

New technologies for biodiesel production using alternative sources

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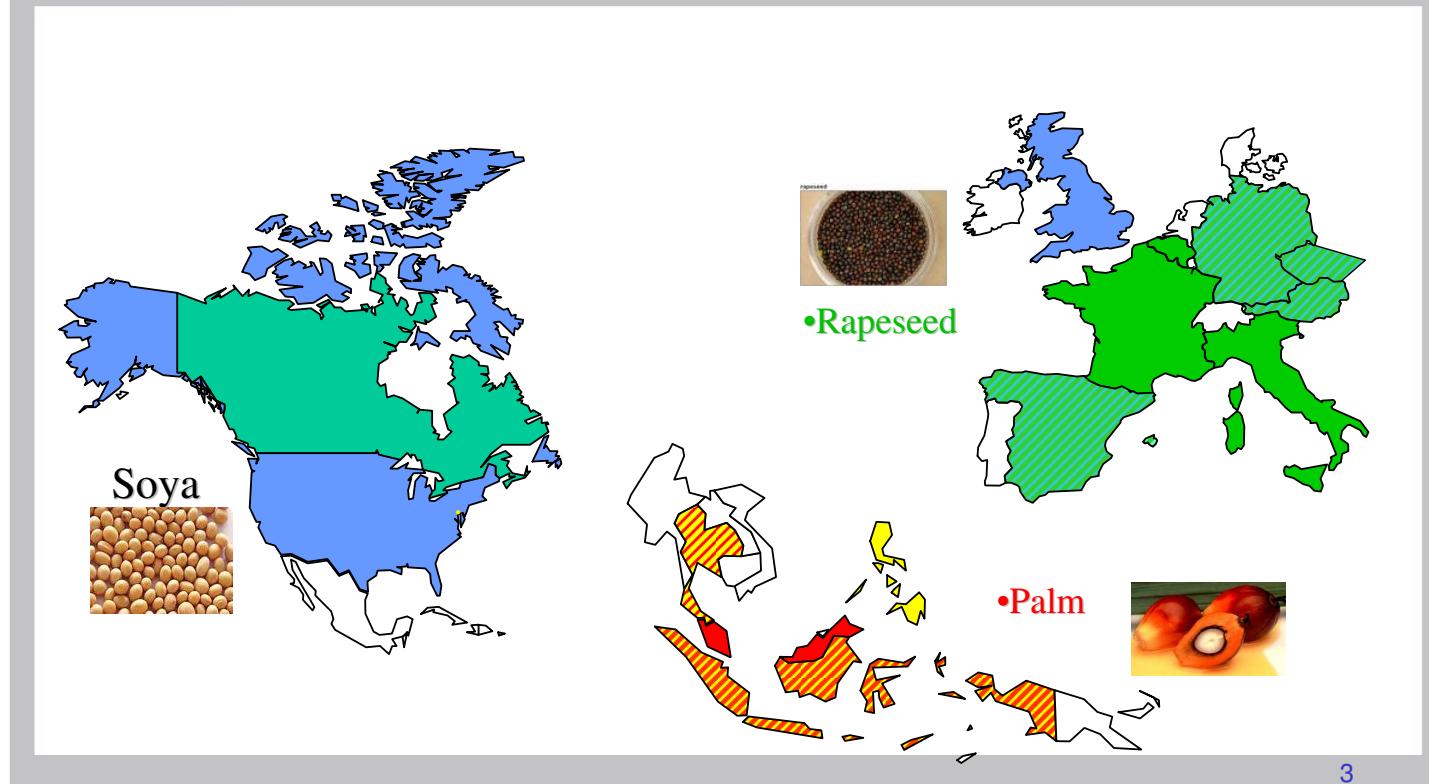
Second Generation Biofuels from Alternative Resources



	First Generation	Second Generation
Final Product	FAME	FAME Green diesel Green biofuel (power, heat, steam)
Feed Stock	Vegetable Food Oil	Crude/waste vegetable oils and animal oil fats Non-edible oils High FFA oils Refining side-streams
Technology	Akaline transesterification	Acid esterification + alkaline transesterification Hydrocracking Refining technology
Considerations	Food ↔ fuel Sustainability ?	Technical, non-food oils High sustainability

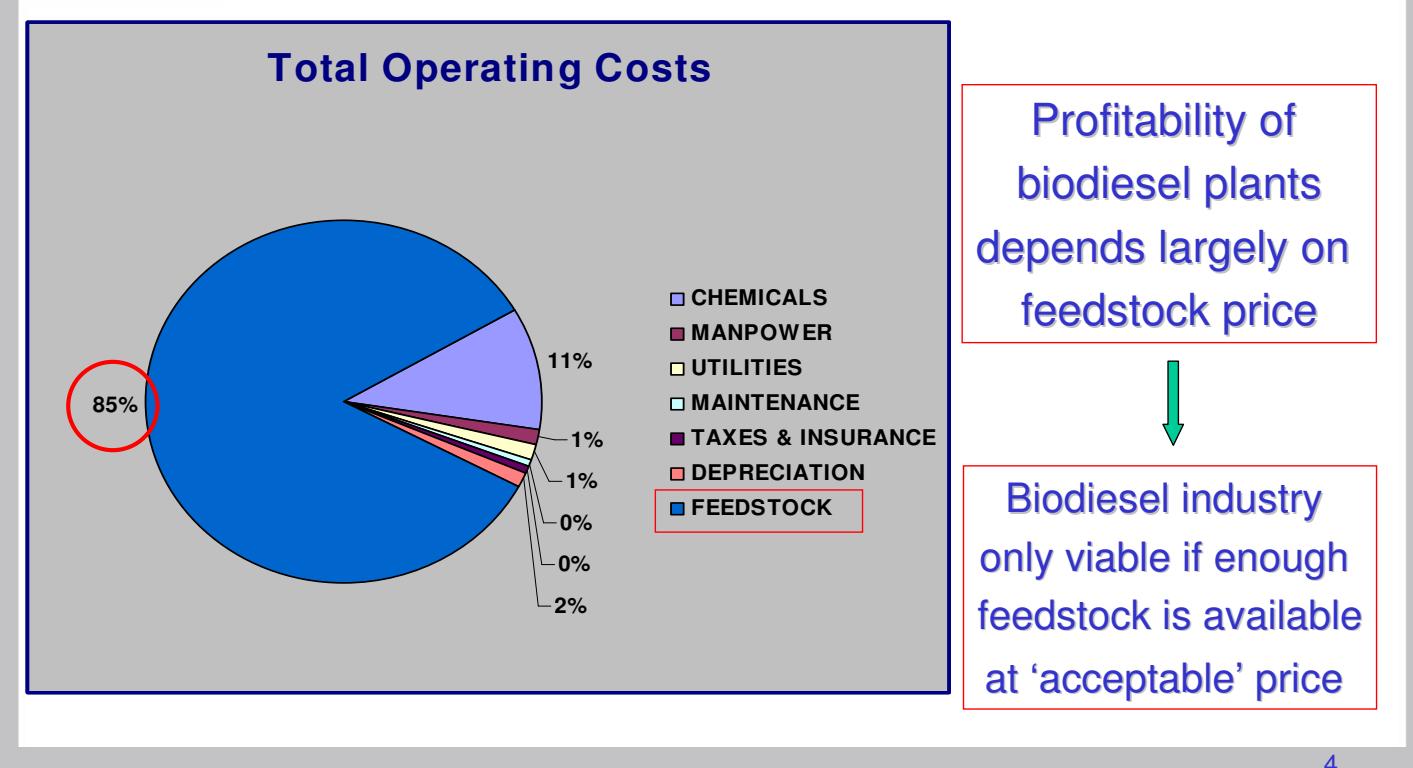
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1st GENERATION FEEDSTOCKS



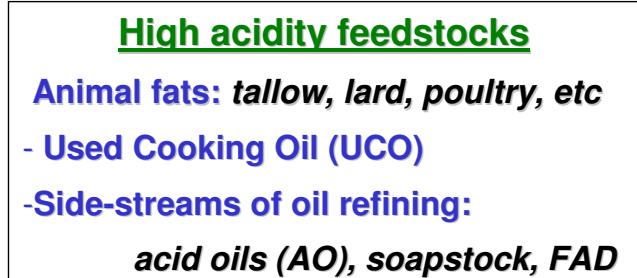
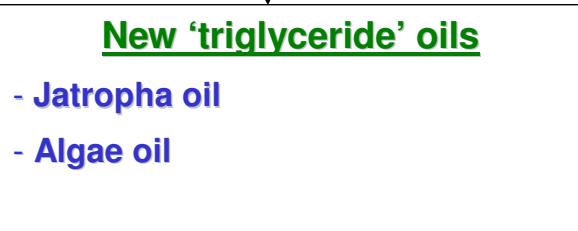
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BIODIESEL PRODUCTION COST



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ALTERNATIVE FEEDSTOCKS



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

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

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- Quality considerations for biodiesel from high acidity feedstocks

→ Case study: crude vegetable oils

→ 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



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	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				

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Conversion of crude oils into biodiesel



Two-step procedures: ratio MeOH/fat: 6 mol/1mol

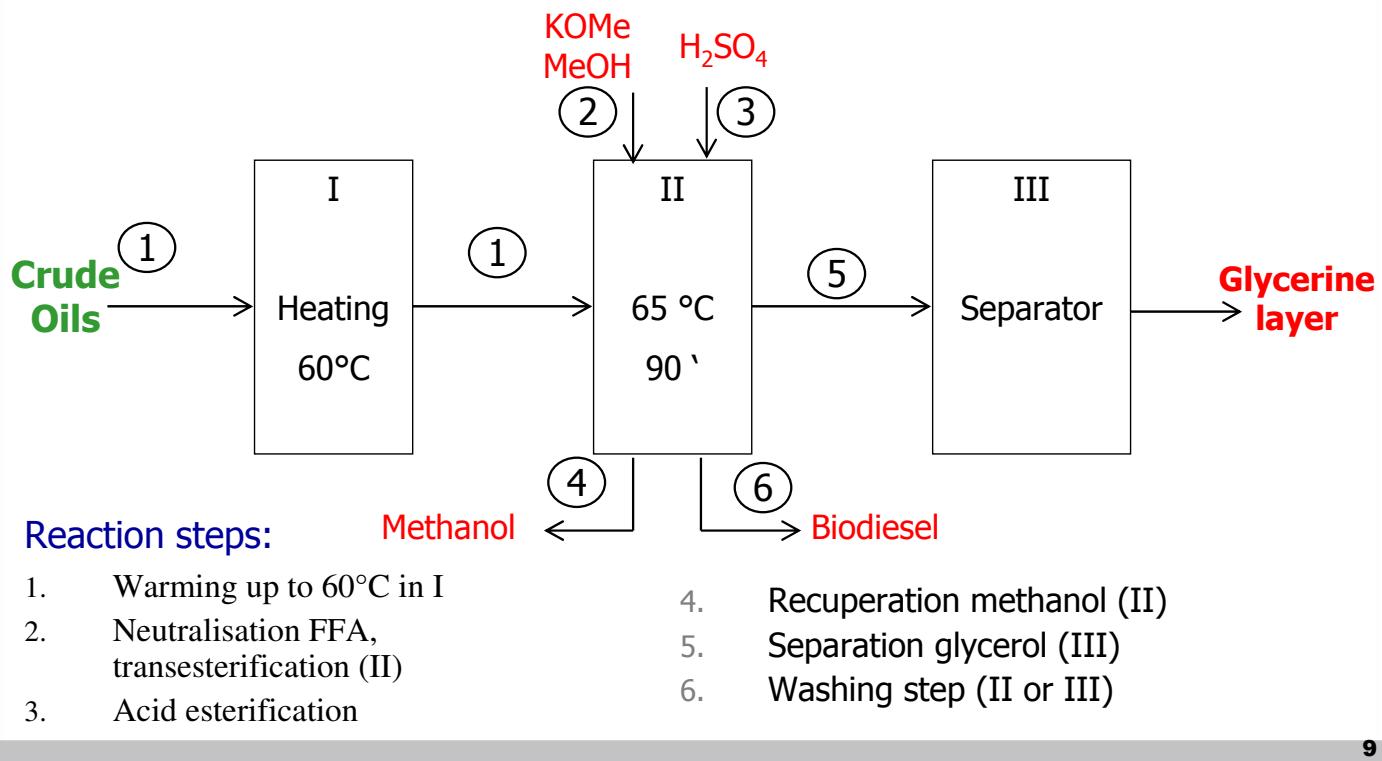
I:

1st step: alkaline transesterification:
catalyst: neutralisation FFA + 5 mol %
2nd step: acid esterification:
 H_2SO_4 : neutralisation catalyst + 5 mol %
Condition: < 10 % FFA

II:

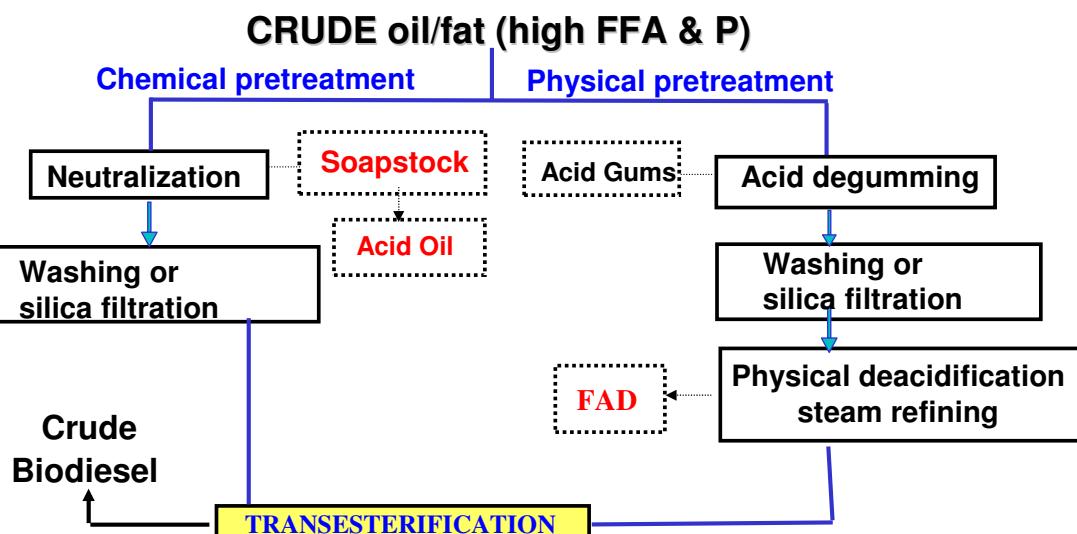
1st step: acid esterification: H_2SO_4 : 20 mol % (FFA)
2nd step: alkaline transesterification:
catalyst: neutralisation H_2SO_4 + 5 mol %

Technology for the conversion of high FFA crude oils into Biodiesel



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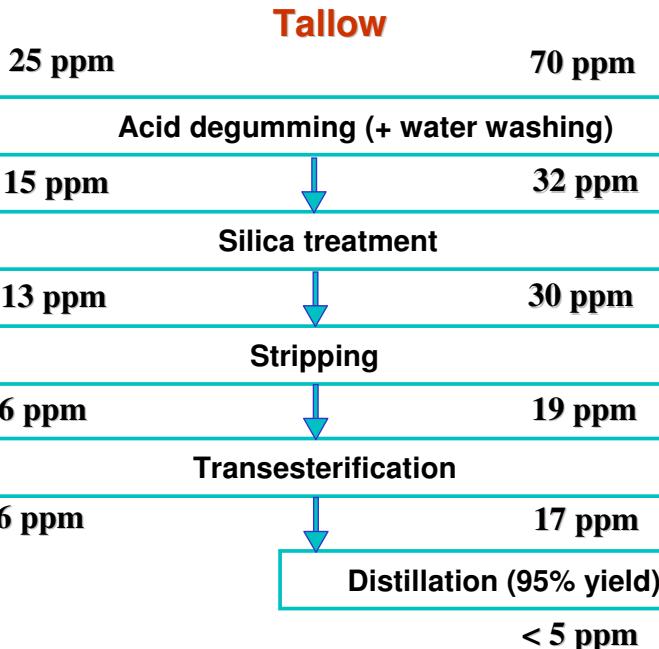
FEEDSTOCK PRETREATMENT



* To avoid process problems and product losses

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

REMOVAL of S-COMPOUNDS from ANIMAL FATS



Good quality feedstocks:

< 10 ppm after
pretreatment

Poor quality feedstocks:

Distillation might
be required

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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

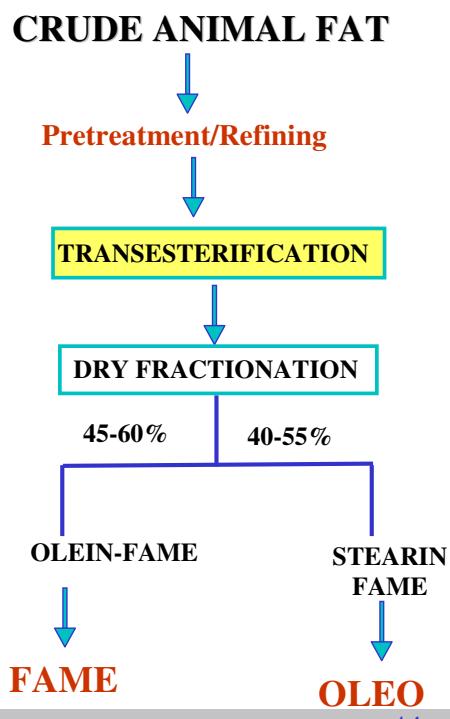
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Feedstock	UCO		Tallow		Chicken Fat		Palm-FAD	
	OIL	FAME	OIL	FAME	OIL	FAME	OIL	FAME
Iodine Value	90	90	62	62	80	80	52	52
Phosphorus	2	< 1	4	< 1	206	N.D.	N.D.	N.D.
Cloud Point (°C)	14	1	--	7.8	11.5	2.3	37.2	10.5
CFPP (°C)		0		9		--	--	> 10
Mono- & diglycerides (%)	--	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

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Feedstock	ANIMAL FAT			
	OIL	FAME	OLEIN FAME	
			1	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



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Definition:

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

Chemical reactions:

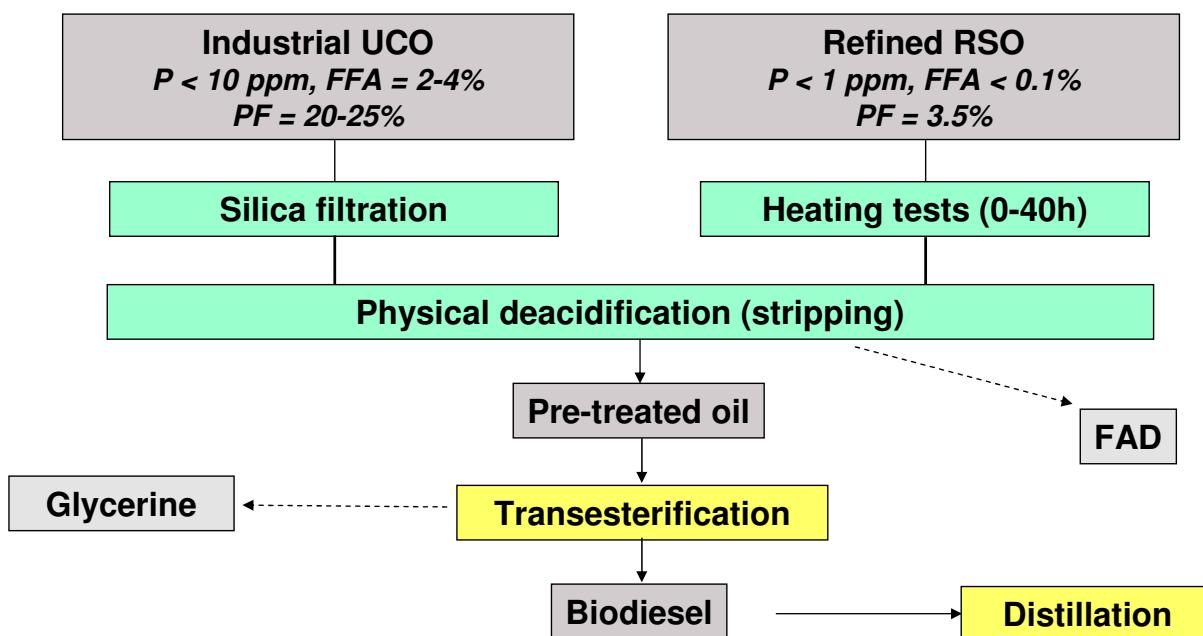
Thermolytic: radical reaction, dimerization/polymerization
Oxidation → polar content
Hydrolysis → FFA

Effect:



Lower ester content, higher FFA
 Higher viscosity and CP: dimers
 Higher total contamination: higher polar content
 Lower oxidative stability

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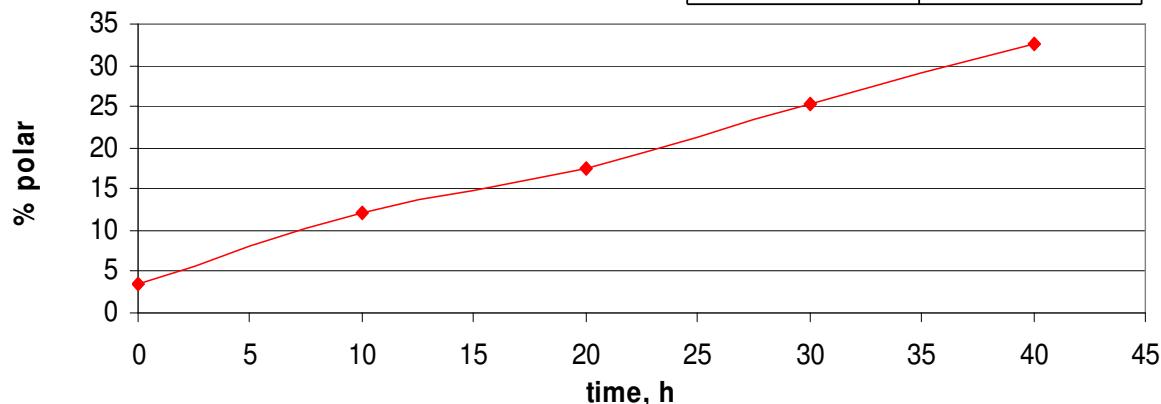


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POLAR CONTENT of RSO

- Polymeric TAG
- Dimeric TAG
- Oxidized TAG

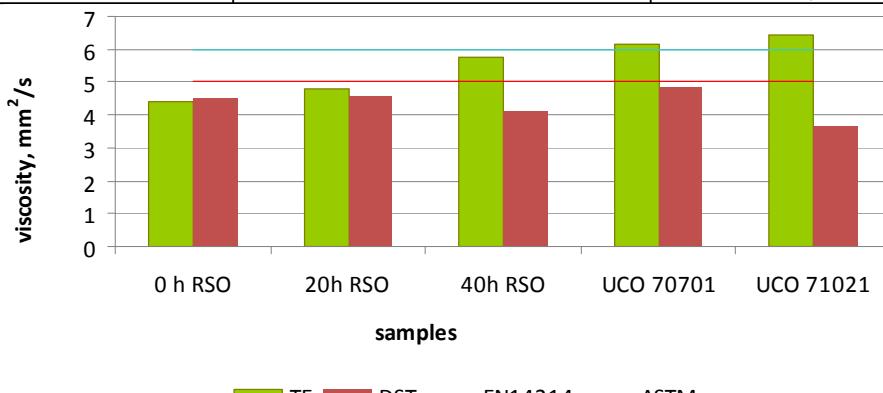
time (h)	% polar
0 h	3,4
10 h	12,0
20 h	17,6
30 h	25,4
40 h	32,7



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

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



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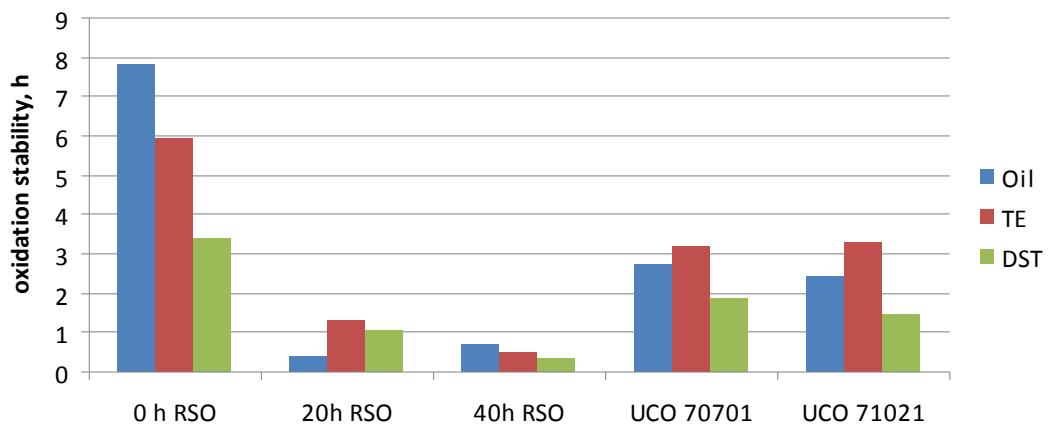
Oxidative Stability Index

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

OSI at 110 °C

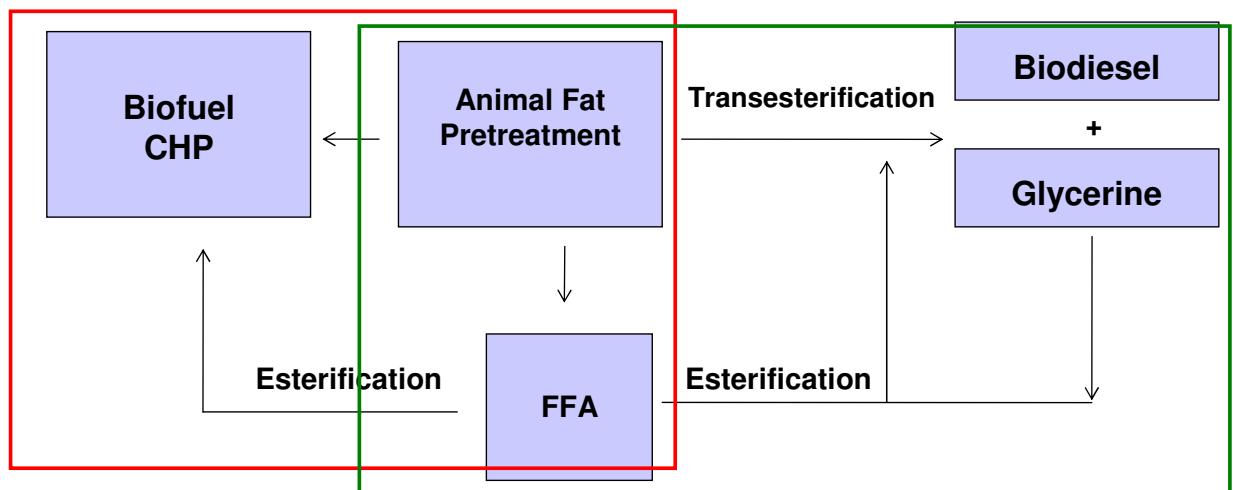
EU: 6 h minimum

ASTM: 3 h minimum



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IMPROVED BIODIESEL PRODUCTION TECHNOLOGY



- via methyl esters

1. stand alone

2. integrated

- via oleochemicals

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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

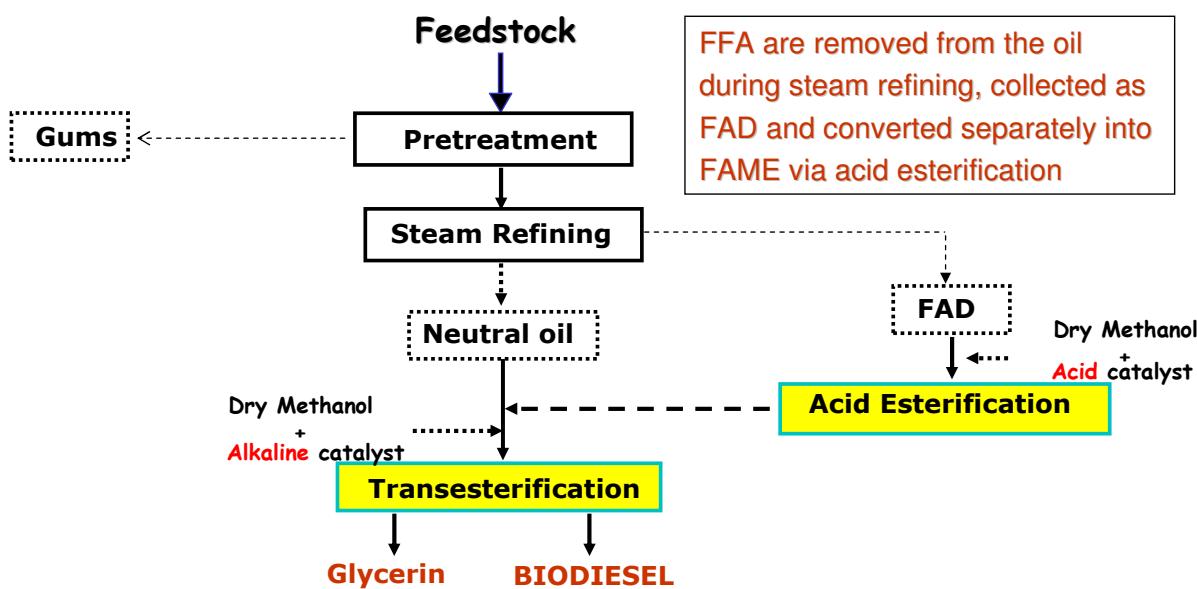
Milder process conditions, no product purification

Solid 'acid' catalyst: Ion exchange Resin type (commercially available)

Enzyme cocktails (technology under development)

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Combination acid esterification and alkaline transesterification

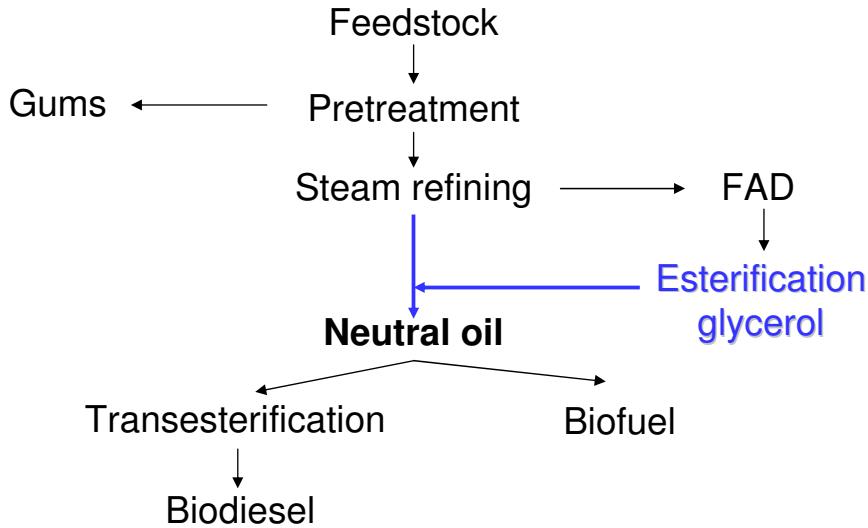


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Strategies for conversion of high acidic oils into biofuels



Removal of FA from oil (b)



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Esterification of high acidic oils with glycerol (1)



- Parameters: T : 200 °C
P : 90 mbar
Ratio: fat/glycerol
Catalyst: without, pTSA

Experimental data:

- Influence of catalyst on FFA-content
- Analysis of acylglycerides (process without catalyst)

Esterification of high acidic oils with glycerol (2)



Influence of catalyst on FFA-content

FFA/glycerol: 1/1 mol (33%)

62 rpm

Time(h)	No catalyst	1% p-TSA
0	71.48	71.48
0.42	66.93	60.31
1.42	39.64	28.25
2.42	23.66	17.71
3.42	15.23	11.50
4.42	10.70	7.88
5.42	7.12	4.99

Esterification of high acidic oils with glycerol (3)

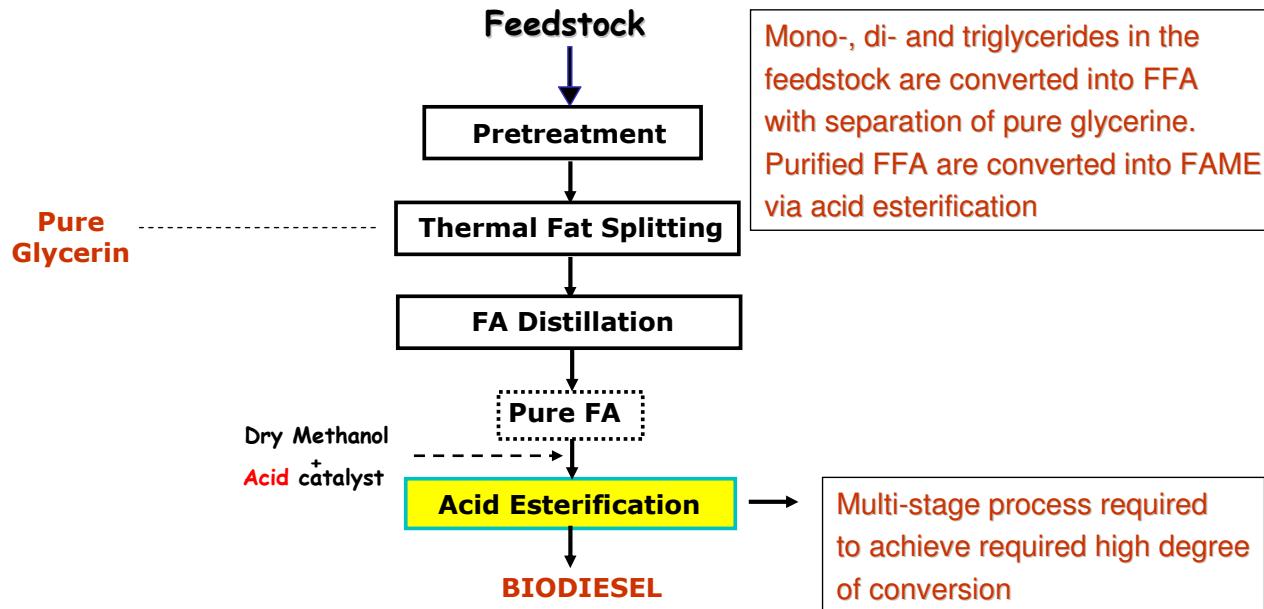


Analysis of acylglycerides

Time	FFA %	Glycerol %	MG	DG	TG
0	70.63	23.31	0	3.78	1.98
1.42	30.57	14.23	25.84	21.33	3.85
2.42	19.66	11.43	29.75	28.32	5.57
3.42	11.29	9.57	31.44	33.87	7.54
4.42	6.96	8.42	31.65	37.11	8.99
5.42	4.62	7.98	36.16	39.00	10.10

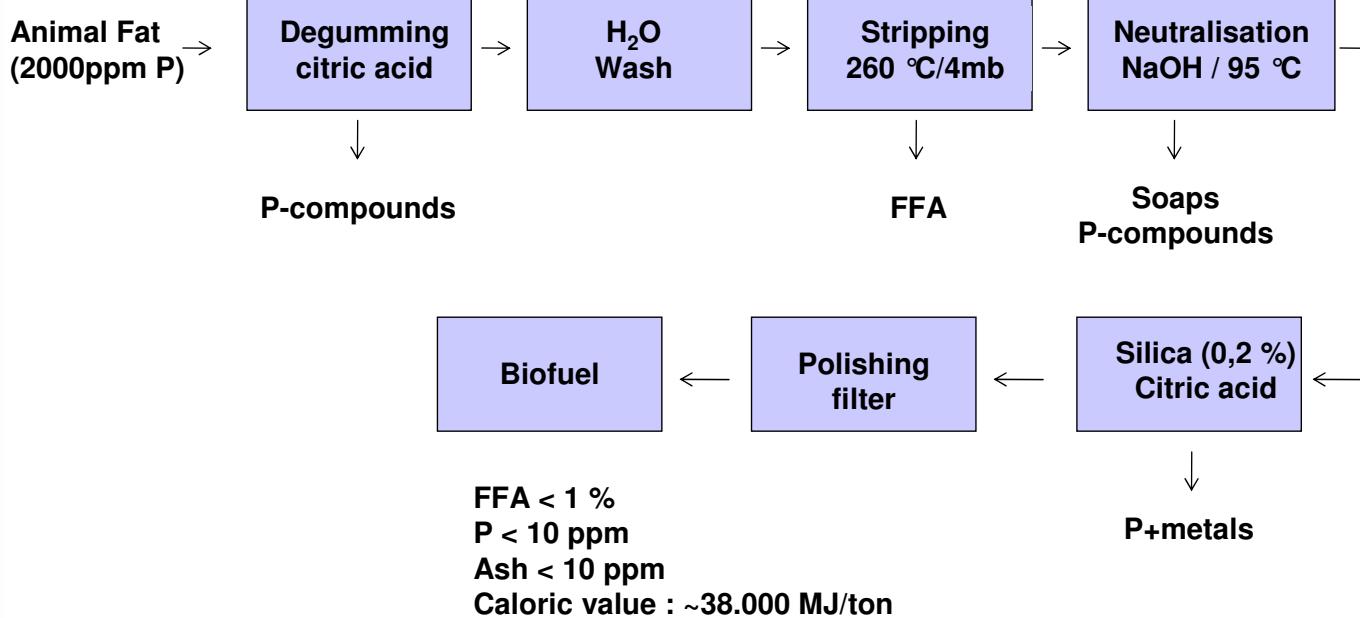
Conditions: 200 °C; no catalyst; FFA/glycerol 1/1; 620 rpm

Thermal Fat Splitting followed by acid esterification



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Refining of Crude Animal Fats for Biofuel Production



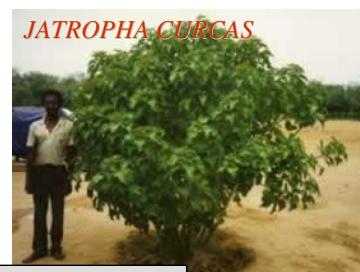
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CONCLUSIONS

- 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

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**THANK YOU
FOR YOUR ATTENTION !**



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