

Biodiesel Technologies and Plant Design

A talk for Design Students
University of Sydney

Dr Wayne Davies

Director R and D, SN2 Pty Ltd

davies@sn2.com.au

August 2005

acknowledgments to:

1. Jon Van Gerpen (whose PPT was the basis for this talk)
2. Institut Francais du Pétrol
3. Journeytoforever.org



In this talk ...

- First half:
 - Background, general info, common knowledge, useful stuff

- Second half:
 - Design considerations and class examples
 - Choices of technology and feedstocks
 - Commercial examples

Biodiesel Benefits and Processes

- Greenhouse
- Definition and standards
- Transesterification
- Fatty acid chains
- Standard recipes
- Competing reactions
- Process issues

Biodiesel and Greenhouse

- Australia uses 14 billion litres/year of diesel
- ARF's total capacity 88.8 million litres/year
- equals 0.63% of total
- © not much of a dent.
- Biodiesel is a niche product until petroleum gets much more expensive

If biodiesel replaced Petroleum Diesel completely using Canola or Rapeseed

Crop yield: 2 tonnes per ha (ha=0.01 km²)

To make 14 billion litres of biodiesel

Use 30 million tonnes of canola

Area needed: 15 million ha = 0.15 million km²

Area of Australia = 7.7 million km²

Fraction under biodiesel crop: 2%

Current crop coverage: 5%

40% increase in crop area needed

Big problem: water for irrigation!

Definition of Biodiesel

- Biodiesel – a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats.

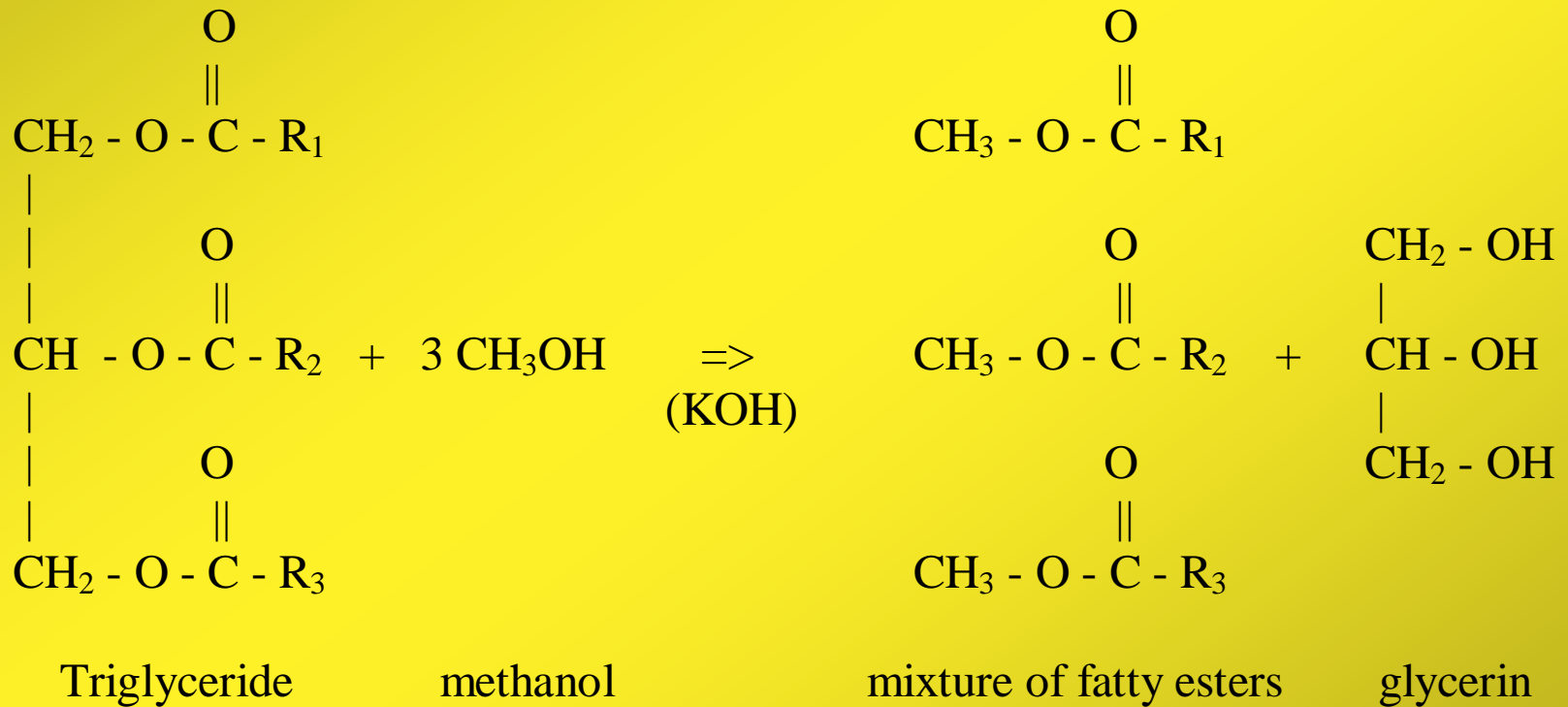
FAME = Fatty Acid Methyl Ester

FAME is not Biodiesel unless it meets the relevant standards

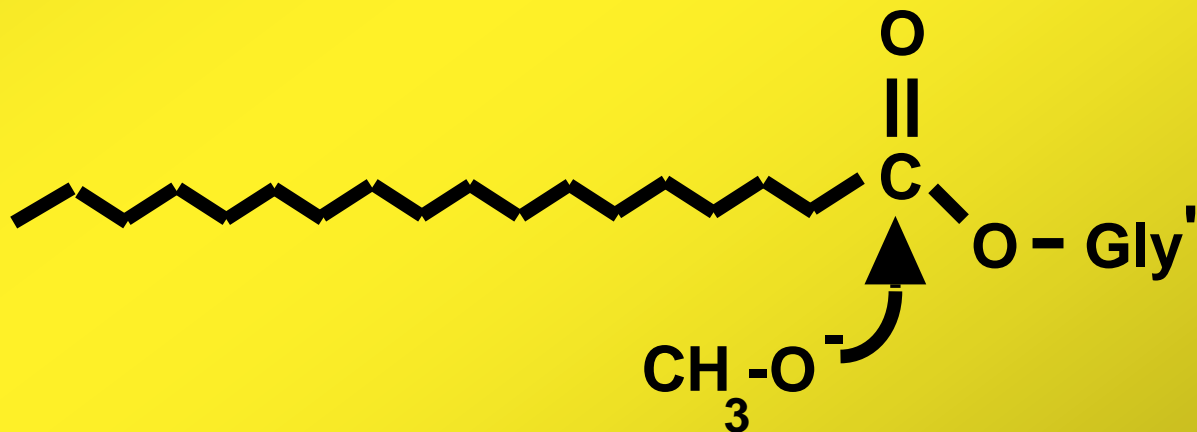
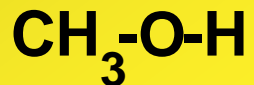
ASTM D 6751-02

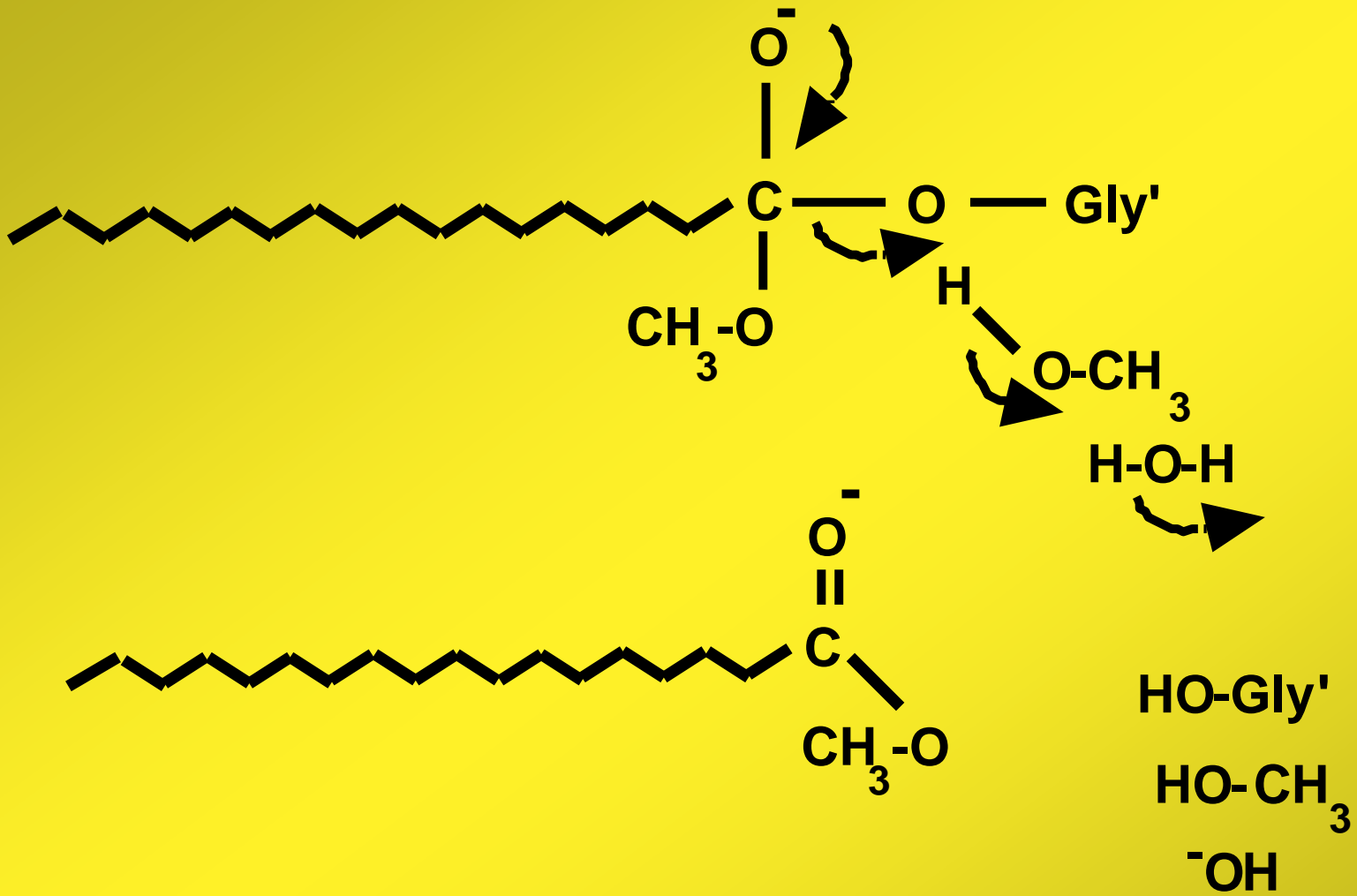
Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm ² /s
Sulfated ash	D 874	0.020 max	wt. %
Total Sulfur	D 5453	0.05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	° C
Carbon residue	D 4530	0.050 max	wt. %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	wt. %
Total glycerin	D 6584	0.240	wt. %
Phosphorus	D 4951	0.0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

Transesterification



Base catalysed SN2 Transesterification





Triglyceride Sources

- Rendered animal fats: beef tallow, lard
- Vegetable oils: soybean, canola, palm, rapeseed etc.
- Chicken, pork fat
- Rendered greases: yellow grease (= waste cooking oil)
- Recovered materials: brown grease (=grease-trap waste), soapstock, etc.
- NB Prices vary a lot!

Standard Recipe

100 kg oil +

21.7 kg methanol

1.5 kg NaOH (or KOH)

100 kg biodiesel + 10.4 kg glycerol + 11.3 kg xs
methanol

Amateurs' Page

Batch homebrew

Thanks to "Journey to Forever" and Mike Pelley

Melted fat



Methanol and Sulfuric acid stage



After acid esterification

Second stage

MeOH and NaOH
addition



Glycerol
layer
settles
out



More
glycerol
settles out

First
wash





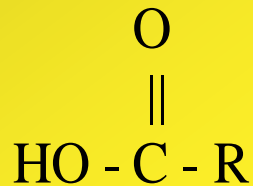
After first wash



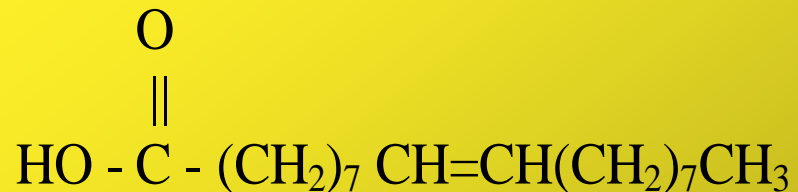
After third wash

Free Fatty Acids (FFAs)

- FFAs are present in oils and fats. Low in virgin and high in low-grade or waste.

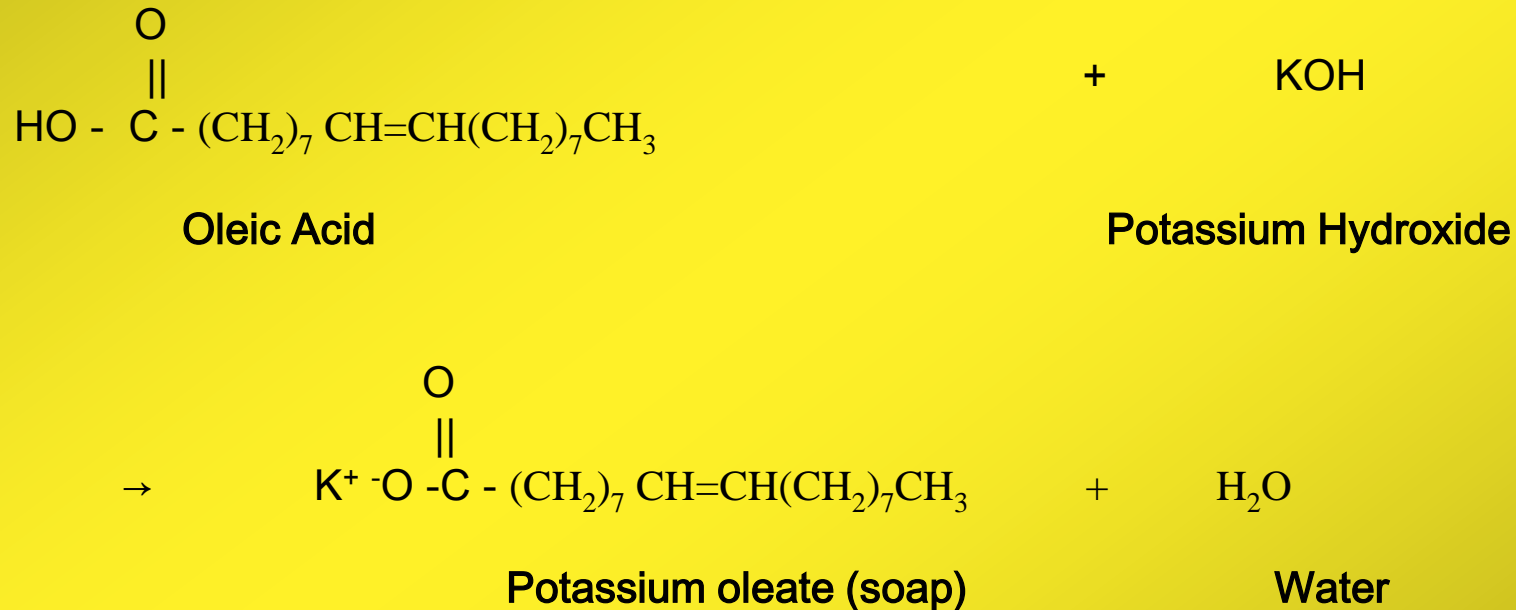


Carboxylic Acid (R is a carbon chain) (i.e. hydrocarbon chain)



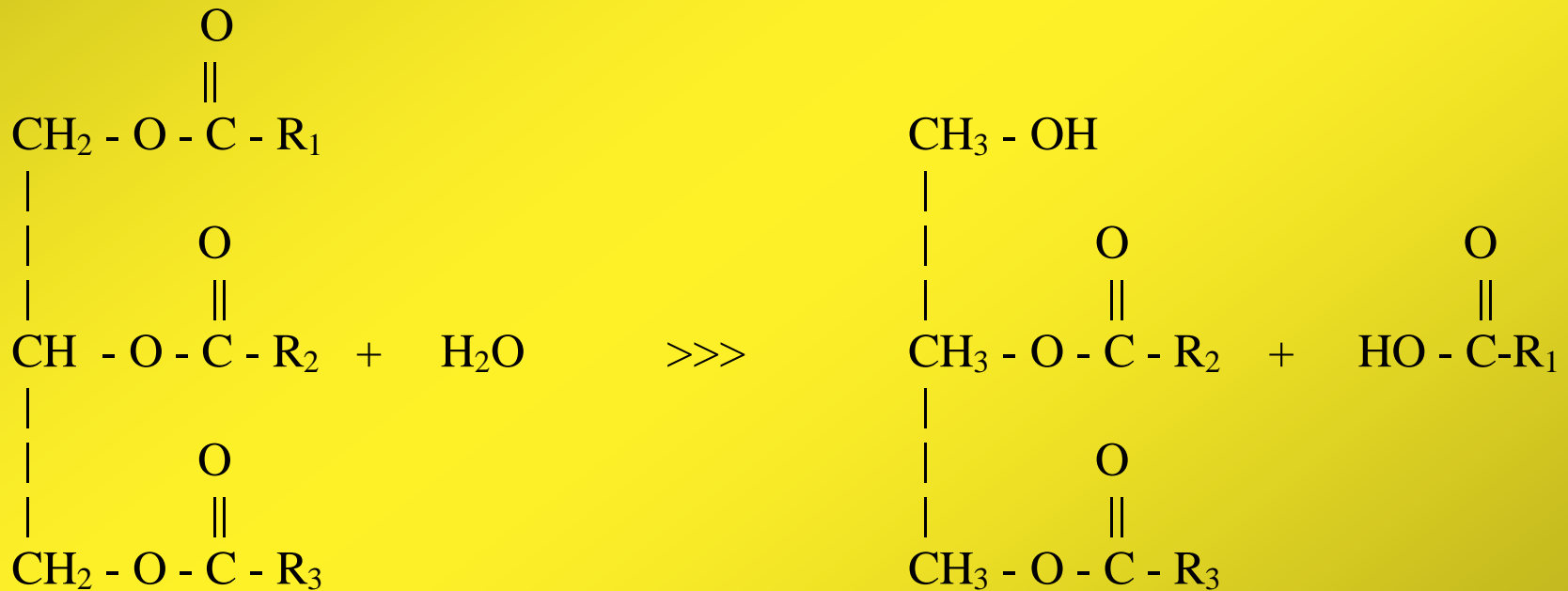
Oleic Acid

Free Fatty Acids react with alkali catalyst to form soap



Water is a problem

Water hydrolyses fats to form free fatty acids, which then form soap. Dry feedstocks best.



Triglyceride

Water

Diglyceride

Fatty acid

Soap generation

- Can cause the the entire product mixture to gel into a semi-solid mass, giving headaches with separation and washing.
- Increased water use and treatment costs
- Loss of biodiesel product

Free Fatty Acid (FFA) levels in Feedstocks

Biodiesel feedstocks vary from edible oils to stinking wastes

- Refined vegetable oils < 0.05%
- Crude soybean oil 0.3-0.7%
- Restaurant waste grease 2-7%
- Animal fat 5-30%
- Trap grease 75-100%

Price decreases as FFAs increase

High FFA feeds need special processing to avoid soap.

But certain processes use FFA as the feed.

COMPARISON OF CERTAIN FEEDSTOCKS WITH Aust Stnd

	Grease Trap Waste	Flux Tallow	Used Cooking Oil	Aust Stnd Notes biodiesel
■ FFA (wt%)	44	83	3.5	<2.5 (implied)
■ Iodine number	34	72	46	120 1
■ Phosphorus (ppm)	250	110	5	10
■ Sulfur (ppm)	< 500	6000	< 500	10 2
■ Potassium	65	22	12	5 3
■ Acid Value †	89	94	8.1	0.8
■ Total Glycerol (wt%)	?	?	?	0.25

- † mg of KOH per gram
- 2. beginning 2006

- 1. European stnd Aust standard is open
- 3. total Na and K

Methods for High FFA feeds: Acid catalysis followed by base catalysis

1. Acid catalysis methylates FFAs to methyl esters, until $\text{FFA} < 0.5\%$.
 - Alkaline esterification of FFA is relatively fast (1 hour) but acid-catalyzed transesterification is slow
 - Water formed by
$$\text{FFA} + \text{methanol} \implies \text{methyl ester} + \text{water}$$
can be a problem.
2. Then separate, add additional methanol and base catalyst to transesterify the triglycerides.

Methoxide Pre-esterification

Dissolving potassium metal in methanol makes dry potassium methoxide (with release of hydrogen). This reacts with FFA to make FAME and KOH but no water is released.

Used to pretreat feeds < 10% FFA

Expensive and hazardous but is in use.

Process Issues

- Feedstock requirements
- Reaction time
- Continuous vs. batch processing
- Processing low quality feedstocks
- Product quality
- Developing process options

Feedstocks

- **Common to all processes**
- “Triglyceride” or fats and oils soybean oil – vegetable oils, animal fats, greases, waste VO, soapstock, etc.
- Primary alcohol: usu. methanol or ethanol (typically in stoichiometric excess)
- **... for conventional process**
- Catalyst (sodium or potassium hydroxide)
- Neutraliser (sulfuric or hydrochloric acid)
- Washwater

Rough Reaction rates

- Transesterification reaction is too slow, at ambient temps i.e. 4-8 hours.
- Reaction time can be shortened to 1-2 hours at 60°C.
- For higher temperatures pressure vessels needed. Methanol boils at 65°C.
- Normally a two-phase mixture, ergo...
- High-shear mixing or use of co-solvents to accelerate reaction rate.
- Reverse reaction occurs, ergo two-stage processes with two reactors are commonly seen.

Process Evolution

- Batch mixing at < 60 deg C
- Continuous < 60 deg C
- Continuous pressurised homogenous catalyst, at say 120 deg C, 6 bar (most common)
- Continuous pressurised heterogeneous catalyst (State of the art?)
- Co-solvent (commercialised as BIOX)
- Supercritical (not commercial)
- Supercritical co-solvent (not commercial)

Batch Processes

Good for smaller plants (<4 million litres/yr).

- Does not require continuous operation.
- Provides greater flexibility wrt feedstock variations.

- Higher labour costs.
- Physically large plant cf continuous.
- Heat integration awkward.
- Greater risk levels:

Heightened Risks of Batch Processes

Due to the inherently large inventory:

- Vapour exposure to workforce, neighbours
- Vapour explosion and fire
- Large leaks

Continuous Processes

- _ Better safety, lower risks
- Lower unit labour costs
- Better economies of scale as capacity goes up
- More compact plant
- Heat recovery inherent
- Allows better use of high-volume separation systems (e.g. centrifuges)
- High capex at small scale but ROI better at larger scale

Innovative Processes

Supercritical
Heterogeneous catalysts

Supercritical Methanol

- SC methanol is a high-density chemically-labile vapour that cannot be compressed into the liquid state. (80 bar 240 deg C)
- It is miscible with oils and fats or FFAs
- It reacts without catalyst to form FAME, glycerol and water.
- Fast reaction ($\tau = 4$ mins)
- See Saka and Kusdiana Kyoto U

- However ...
- Not commercial as yet.
- Large xs methanol required 42:1 mole ratio.
- MeOH recycle costs are significant

Heterogeneous Catalysis

WHY ?

1. Homogenous catalysts are used up
2. They make soap with FFAs
3. Product needs lots of washing, ergo wastewater costs

Can we use a solid that has catalytic properties that will stay in the reactor?

YES we can ... enter the Heterogeneous Catalyst. More later ...

Summary (so far)

- Biodiesel can be made from virtually any oil or fat.
- The technology choice must consider: capacity, feedstock type and quality, catalyst consumption, methanol:oil ratio etc.
- Biodiesel is regarded as a “green” fuel but there is not enough oil and fat made to replace more than 20% of petroleum diesel.
- Sustainability of biodiesel is >> petroleum diesel but it is a niche product for the time being.

Summary cont.

Biodiesel from Waste Oil is much more “green” because it can be reasonably regarded as having near zero embodied energy debt.

BUT

There is not enough of it to make a great difference.

Compare what you consume:

(i) ? Litres per year of petrol vs

(ii) ? Litres/year of cooking oil

Part 2:

Class Exercises

Kinetics

Commercial Examples

Kinetics of Transesterification

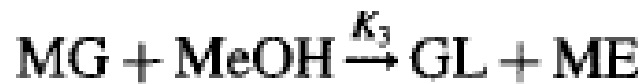
- Class Exercise:
- Consider vegetable oil and methanol
- Write down the relevant parameters for designing a reactor!

- 3 minutes then show and tell.

Kinetics of Transesterification

- Temperature
- Oil/fat type
- Ratio of methanol to oil/fat
- Catalyst concentration
- Catalyst type
- Mixing (esp. if single phase system)
- Water content of feed

Kinetics of υπερεστεροποίηση



Dissakou, et al

No catalyst, high temps.

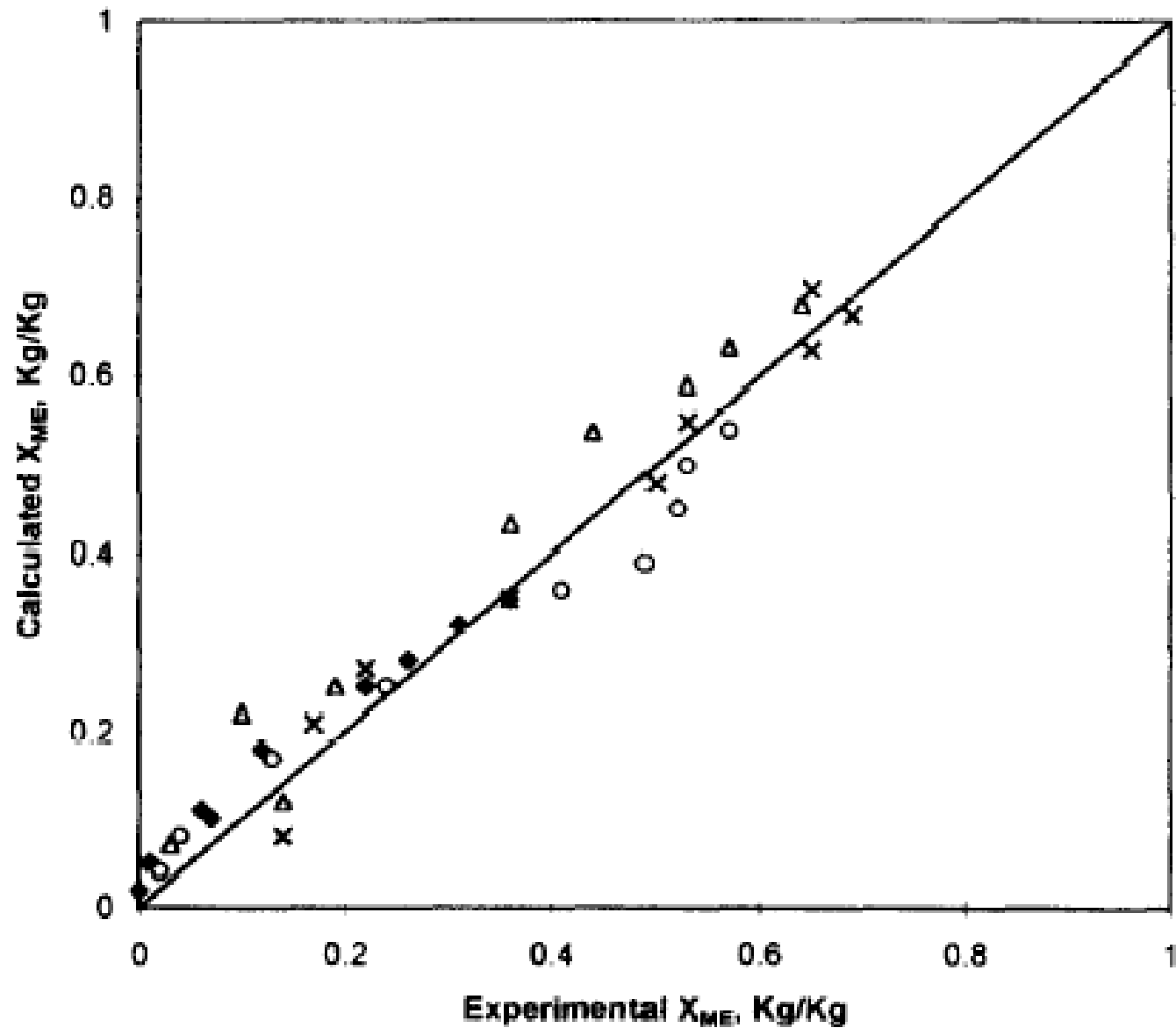
Co-solvent

$$\frac{dC_{\text{TG}}}{dt} = -K_1 C_{\text{TG}} C_{\text{MeOH}} \quad (4)$$

$$\frac{dC_{\text{DG}}}{dt} = K_1 C_{\text{TG}} C_{\text{MeOH}} - K_2 C_{\text{DG}} C_{\text{MeOH}} \quad (5)$$

$$\frac{dC_{\text{MG}}}{dt} = K_2 C_{\text{DG}} C_{\text{MeOH}} - K_3 C_{\text{MG}} C_{\text{MeOH}} \quad (6)$$

This is curve fitting not "Prediction" as stated



Kinetics of transesterification of soybean oil Nouredдини, H. and Zhu, D.,

Journal of the American Oil Chemists' Society , 74, n11, 1997, 1457-1463

Abstract rewritten by WD with apologies

Three stepwise and reversible reactions are believed to occur. The effect of variations in mixing intensity and temperature on the rate of reaction were studied at constant molar ratio (methanol:triglyceride = 6:1) and constant concentration of catalyst (0.20 wt% based on soybean oil). Variations in mixing intensity appeared to affect the reaction as did variations in temperature. A 2-step reaction mechanism consisting of an initial mass transfer-controlled step followed by a kinetically controlled step is proposed. Experimental data for the latter step were consistent with second-order kinetics. The reaction rate constants and the activation energies were determined for all the forward and reverse reactions.

WAD suggests: compare rate constants with [Dissakou et al.](#)

Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst

Kim, Hak-Joo (Department of Chemical Engineering, Korea University)
;Kang, Bo-Seung ;Kim, Min-Ju ;Park, Young Moo ;Kim, Deog-Keun
;Lee, Jin-Suk ;Lee, Kwan-Young : ***Catalysis Today*** , v 93-95, Sep 1,
2004.

WAD rewritten Abstract: Na/NaOH/gamma-Al₂O₃ heterogeneous base catalyst was adopted for the production of biodiesel. A study of the reaction conditions: reaction time, stirring speed, use of co-solvent, oil to methanol ratio, and amount of catalyst, was performed. The heterogeneous base catalyst showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst.

WAD notes: 80% of the yield is not “almost the same”. Large ratio of co-solvent and excess methanol suggest significant recycle costs. Slow rates of reaction. Why did they not heat it up and run under pressure?

Design a Reactor

- Your task: to design a continuous plug flow reactor for 160,000 tonnes per year of biodiesel.
- Density 0.88 tonne/m³
- 320 days/year
- Determine: length of pipe for "best diam."
- Pipe sizes available (mm):
 - 50, 100, 150, 200, 300
- Two alternative residence times:
 - A: Low temp: 2 hours
 - B: Hi temp: 20 mins
- 10 minutes to do this then show and tell.

REACTOR DESIGN FOR A CONTINUOUS PLANT

- Based on Esterfip plant capacity (Sête France)

-

- **Capacity** tonne per year 160000

- **Flowrate** m3 per year 188235

- **Flowrate** m3/hour 23.8

-

- **Reactor Volumes** **WAD's intuition**

- **Residence time**

- 2 hours m3 47.5 too big

- 20 minutes m3 7.9 still pretty big

- 4 minutes m3 1.6 too good to be true

Design pipe reactor (cont. a)

■			
■	Conditions	Length (m)	WAD's intuition
■	2 hours, 50 mm ID	24209	not feasible
■	20 minutes, 50 mm ID	4034	still too long
■	20 minutes, 150 mm ID	448	more practical
■	4 minutes, 50 mm ID	807	a bit long
■	4 minutes, 75 mm ID	359	you wish

Design pipe reactor (cont. b)

	no. of 6-m pipe runs	Dimensions* W and H (m)
Conditions		
2 hours 50 mm ID	4035	6.4
20 minutes 50 mm ID	672	2.6
20 minutes 150 mm ID	75	2.6
4 minutes 50 mm ID 135		1.16
4 minutes 75 mm ID 60		1.16
* Allows for insulation thickness = (guess) half pipe diam.		

Reactor Optimisation

- A small high-temperature reactor is desirable because it saves CAPEX (less metal, fabrication and installation costs, footprint)
- Temp up, rate up, reactor size down, CAPEX down
- BUT both CAPEX and OPEX can increase when...
- Heating to greater temperatures -> OPEX up as fuel consumption (and cooling water) up.
- Bigger heat exchanger -> CAPEX up
- Reactor wall thickness up as pressure up -> CAPEX up
- Thicker insulation -> CAPEX up.
- Bigger pump for increased pressure -> CAPEX up.
- Heterogeneous catalyst life down -> OPEX up.

Actual Commercial Processes

BIOX Process

- Uses co-solvent usually MTBE
- Low temperature operation
- Claimed 7 min residence time
- Needs alkaline homog. catalyst (and acid)
- Requires large ratios of methanol to oil
- Commercialised at 67 million litres/annum
- Inventor Em. Prof. D. Boocock Toronto Canada

Energea Process

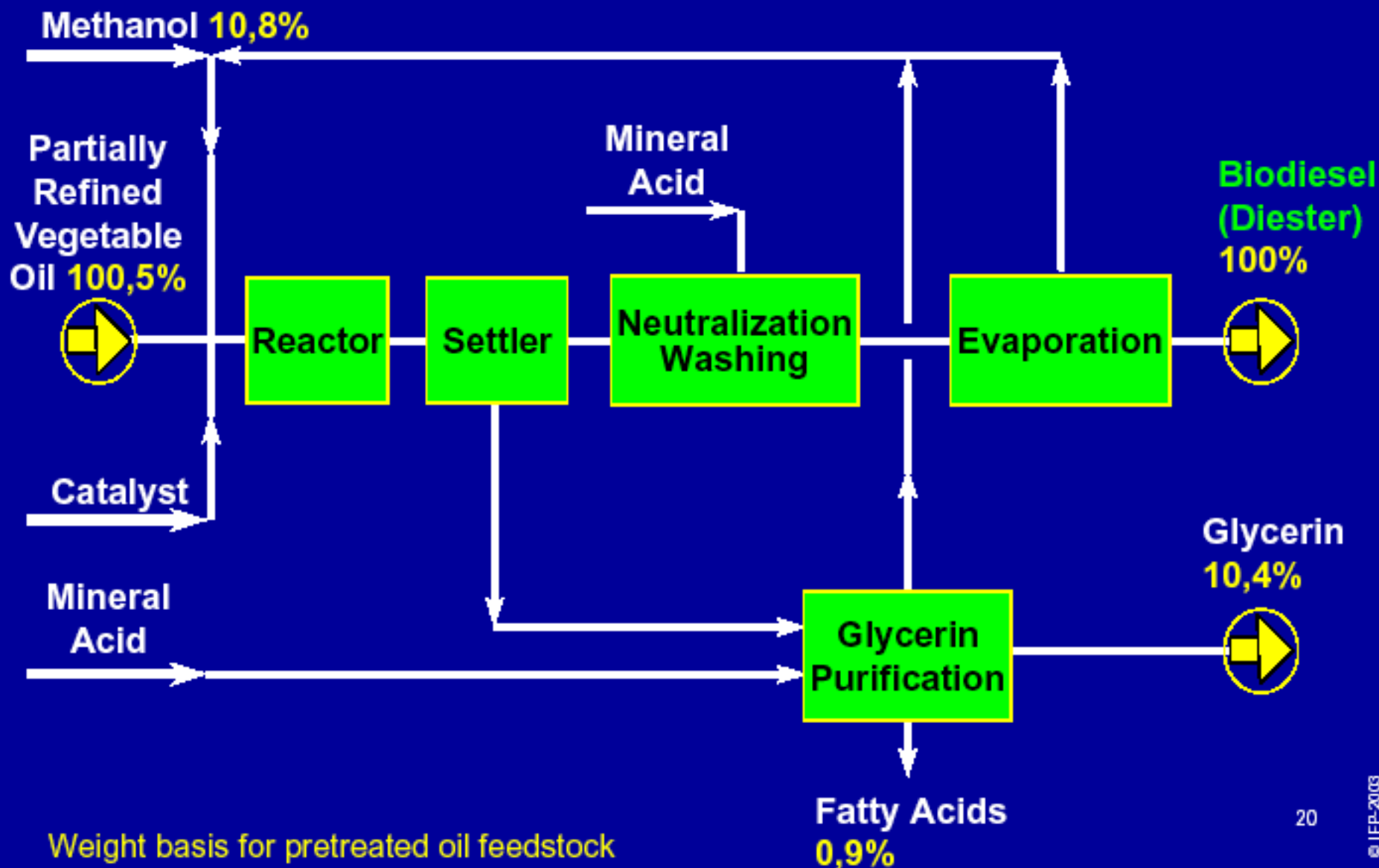
- Pressurised continuous
- Elevated temperature
- Residence time probably 20 mins
- Uses alkaline catalyst and acid
- Low ratios of methanol to oil
- Chosen by ARF (SA and WA)
- Look for Dr Richard Gapes at Vienna Tech. U

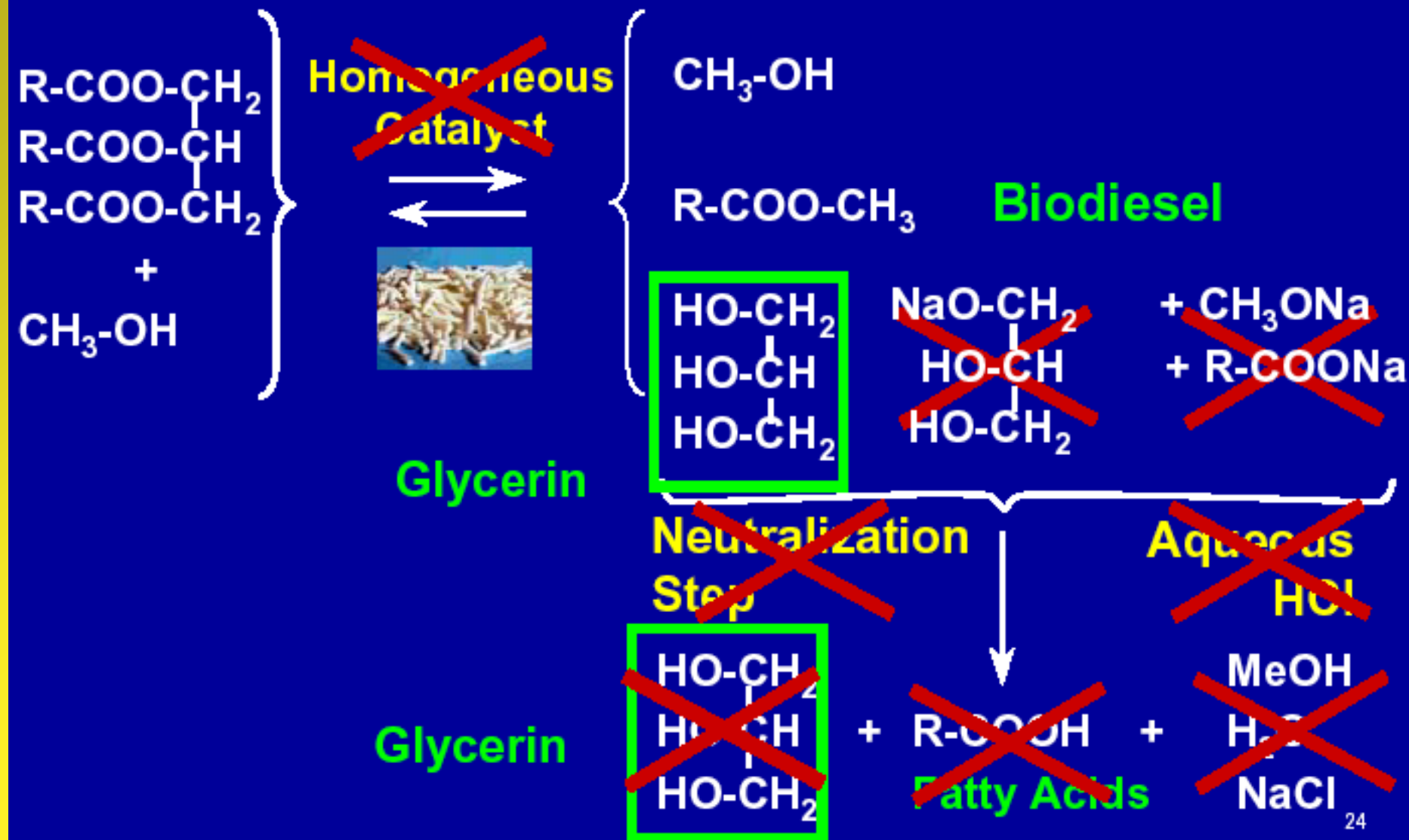
Lurgi Process

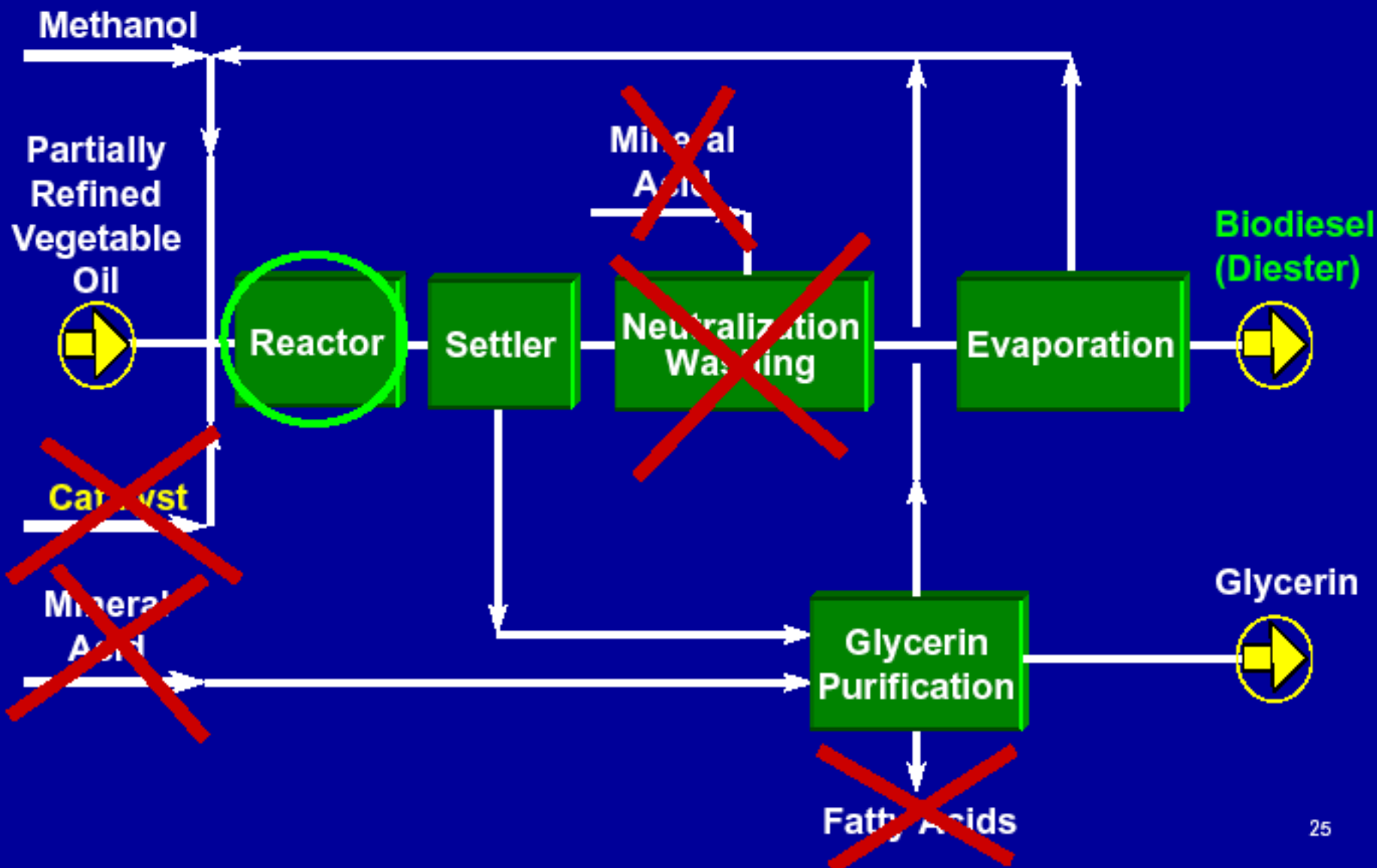
- Similar to Energea
- Two stage CSTR reactor (?)
- 100,000 tonne per annum plant in California
- Flowsheet (for PR purposes) has washwater in but not out

Institut Francais du Pétrol,

- Hetero aluminate catalyst (no caustic soda, potash)
- Clean glycerol, little washing needed
- Temperature ca 200 deg C (? ex patent)
- Pressure ca 62 bar (?)
- Residence time 2 hours (? ouch!)
- Max water allowed in = 1000 ppm
- 160,000 tonne per year at Sete France
- **See Bournay , et al. Inventor US Patents**









Heterogeneous Process Highlights

- New continuous technology based on solid catalyst
- Exceptional glycerol purity >98%
- Very high ester yield: close to 100%
- No waste production of low-value fatty acids
- No waste saline streams that require disposal
- No consumption / no handling of chemicals
- Much lower catalyst requirements (per ton of FAME) compared with other processes

Cao et al. (not commercial)

- Supercritical process no catalyst
- Temps 260 to 300 deg C
- Propane:methanol = 0.05 to lower SC temp
- Large ratio methanol:oil
- High pressure (>100 bar)
- Fast reaction $\tau = 10$ □ □ □ □
- Not costed (methanol recycle might be a worry)

Local Manufacturers

- Australian Biodiesel Group (also see Australian Biodiesel Consultancy. Plant at Berkeley Vale NSW (home made, conventional)
- Australian Renewable Fuels (ARF) floated \$20 M. Total capacity 88.8 million litres/year in SA and WA (Uses Energea technology)

Economics (ex ARF prospectus)

Revenue: 0.96 \$A/litre biodiesel

- Feedstock tallow: 560 A\$/tonne
- Methanol: 443 \$A/tonne
- Converter margin on feedstocks only
- $\$960 * 0.86 - \$560 - \$0.11 * 443 = \217 per tonne
- Equals 19 cents per litre.
- Total income/year \$16.9 million
- Cf prospectus \$37 million
- (what the...?)

Relevant Unit Operations

- Phase separation (gravity, 'fuges)
- Washing (cc gravity, 'fuges etc)
- Evaporation (distillation less relevant)
- Heat exchange
- Drying

Summary and conclusions

- Feedstocks are a major cost component.
- Oils and tallows more available but expensive.
- Waste VO, yellow grease limited supply
- Design plant to be cheap to run: energy costs, labour costs and utilities. Robots might be useful.
- Capex is important too but it should make less impact on a large-scale plant.
- You must optimise your design for it to have any engineering significance.

References

- John Duncan “Costs of biodiesel production” (use Google to find)
- Barry Judd “Biodiesel from Tallow” (use Google to find)
- Nelson and Schrock “Economics of biodiesel production from tallow”
- Anneliese Niederl and Michael Narodoslawsky “. LCA study of biodiesel from tallow and used vegetable oil (use Google to find)
- Australian Renewable Fuels prospectus (use Google to find)
- Ma, F. and Hanna, M.A. “Biodiesel production: A review” *Bioresource Technology*, 70, 1999, 1-15
- Dissakou, M et al. “Kinetics of the non-catalytic transesterification of soybean oil” *Fuel*, 77 1998, 1297-1302
- Nouredini, H. and Zhu, D., “Kinetics of transesterification of soybean oil *Journal of the American Oil Chemists' Society* , 74, n11, 1997, 1457-1463
- http://journeytoforever.org/biofuel_supply.html#biodiesel

References cont.

- Van Gerpen et al. “Biodiesel production technology: Aug 02-Jan 04” NREL/SR-510-36244 (use Google)
- [PDF] “Biodiesel Report Outline”
- Cao et al. “Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent” Fuel, 84, 2005 p347-351
- TIP: Visit US Patent Office for kinetic data described in patents and not in the general literature.

References cont.

“Assessment of biodiesel and ethanol diesel blends, greenhouse gas emissions, exhaust emissions, and policy issues” prepared by Levelton Engineering Ltd. (**NB good for costing processes and energy usage etc**)