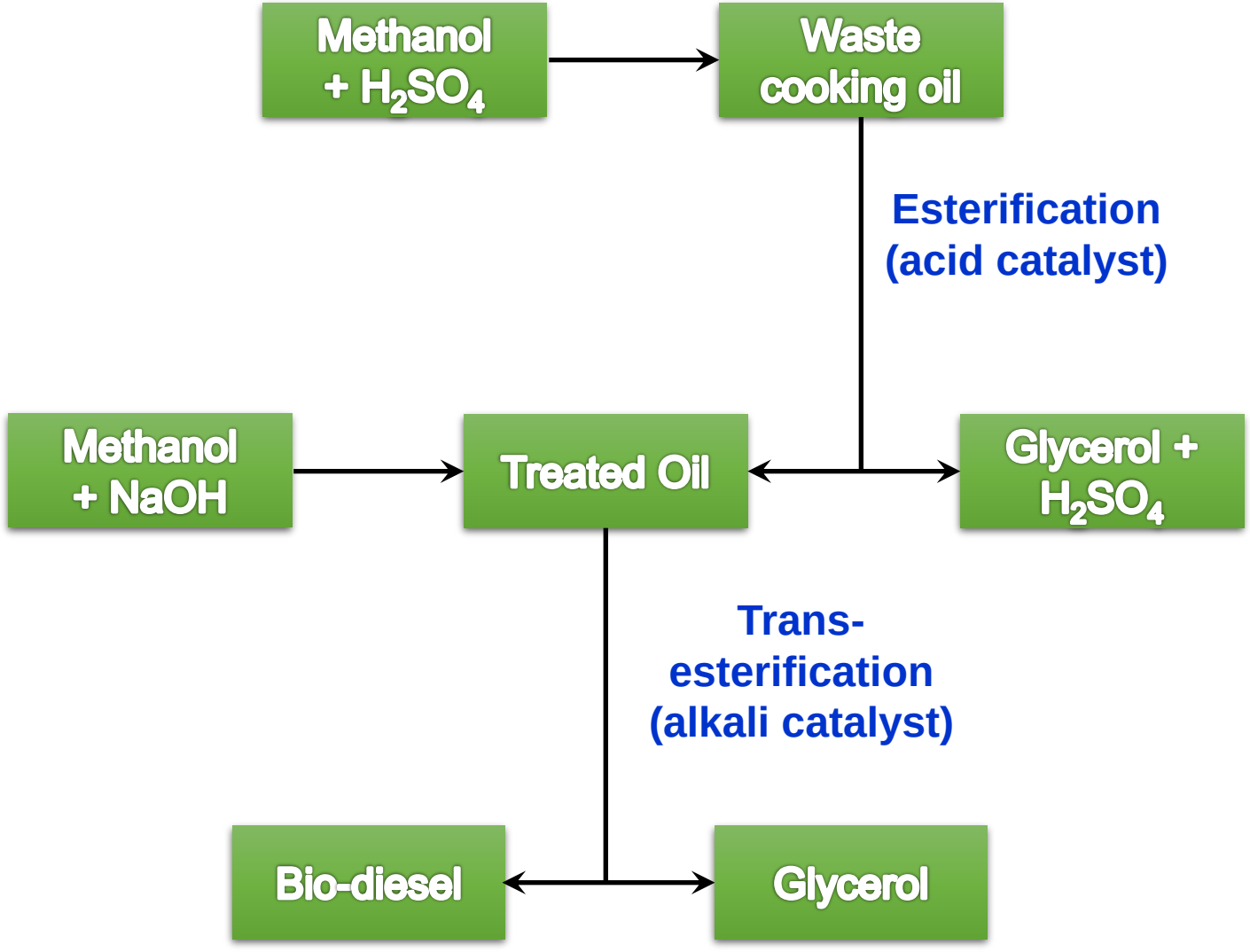
Acid Catalyst

$R1COOH + CH_3OH \Leftrightarrow R1COOCH_3 + H_2O$
(Biodiesel)

Alkali Catalyst (KOH)

$R1COOH + CH_3OH \Leftrightarrow R1COOK + H_2O$
(Soap)

Biodiesel Process: WCO



Biodiesel Process: Simulation

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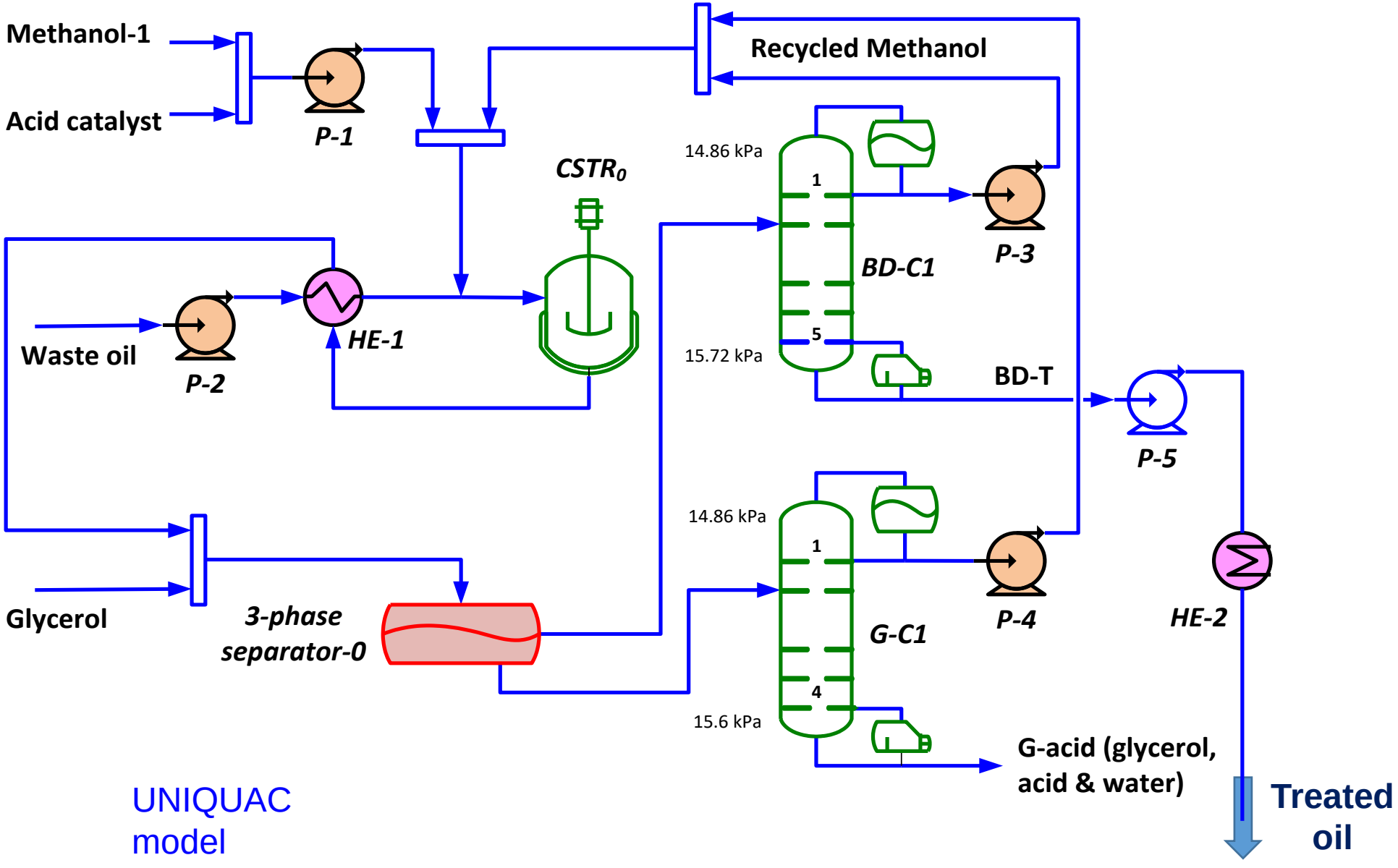
- ✓ Aspen Hysys V 7.2
- ✓ UNIQUAC* thermodynamic model has been used.
- ✓ Triolein is used to represent triglycerides in waste cooking oils.
- ✓ Physical properties of mono-, di- and triolein are taken from Aspen Plus database.
- ✓ Feed waste cooking oil contains FFA (6 mole %) and triolein.

Average Plant Capacity (USA) ~ 24 million gallons per year

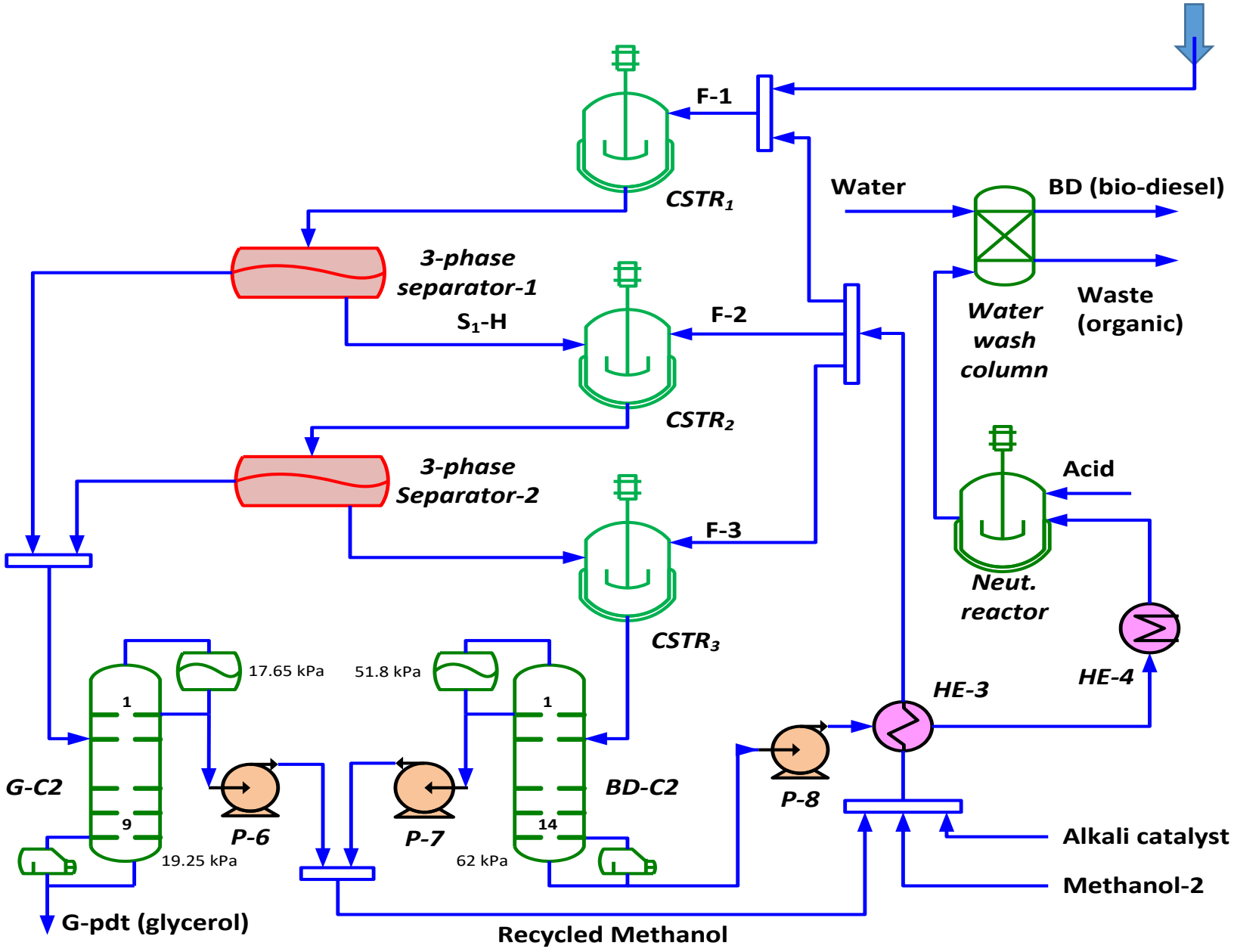
* Franca et al., J. Chem. Eng. Data., 2009

Biodiesel Process: Pretreatment



UNIQUAC model

Biodiesel Process: Main Process



Biodiesel Process: Cost

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- ✓ Inputs: oil, methanol and catalyst (utilities: steam and water)
- ✓ Outputs: biodiesel and crude glycerin

Pre-reaction requirements

- Oil storage tank
- Alcohol storage tank
- Catalyst storage
- Biodiesel reactor

Post-reaction requirements

- Settling tank
- Separation column
- Washing tank
- Biodiesel storage tank
- Glycerin storage tank

Biodiesel Process: Cost

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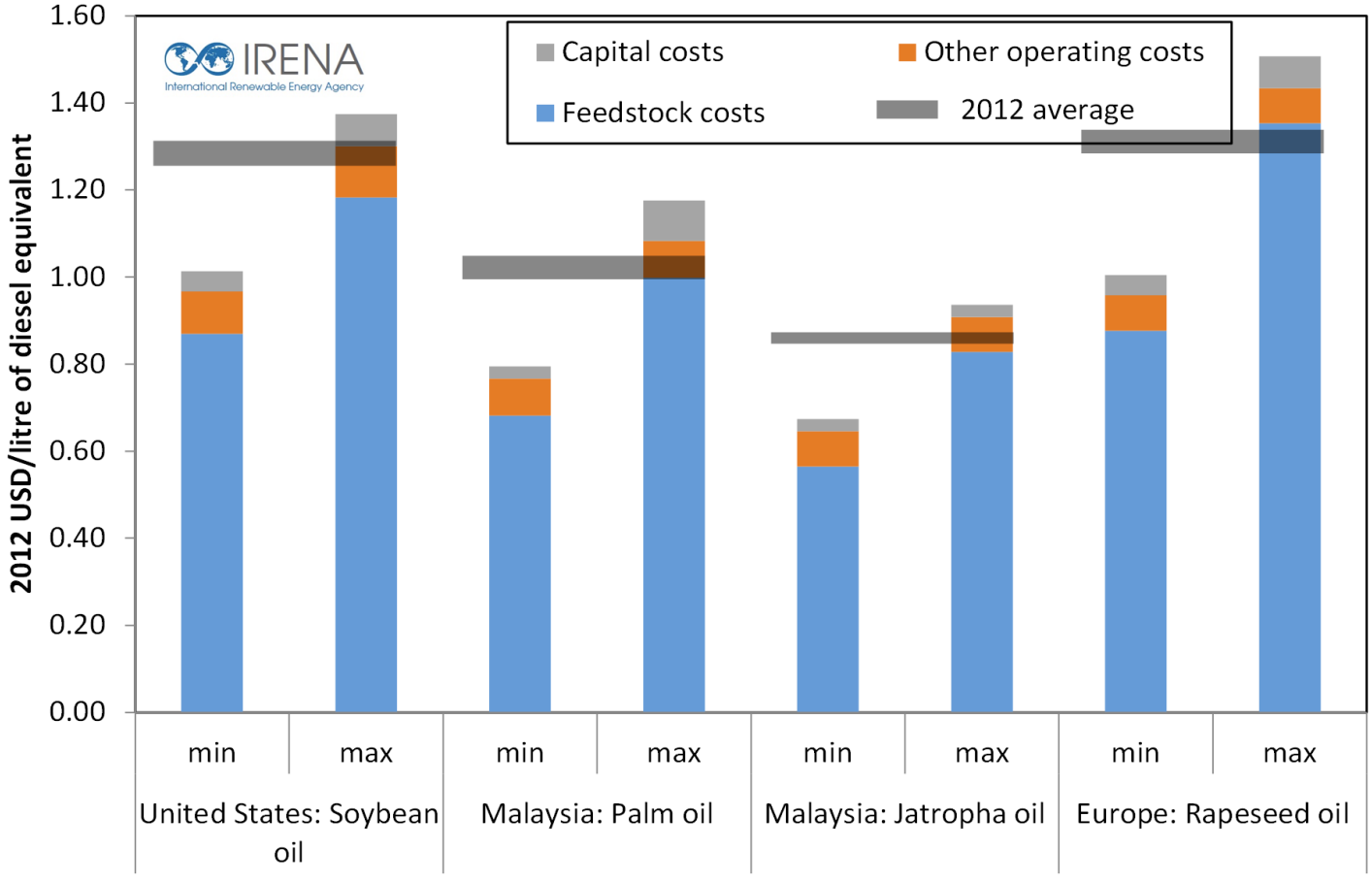
Total production cost of biodiesel using different feed-stocks.



Feed stocks cost is the major contributor in the cost of biodiesel.

Biodiesel Standard & Properties

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Biodiesel Standard

International standard (EN 14214) requirements for biodiesel

Property	*Unit*	*Lower limit*	*Upper limit*
Ester content	% (m/m)	96.5	–
Density	Kg/m^3	860	900
Viscosity	mm^2/sec	3.5	5.0
Flash point	°C	>101	–
Sulphur content	mg/kg	–	10
Cetane number	–	51.0	–
Sulphated ash content	% (m/m)	–	0.02
Water content	mg/kg	–	500
Acid value	mg KOH/g	–	0.5
Methanol content	% (m/m)	–	0.2
Total glycerol	% (m/m)	–	0.25

Properties of biodiesel produced from different oils

Vegetable oil methyl esters (biodiesel)	Kinematic viscosity (mm^2/s)	Cetane no.	Lower heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Peanut	4.9	54	33.6	5	–	176	0.883
Soya bean	4.5	45	33.5	1	−7	178	0.885
Babassu	3.6	63	31.8	4	–	127	0.875
Palm	5.7	62	33.5	13	–	164	0.880
Sunflower	4.6	49	33.5	1	–	183	0.860
Tallow	–	–	–	12	9	96	–
Diesel	3.06	50	43.8	–	−16	76	0.855
20% biodiesel blend	3.2	51	43.2	–	−16	128	0.859

Glycerin Use

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

No ready market for crude glycerin

Quantity produced = 10% to 20% of biodiesel production

Contains methanol and catalyst

Possible Uses:

- Fuel
- Compost
- Soap production
- Refine to pharmaceutical grade glycerin

Further Studies

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- Sharma S, Rangaiah GP, Multi-objective optimization of a bio-diesel production process, Fuel 2013.

Thank You