UNIVERSITEIT GENT
Faculty of Bioscience Engineering

RRB Renewable Resources & Biorefineries
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oleochemicals & biodiesel
desmet ballestra

Valorization of alternative lipid resources for bioenergy

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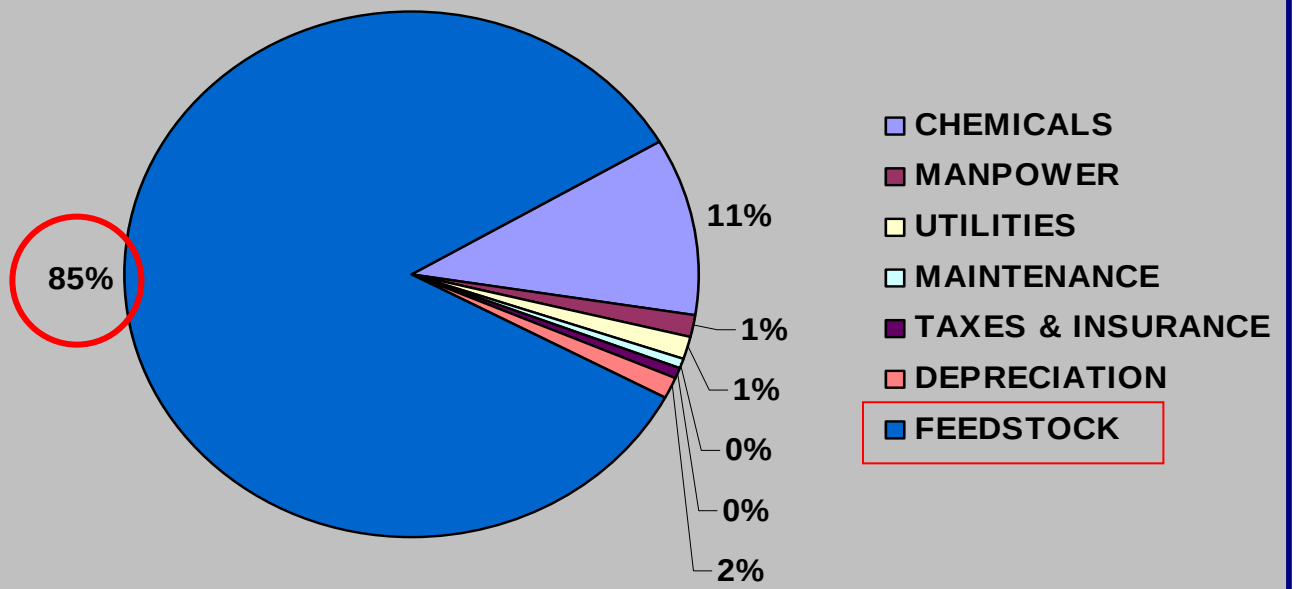
FIRST and SECOND GENERATION BIOFUELS

	First Generation	Second Generation
Final Product	FAME	FAME (Branched Hydrocarbons)
Feedstock	Vegetable Food Oils	Vegetable oils, animal fats Used oils, high FFA oils
Technology	Alkaline transesterification	Acid esterificiation + TE (Hydrocracking)
Considerations	Food *vs* Fuel conflict Sustainability issue	Technical, non-food oils Better sustainability

BIODIESEL PRODUCTION COST



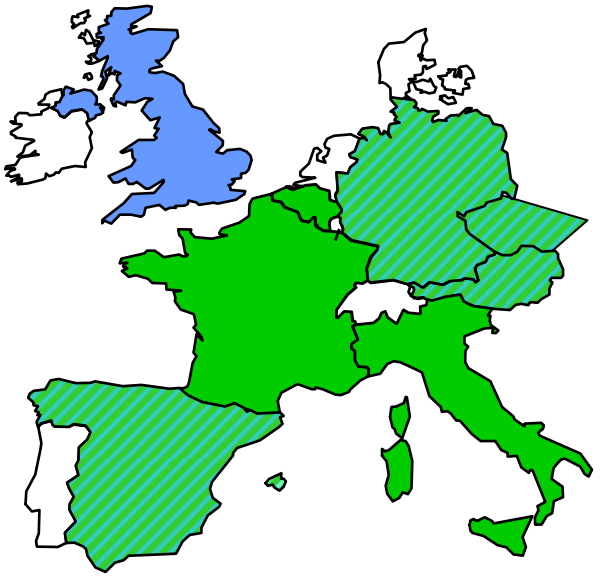
Profitability of biodiesel plants depends largely on feedstock price

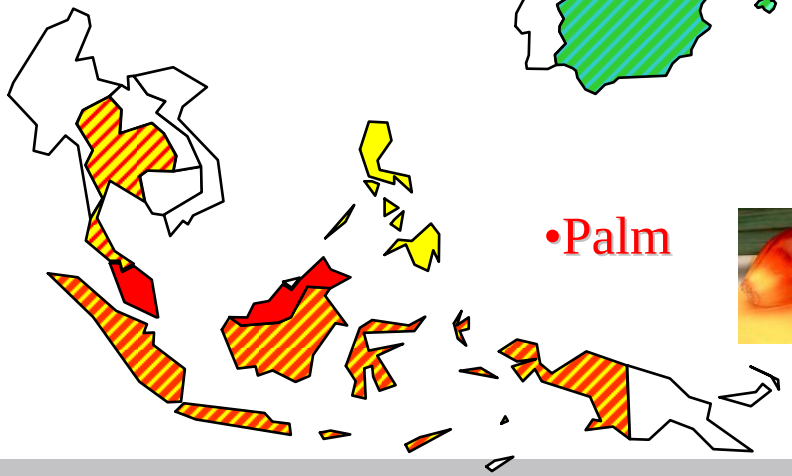
Biodiesel industry only viable if enough feedstock is available at 'acceptable' price

1st GENERATION FEEDSTOCKS

Soya

•Rapeseed





•Palm

ALTERNATIVE FEEDSTOCKS

New 'triglyceride' oils

- Jatropha oil
- Algae oil

- Standard technology can be used
- High quality BIODIESEL at high yield

High acidity feedstocks

Animal fats: ***tallow, lard, poultry, etc***

- Used Cooking Oil (UCO)
- Side-streams of oil refining:

acid oils (AO), soapstock, FAD

- Cheaper feedstocks
- More complex process (extraction, pretreatment, acid esterification)
- BIOFUEL & BIODIESEL

CONTENT

- **Quality considerations for biodiesel from high acidity feedstocks**

  → **Case study: various animal fats**

- **Issues specific for biodiesel from used cooking oils**

  → **Physical & chemical changes during frying**

- **Improved technologies for processing the alternative feedstocks**

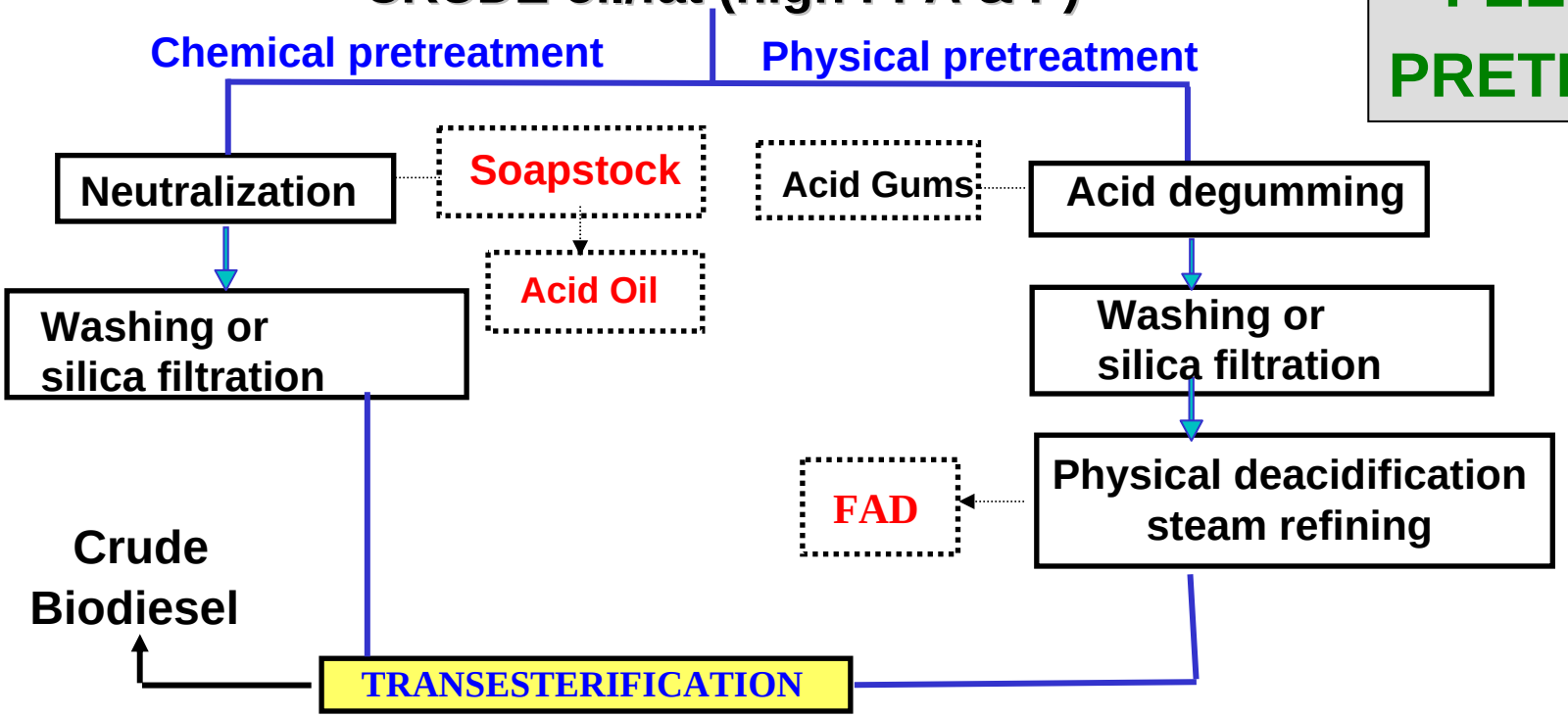
  → **Stand alone process**
  Integrated
  Via oleochemicals

BIODIESEL QUALITY STANDARDS

	ASTM D6751 (USA)	Soybean biodiesel	EN14214 (EU)	Rapeseed biodiesel
Viscosity at 40°C (cST)	1.9-6.0	3.1-4.1	3.5-5.0	3.5-5.0
Total sulphur (ppm)	< 15	N.D.	< 10	< 10
Acid value (mg KOH/g)	< 0.5	0.1	< 0.5	< 0.1
Ester content (%w/w)	--		> 96.5	
Phosphorus (ppm)	< 10	< 1	< 10	1 - 3

+ CFPP & CP

FEEDSTOCK PRETREATMENT



* To avoid process problems and product losses

* Removal of free fatty acids, gums, polyethylene, sulphur, insoluble impurities, …

REMOVAL of S-COMPOUNDS from ANIMAL FATS

Tallow

25 ppm — 70 ppm

Acid degumming (+ water washing)

15 ppm — 32 ppm

Silica treatment

13 ppm — 30 ppm

Stripping

6 ppm — 19 ppm

Transesterification

6 ppm — 17 ppm

Distillation (95% yield)

< 5 ppm

Good quality feedstocks:

< 10 ppm after pretreatment

Poor quality feedstocks:

Distillation might be required

FATTY ACID COMPOSITION

	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	Other
Soybean	----	----	8	4	28	53	7
Palm	----	2	42	5	41	10	----
Rape Seed	----	----	4	1	60	20	15
Sunflower	----	----	6	4	28	61	1
Chicken fat	----	1	23	6	42	19	9
Lard	----	2	26	18	37	10	7
Beef tallow	----	3	25	19	40	4	9
Jatropha	----	----	15	7	41	36	1

QUALITY of BIODIESEL

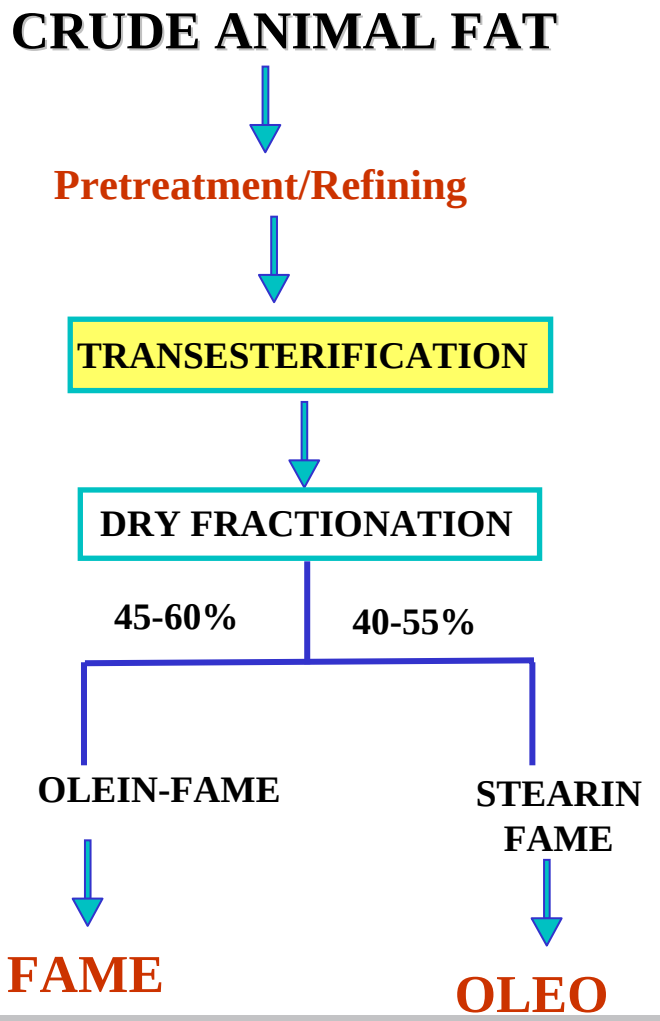
Feedstock	UCO		Tallow		Chicken Fat		Palm-FAD	
	OIL	FAME	OIL	FAME	OIL	FAME	OIL	FAME
Iodine Value	90	**90**	62	**62**	80	**80**	52	**52**
Phosphorus	2	**< 1**	4	**< 1**	206	**N.D.**	N.D.	**N.D.**
Cloud Point (°C)	14	**1**	--	**7.8**	11.5	**2.3**	37.2	**10.5**
CFPP (°C)		**0**		**9**		--	--	**> 10**
Mono- & diglycerides (%)	--	**N.D.**	--	**N.D.**	--	**0.15**	--	**0.20**
Acid value (mg KOH/g)	8.0	**0.25**	15.4	**0.4**	3.7	**0.16**	183	**0.8**
Viscosity at 40°C (cST)	--	--	--	**4.5**	--	**5.1**	--	--

FAME from alternative feedstocks has too high Cloud Point and CFPP for direct use as BIODIESEL

FRACTIONATION

ANIMAL FAT

Feedstock	OIL	FAME	OLEIN FAME 1	OLEIN FAME 2
Iodine Value	62	62.6	76.6	84.1
Phosphorus (ppm)	4	< 1	< 1	<1
Acid value (mg KOH/g)	3.0	0.2	0.2	0.3
Mono- & diglycerides (%)	--	0.15	0.1	0.1
Cloud Point (°C)	--	**5.0**	**-0.5**	**-4.5**
Fractionation yield (%)	--	100	60	45



BIODIESEL from USED COOKING OIL

Definition: Oils and fats that have been used for cooking and deep-frying, leading to oxidation and thermal degradation

Chemical reactions:

Thermolytic: radical reaction, dimerization/polymerization

Oxidation → polar content

Hydrolysis → FFA

Effect:

Lower ester content, higher FFA

Higher viscosity and CP: dimers

Higher total contamination: higher polar content

Lower oxidative stability

EXPERIMENTAL DESIGN

Industrial UCO
P < 10 ppm, FFA = 2-4%
PF = 20-25%

Refined RSO
P < 1 ppm, FFA < 0.1%
PF = 3.5%

Silica filtration

Heating tests (0-40h)

Physical deacidification (stripping)

Pre-treated oil

FAD

Glycerine

Transesterification

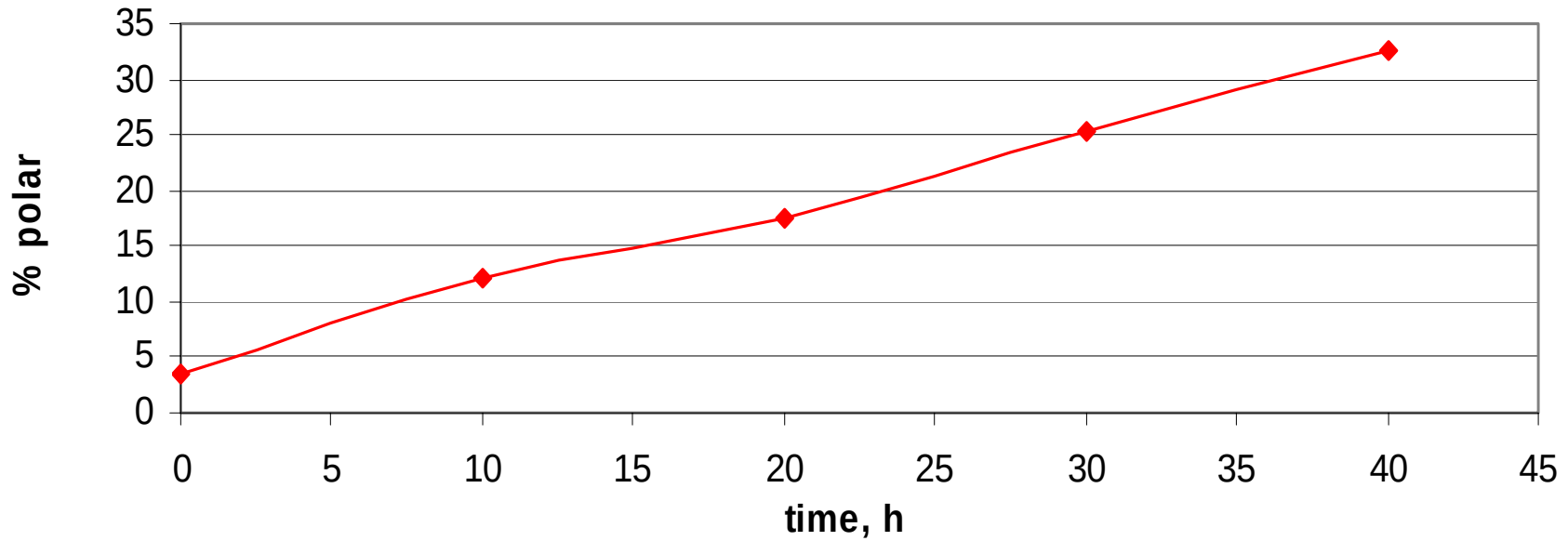
Biodiesel

Distillation

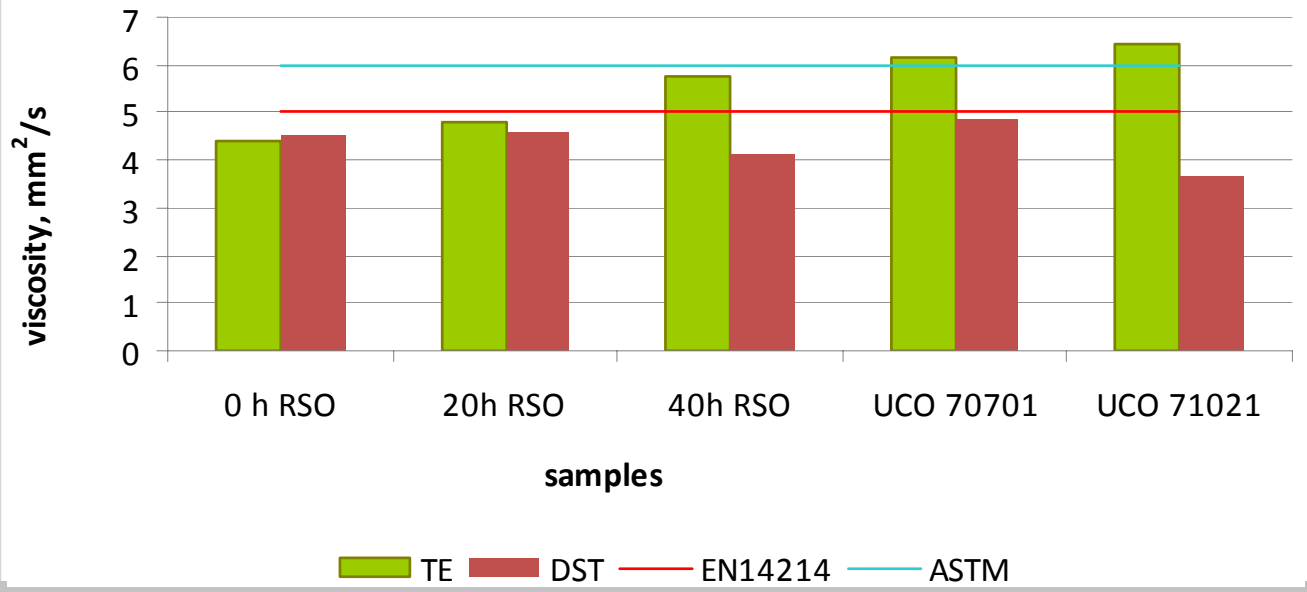
POLAR CONTENT of RSO

- **Polymeric TAG**
- **Dimeric TAG**
- **Oxidized TAG**

time (h)	% polar
0 h	3,4
10 h	12,0
20 h	17,6
30 h	25,4
40 h	32,7



Samples	Viscosity of transesterified oils, mm^2/s	Viscosity of distilled FAME, mm^2/s
0 h RSO	4,43	4,51
20 h RSO	4,79	4,56
UCO 1	6,13	4,11
UCO 2	6,42	4,87
40 h RSO	5,78	3,69



Viscosity (at 40 °C) of transesterified and distilled samples

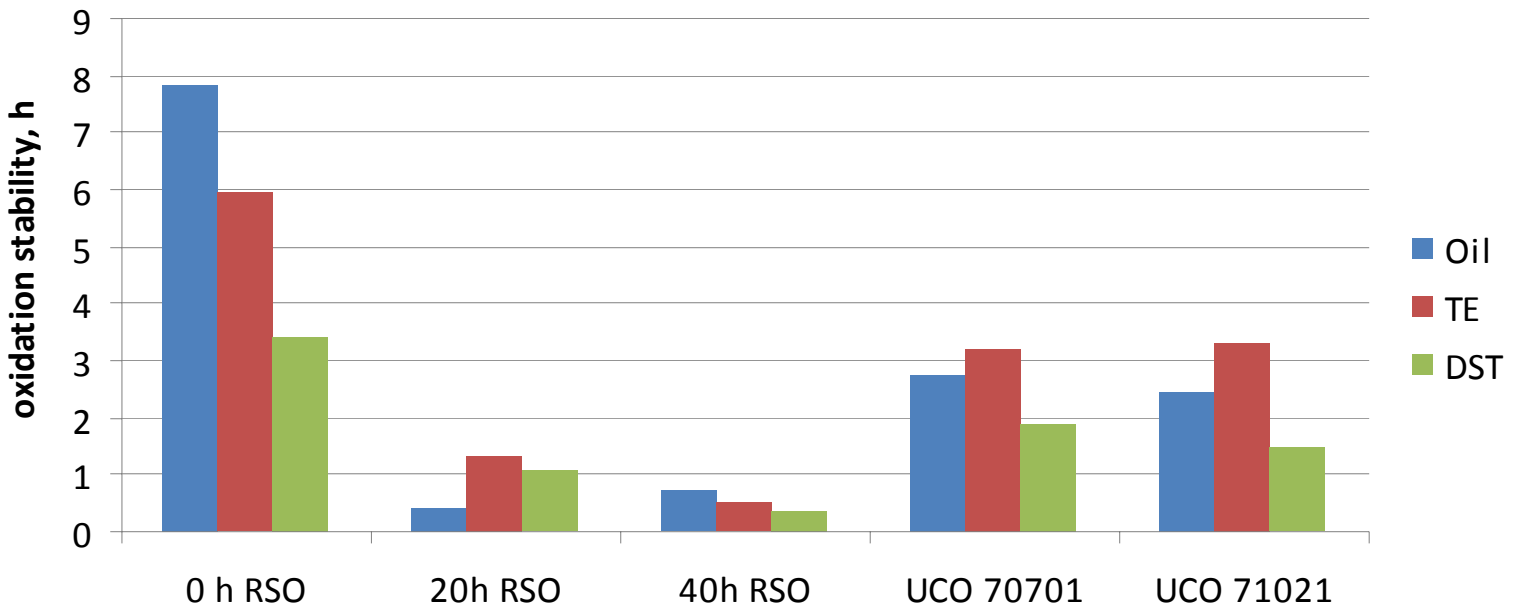
Samples	OSI of oil, h	OSI of TE oils, h	OSI of DST, h
0 h RSO	7,83	5,95	3,4
20 h RSO	0,43	1,33	1,05
40 h RSO	0,73	0,53	0,38
UCO 1	2,75	3,2	1,88
UCO 2	2,45	3,3	1,45

Oxidative Stability Index

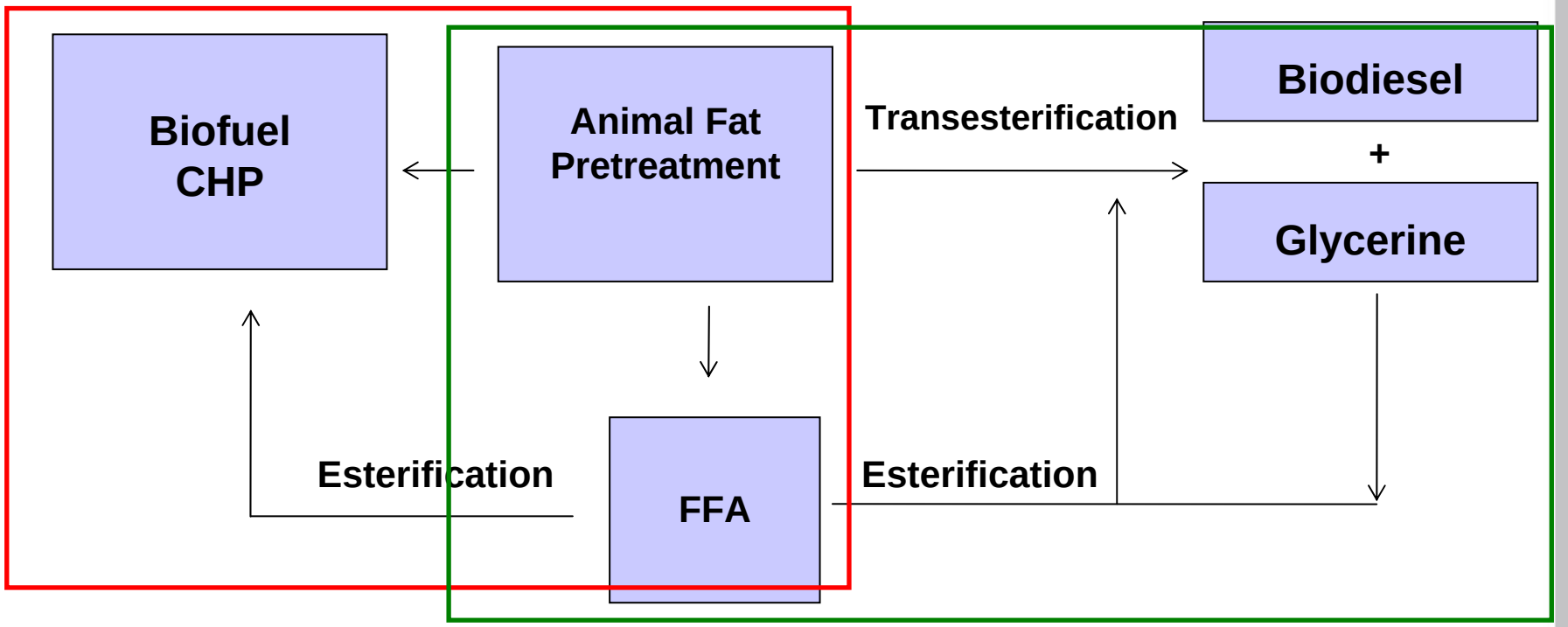
OSI at 110°C

EU: 6 h minimum

ASTM: 3 h minimum



IMPROVED BIODIESEL PRODUCTION TECHNOLOGY

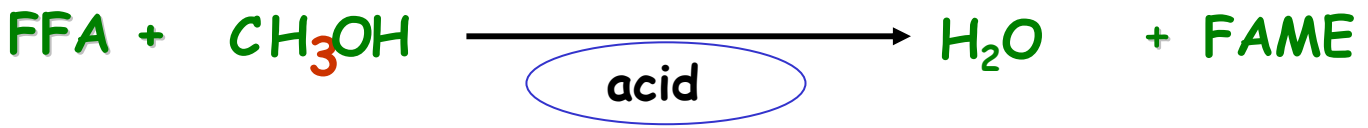


- via methyl esters
  1. stand alone
  2. integrated

- via oleochemicals

Stand alone AE process

Objective: Conversion of poor quality feedstocks with high acid value into high quality biodiesel at the highest possible yield

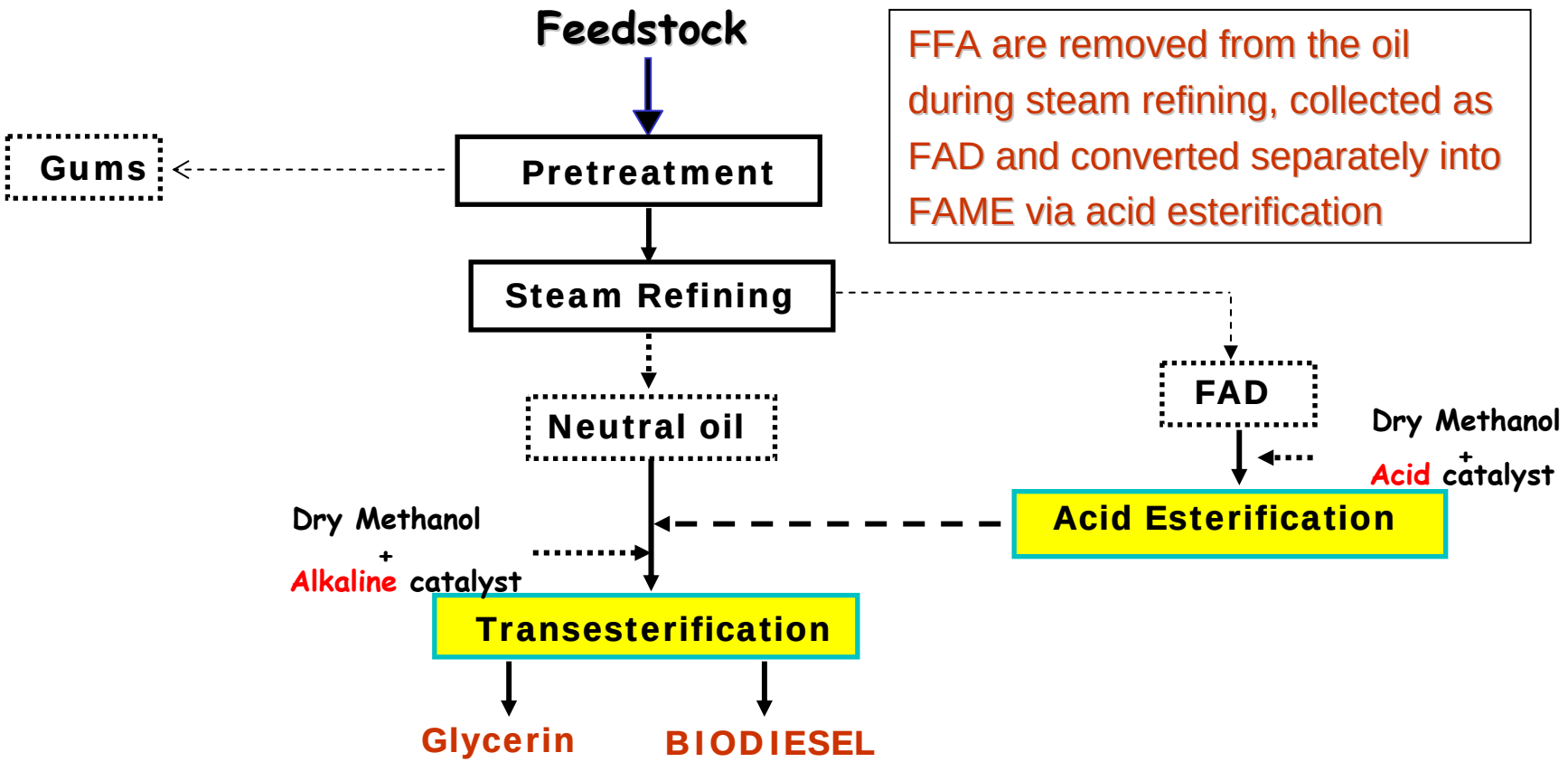


Current technology: Process with liquid sulphuric acid as catalyst
Undesired process (High temperature/pressure)
Strict construction material requirements

New technology: Process with solid 'acid' catalyst
Milder process conditions, no product purification

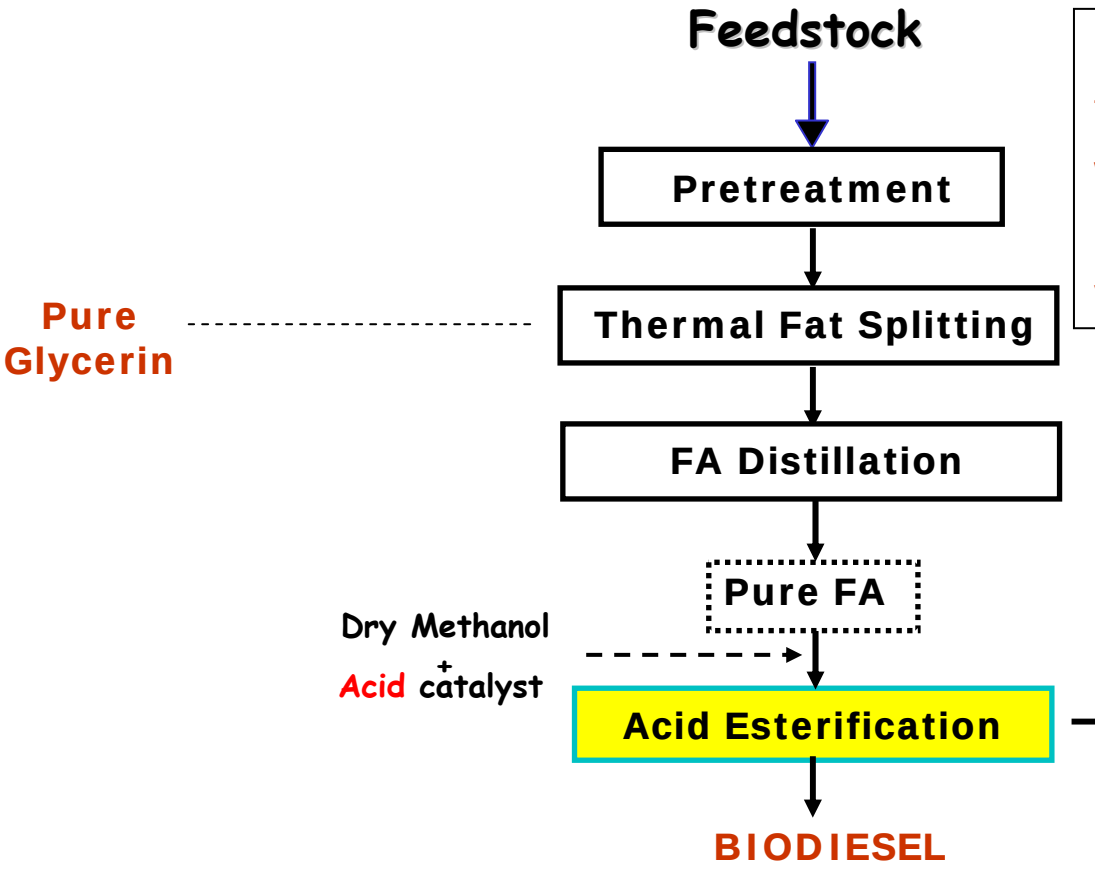
Solid 'acid' catalyst: Ion exchange Resin type (commercially available)
Enzyme cocktails (technology under development)

Combination of acid esterification and alkaline transesterification



FFA are removed from the oil during steam refining, collected as FAD and converted separately into FAME via acid esterification

Thermal Fat Splitting followed by acid esterification



Mono-, di- and triglycerides in the feedstock are converted into FFA with separation of pure glycerine. Purified FFA are converted into FAME via acid esterification

Multi-stage process required to achieve required high degree of conversion

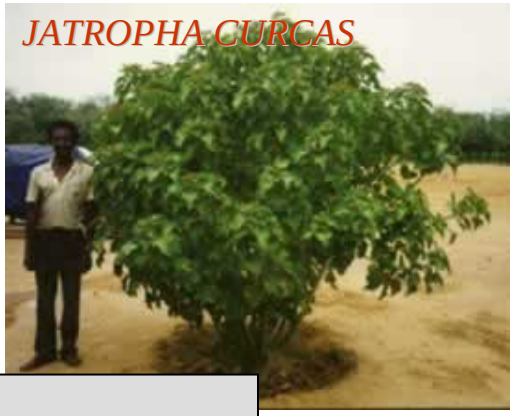
CONCLUSIONS

- **Processing low quality raw materials allows to a biodiesel producer to:**
  - **Decrease the overall production cost**
  - **Enlarge the plant flexibility**
  - **Avoid the « food *vs* fuel » debate**

- **Important biodiesel quality parameters are feedstock related:**
  - **Animal fats: S-content; PE content; cold flow properties**
  - **UCO: ester content; viscosity; OSI; total contamination**

  ⇨ **post-treatment is often required**

- **Improved production technologies are needed to convert such feedstocks into high quality biodiesel at the highest possible yield**



THANK YOU
FOR YOUR ATTENTION !