UGent Francqui Chair 2013 / 2nd Lecture

Studies on esterification of Free Fatty Acids in biodiesel production

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Contents

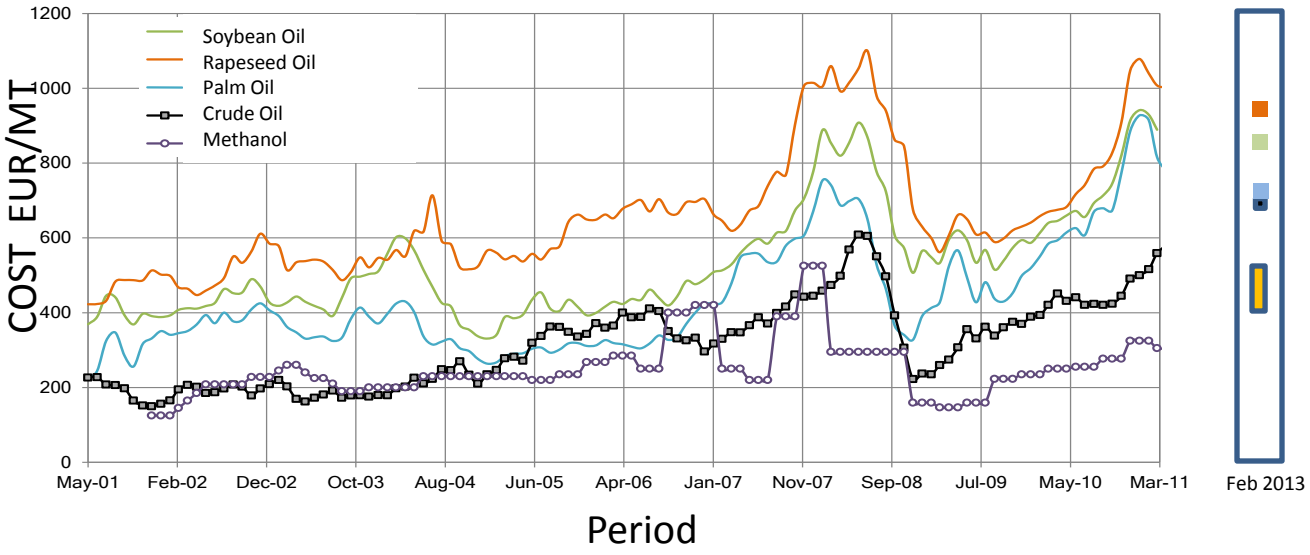
1st Lecture

- Production of Biodiesel through Transesterification of Triglycerides in Vegetable Oils and Fats
  - Homogeneous Thermal (No catalyst Use)
  - Homogeneous Catalytic (Acid catalyst – Base catalyst)
  - Heterogeneous Catalytic (Solid catalyst/carriers – Active Phase)

- Catalytic effect of Free Fatty Acids (FFAs) present in Vegetable Oils and Fats on Transesterification reactions

- Raw Materials : Refined Vegetable Oils and Fats
  At Least De-gummed and Neutralized

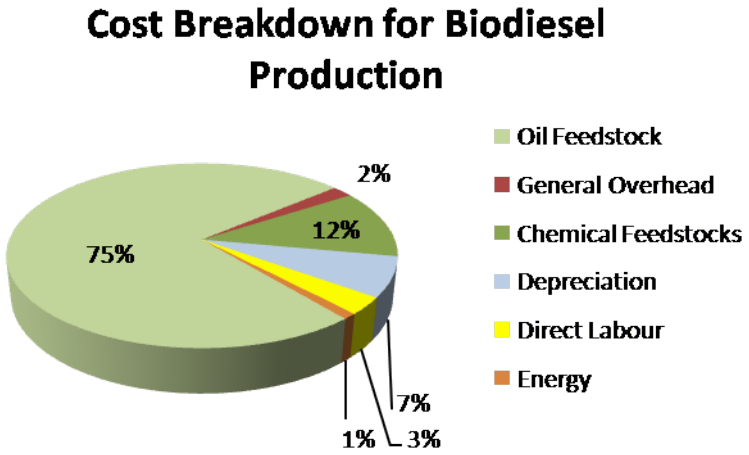
Cost of Raw Materials and Crude Oil



Acidic Vegetable Oils and Cooking Oils have a price of 400 – 550 EUR/MT

Sources : http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/
http://www.indexmundi.com/commodities/?commodity=crude-oil

- ✓ Acidic Vegetable Oils / Fats and Cooking Oils are considered as very attractive alternative Raw materials and the Biodiesel from them may not need subsidizing to be used as (Bio)Fuel
- ✓ Convert Waste to Fuels (High acidity Oils and Fats)



http://www.epa.gov/region9/waste/biodiesel/questions.html

Alternative Raw Materials for Biodiesel Production

Acidic Vegetable Oils *(FFAs > 1 wt %)*

Animal Fats *(FFAs > 5 wt %)*

Cooking Oils *(FFAs > 2.5 wt %)*

Fatty Acid	Beef Tallow	Pork Lard	Chicken Fat
Myristic 14:0	1.4 – 6.3	0.5 – 2.5	1
Palmitic 16:0	20 – 37	20 – 32	25
Palmitoleic 16:1	0.7 - 8.8	1.7 – 5	8
Stearic 18:0	6 – 40	5 – 24	6
Oleic 18:1	26 – 50	35 – 62	41
Limoleic 18:2	0.5 – 5	3 – 16	18
Typical Saturation*	40	40	30 – 33
Typical form RT	Solid	Solid	Thick liquid/Solid
Sulphur, ppm	Up to 100	Up to 100	Up to 100

* Compare with 15 % in Soya bean Oil and 10% in Rape seed oil

http://www.extension.org/pages/30256/animal-fats-for-biodiesel-production

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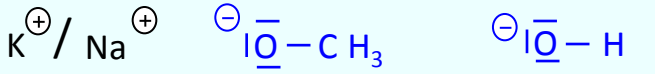
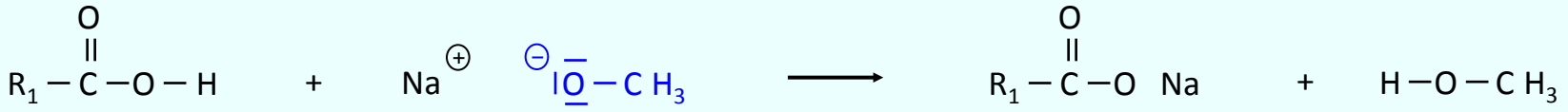
Base Catalyst



Potassium/Sodium **Methylate** **Hydroxide**

Saponification Reaction



Fatty Acid **Sodium Methylate** **Soaps** **Methanol**

Catalyst !!!

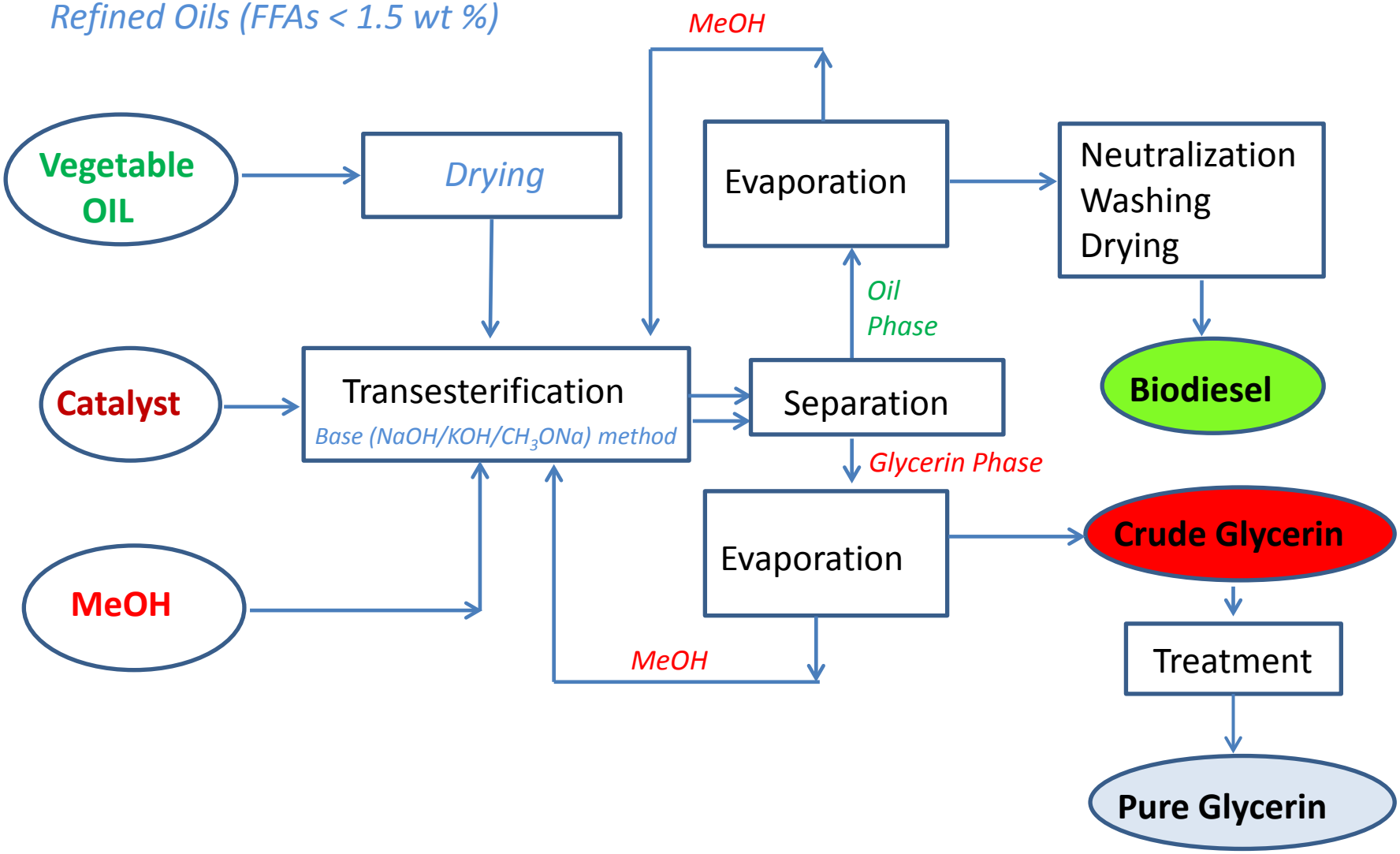
High Soap content

- Reduces the amount of Catalyst for transesterification
- Causes problems in Downstream/Cleaning Processing

The presence of Free fatty Acids is The CONTROLLING Parameter Of the Method (Process) used for Biodiesel production

BIODIESEL Production

Refined Oils (FFAs < 1.5 wt %)



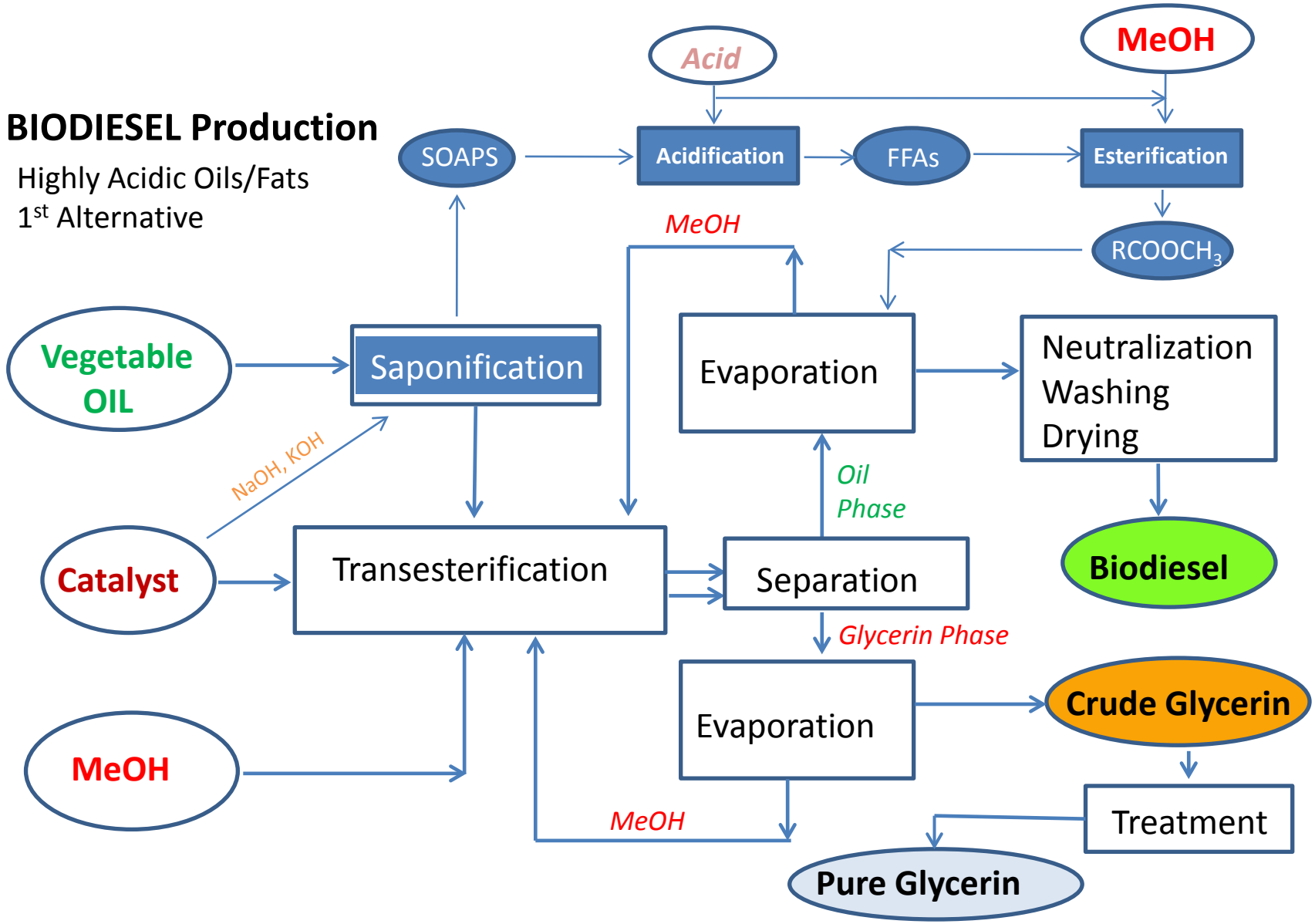
For higher FFA content (> 1.5 wt%) alternative strategies must be applied in Biodiesel production Process

1st alternative : Remove the FFAs from the OIL

- In the Pretreatment step before transesterification, FFAs are converted into soaps and removed from the Oil (triglycerides)

2nd alternative : Transform FFAs and Triglycerides to Methylesters

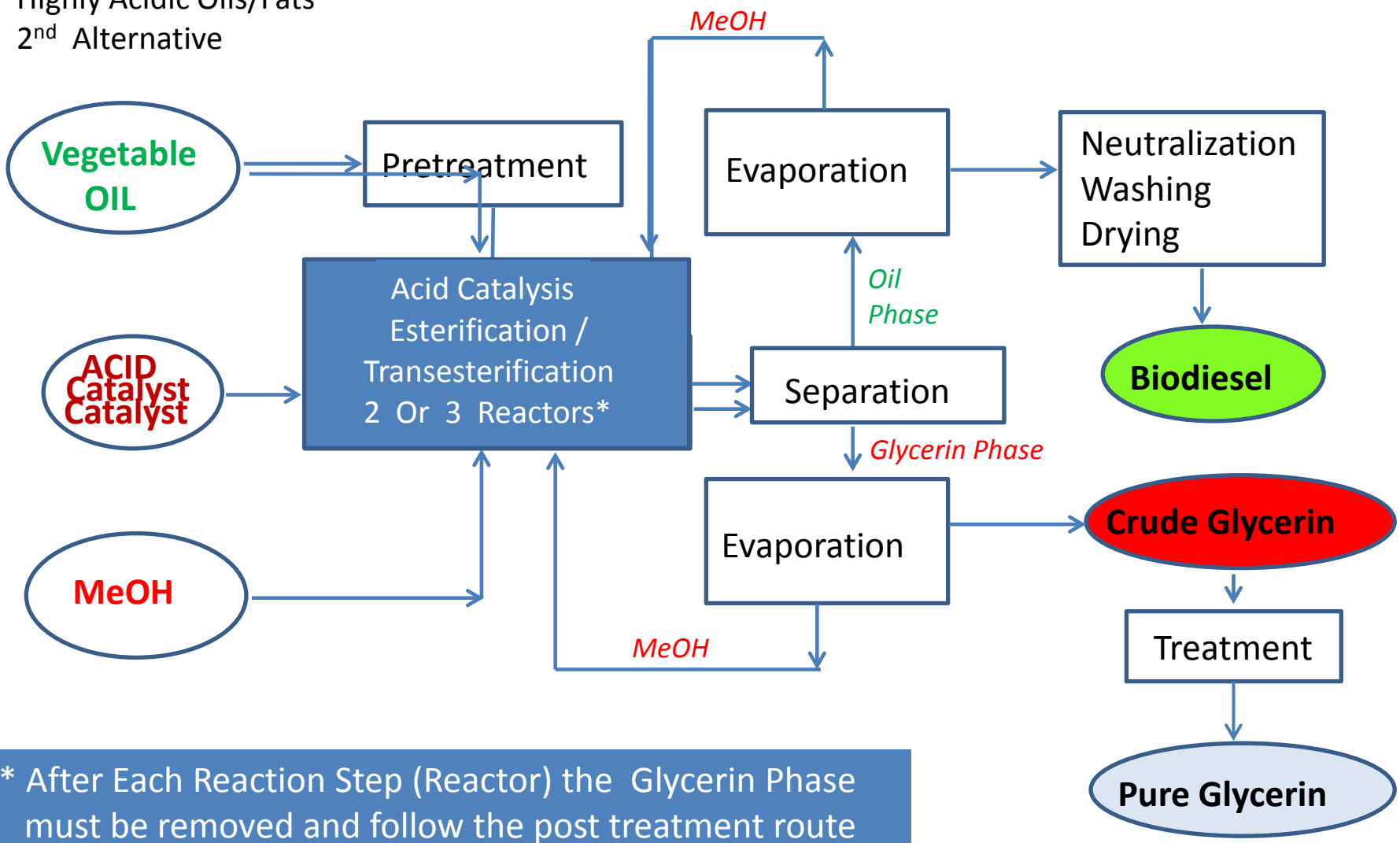
- Application of the Acid Catalysis Method to transesterify the triglycerides and Esterify the FFAs in parallel in the same reactor


BIODIESEL Production
Highly Acidic Oils/Fats
1st Alternative
Acid
MeOH
SOAPS
Acidification
FFAs
Esterification
MeOH
RCOOCH3
Vegetable OIL
Saponification
Evaporation
Neutralization
Washing
Drying
NaOH, KOH
Oil Phase
Catalyst
Transesterification
Separation
Biodiesel
Glycerin Phase
Evaporation
Crude Glycerin
MeOH
MeOH
Treatment
Pure Glycerin

BIODIESEL Production

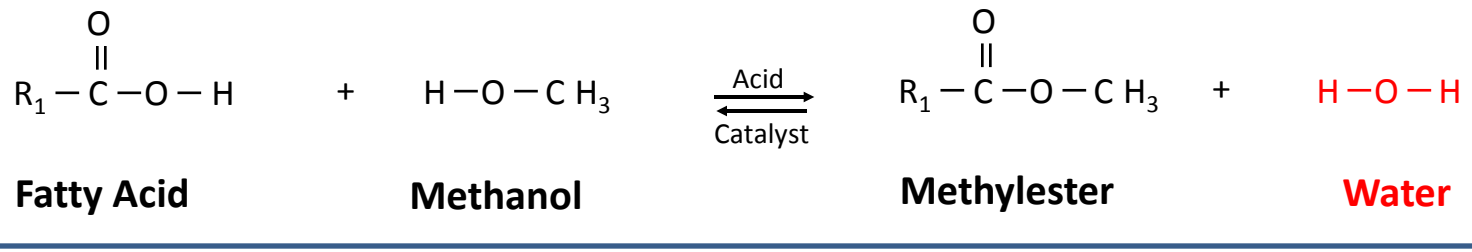
Highly Acidic Oils/Fats

2nd Alternative

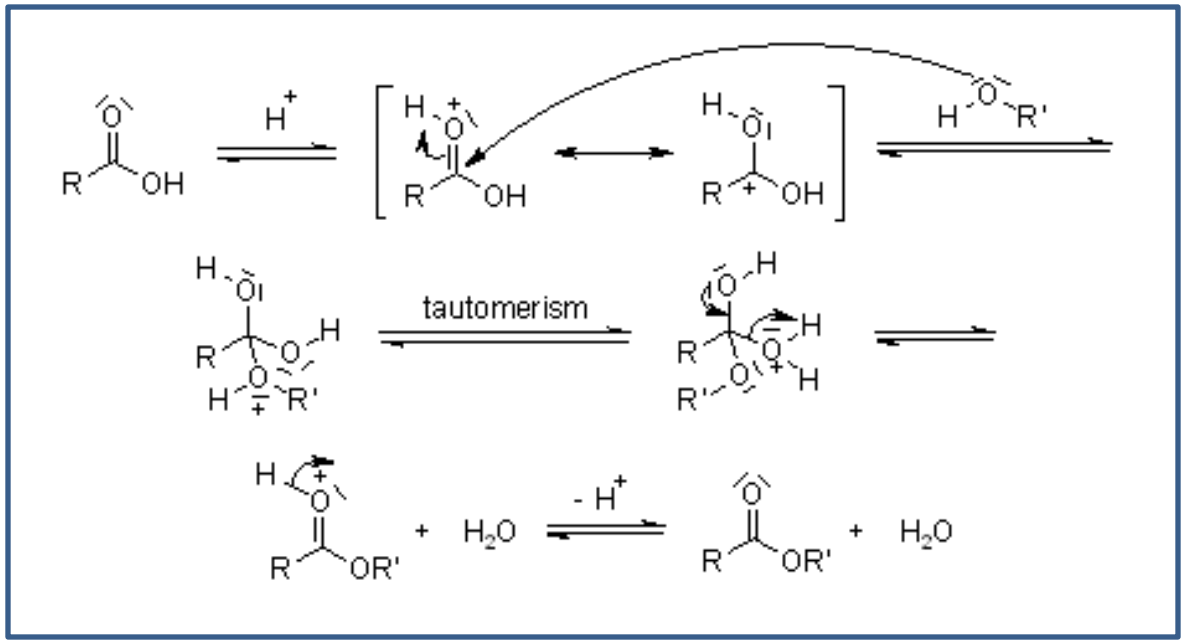


* After Each Reaction Step (Reactor) the Glycerin Phase must be removed and follow the post treatment route

Esterification – Hydrolysis Reaction



Mechanism of Esterification Reaction



The Use of a Solid Catalyst for FFAs Esterification simplifies the Process

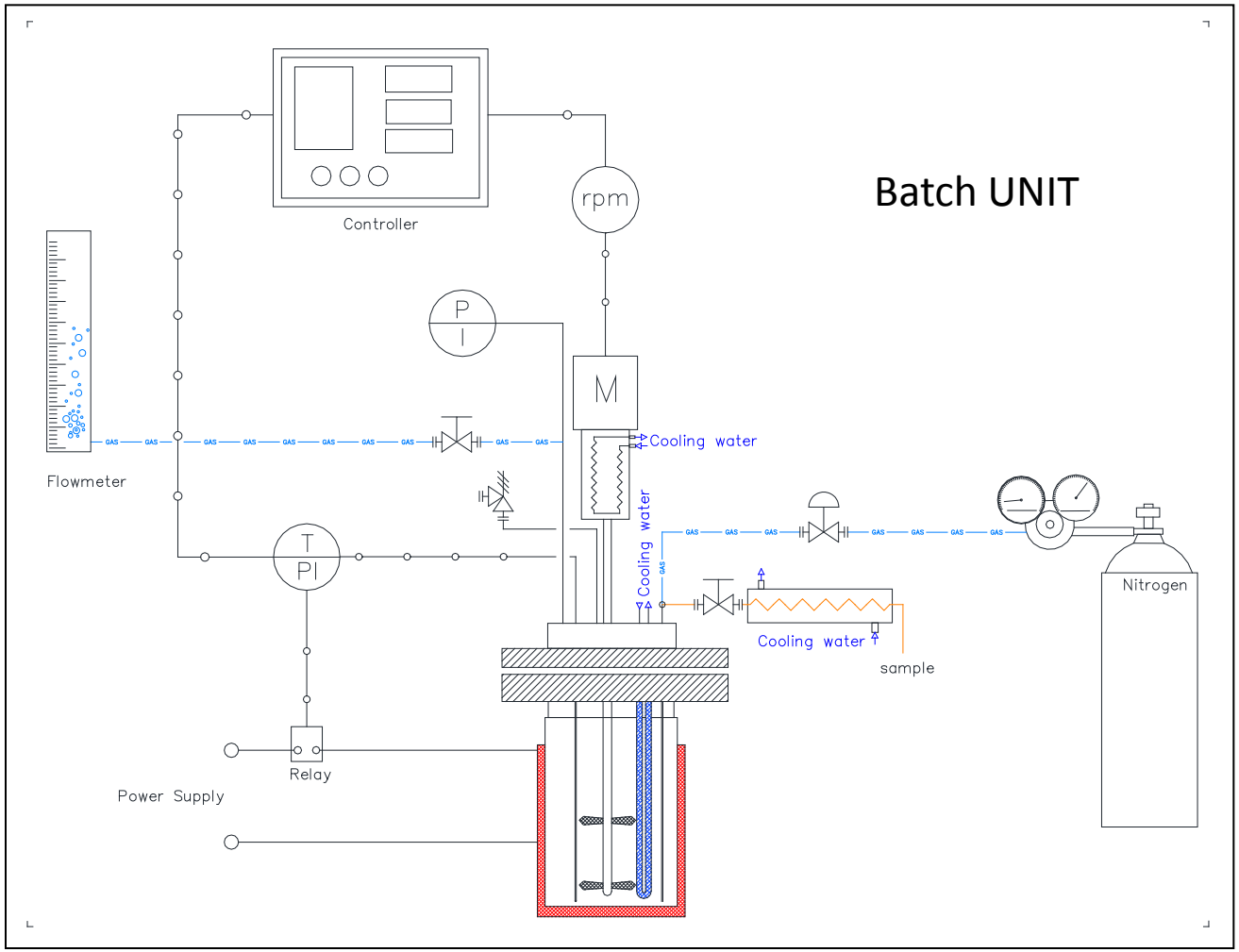
Benefits :

- The Catalyst is not consumed
- The resulting mixture consisting of :
  Methyl-Esters from FFAs,
  Triglycerides from the initial Oil and
  non-reacted MeOH
  can be treated for the final transformation to Biodiesel with <u>any process</u>
- Super-acid catalysts can be used at temperatures 70 – 110 C and molar ratios MeOH/FFAs = 5/1 – 20/1

For Oils with high FFA content a two step esterification may be needed

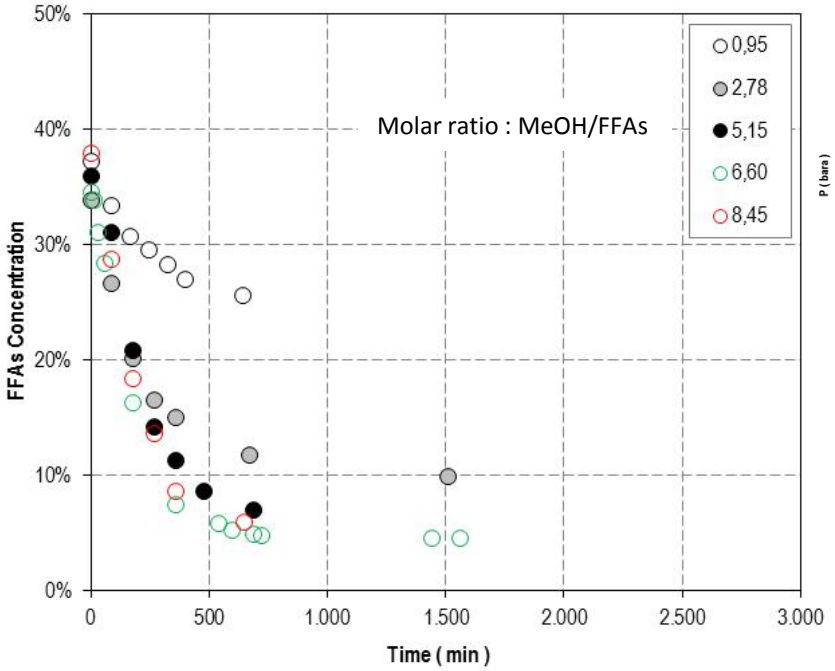
- **Catalyst**
  - Commercial super acid resin : Purolite CT-275
  - Acidity ($eqH^{+}kg^{-1}$) : 5.20
  - S_g (m^2kg^{-1}) : $31x10^{-3}$
  - T_{max} (^oC) : 145

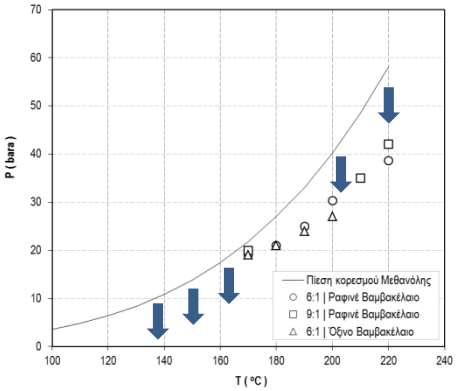
- **Reaction Systems**
  - Batch reactor
  - Tubular reactor
- **Conditions**
  - Temperature range : 70 - 120 ^oC
  - Operation pressure : 3 - 12 bara
- **Feedstocks**
  - Free fatty acids oil refinery by-product (Palm Oil): 38.1 wt.%, 58 wt.% and 100 wt.% acidity
  - Crude sunflower seed oil: 2.93 wt. % acidity
  - Acid cottonseed oil: 3.03 wt. % acidity
  - Analytical grade (99.9 %) Methanol



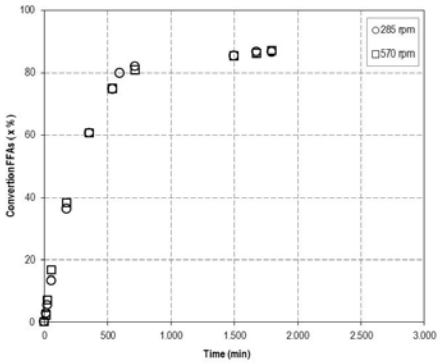
Batch Reactor

Effect of molar ratio & External mass transfer phenomena





$P_{0,Syst} < P_{T,MeOH}$



- The maximum dissolved methanol in the system was 6.6 / 1 molmol^{-1}
- Minimal external transport phenomena in the system
- From experiment with crushed catalyst concluded that there are no internal transport phenomena

- **Batch reactor**
  - Homogeneous mixture with constant density (d mixture = constant)
  - Isothermal - single phase mixture, apparent constant rates

- **Single reaction first order with respect to each reacting component**

Total Esterification Rate :

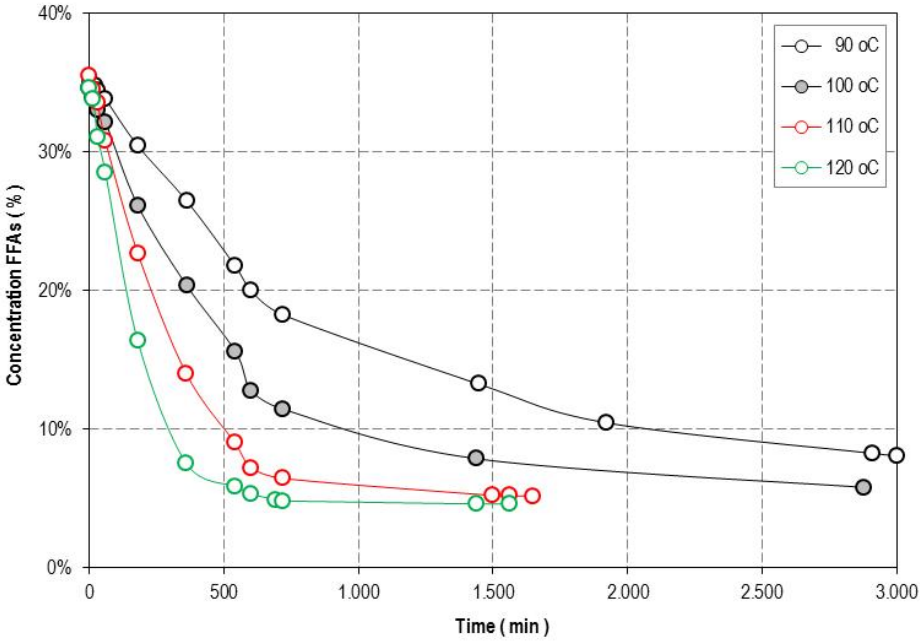
$$\frac{dN_{FFA}}{dt} = -\left(-r_{FFA}\right)_{th} \times M_{mix} - \left(-r_{FFA}\right)_{cat.} \times m_{cat}$$

$$\left(-r_{FFA}\right)_{th} = -\left(k_{FFA,th} C_{FFA} C_{MeoH} - k_{-FFA,th} C_{ME} C_{H_2O}\right) \times C_{FFA}$$

$$\left(-r_{FFA}\right)_{cat.} = -\left(k_{FFA,cat} C_{FFAs} C_{MeOH} - k_{-FFA,cat} C_{MEs} C_{H_2O}\right)$$

- **Equilibrium**

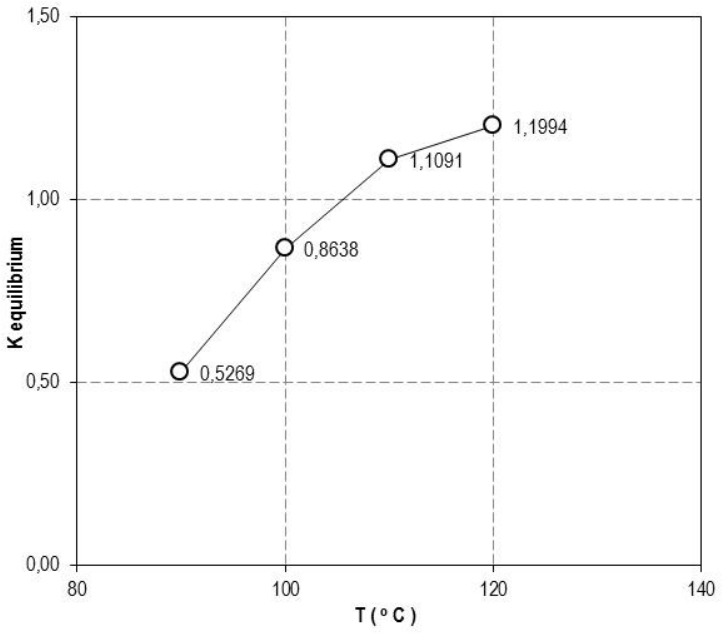
$$K_{eq} = \frac{k_{FFAs}}{k_{-FFAs}} = \frac{C_{MEs(eq)} \times C_{H_2O(eq)}}{C_{FFAs(eq)} \times C_{MeOH(eq)}}$$

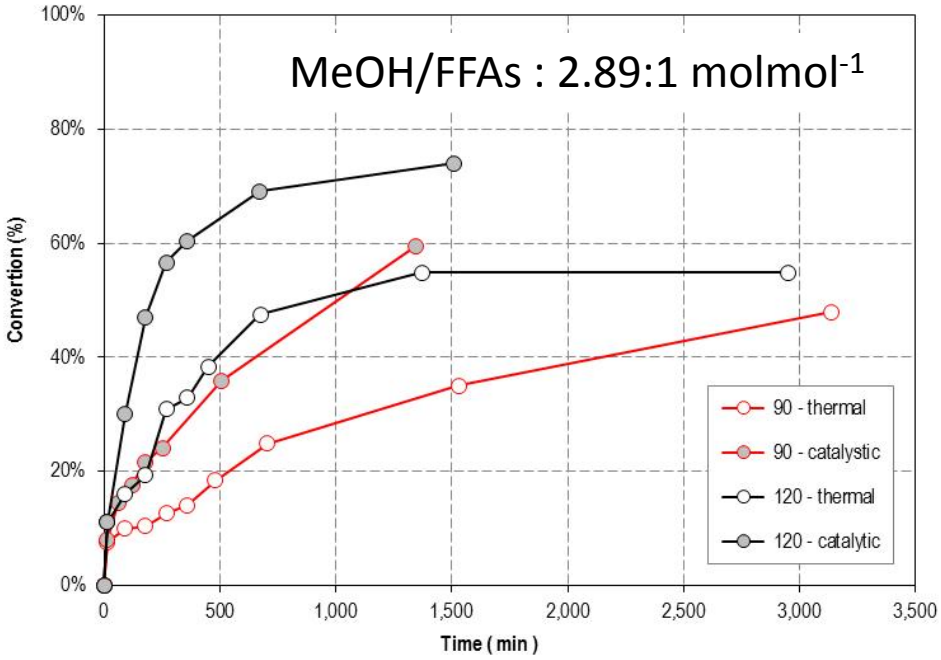


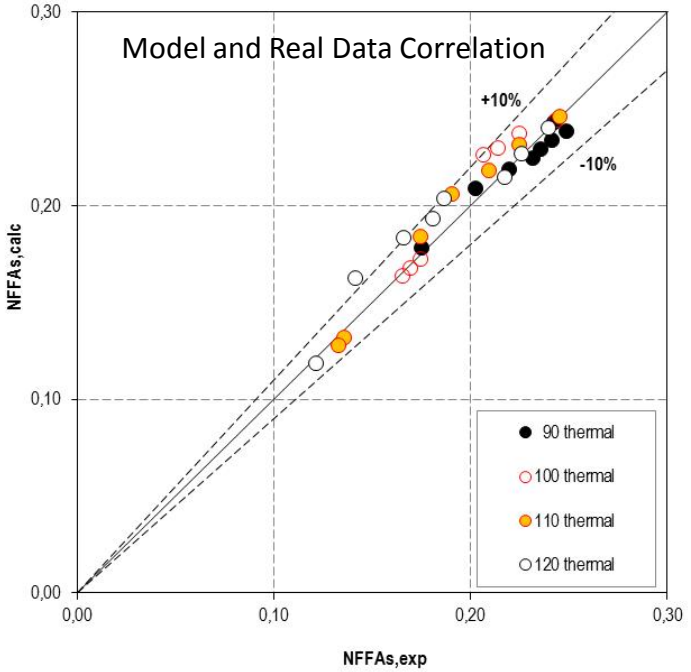
- Temperature range : 90 - 120 ^{o}C
- Free fatty acids mixture : 38.1 wt. %
- Methanol / FFAs molar ratio : 6.6/1 molmol^{-1}
- Reaction time : up to 50 h

Temperature T (^{o}C)	Initial acidity (%)	Final acidity (%)	Keq
120	38.1	4.59	1.1994
110	38.1	4.78	1.1091
100	38.1	5.58	0.8638
90	38.1	7.44	0.5269

Batch Reactor
Equilibrium constant

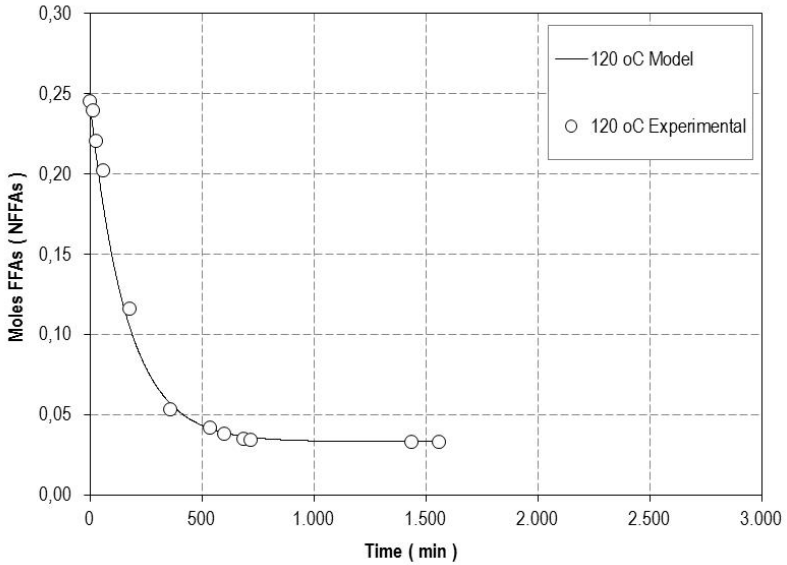


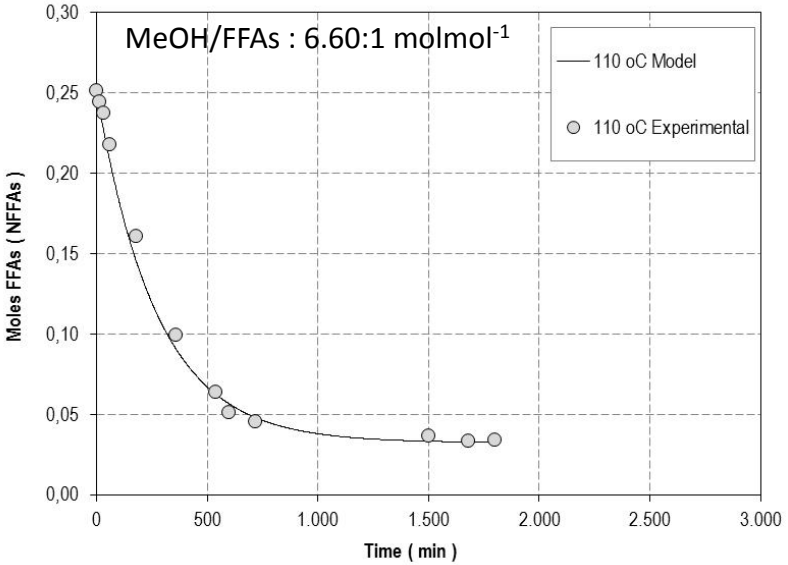


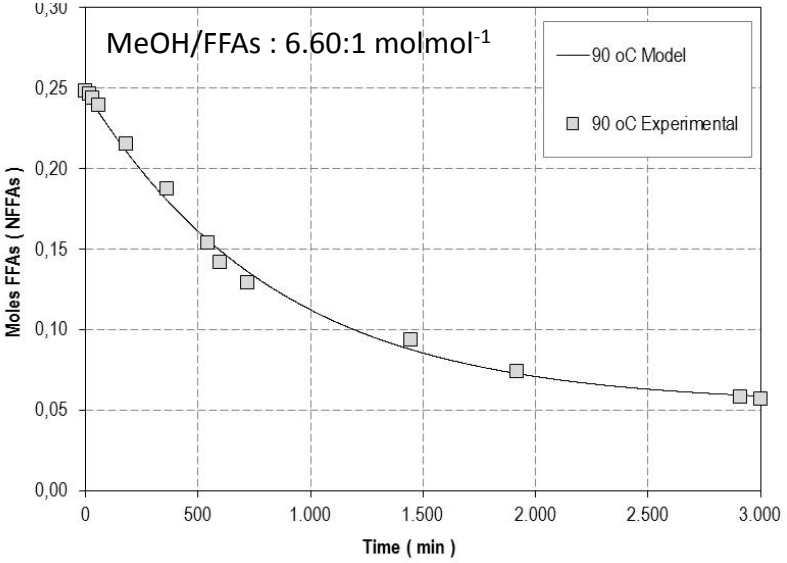


- Significant catalytic effect of free fatty acids
- Very good mathematical model fitting with the use of reverse reactions

MeOH/FFAs : 6.60:1 mol·mol^{-1}





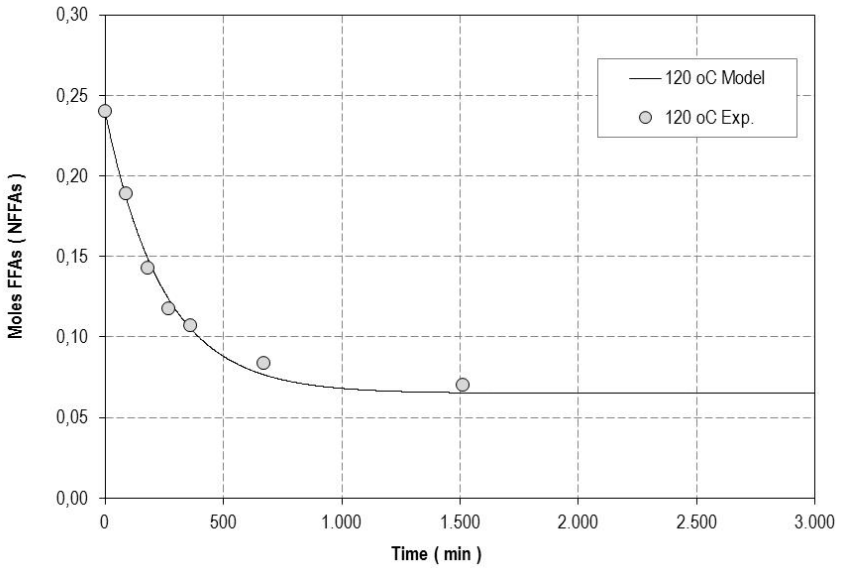


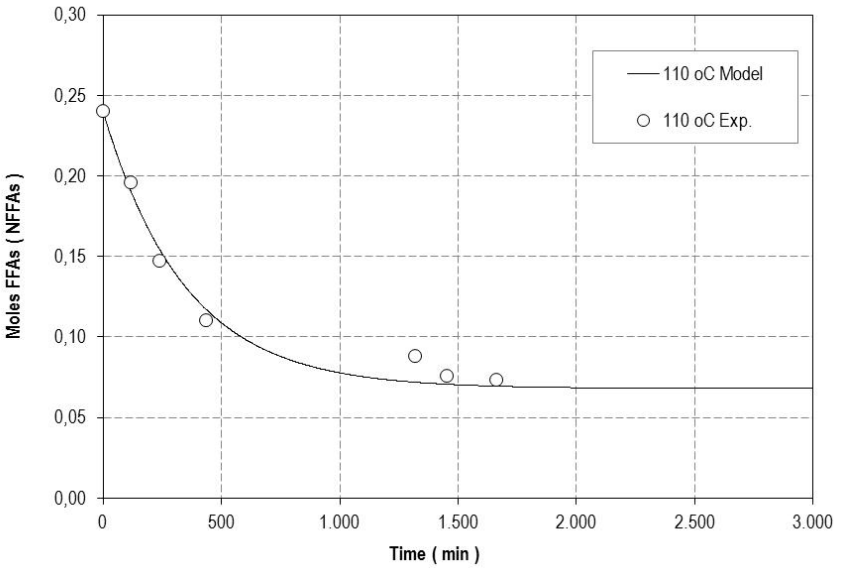
Esterification reaction rate, k_{FFA}

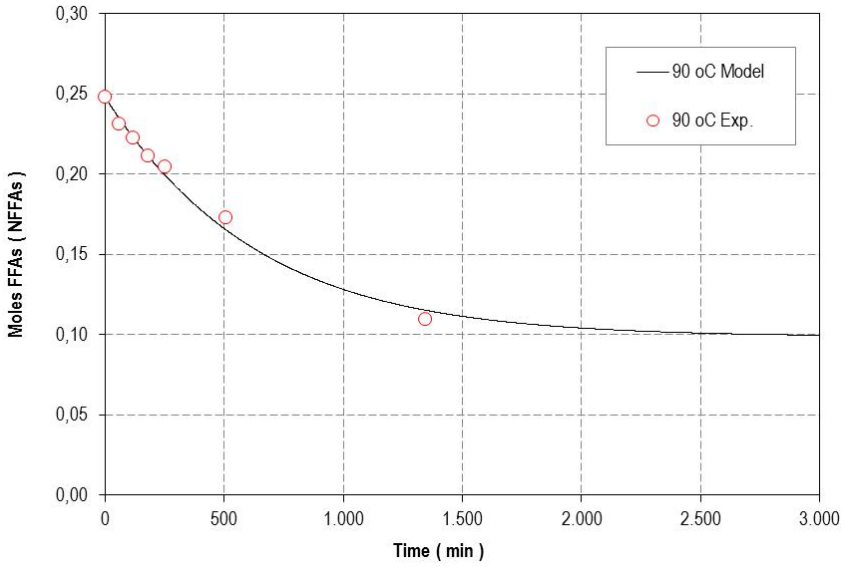
$$g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$$

T (ºC)	k_{ffas}	k_{-ffas}	Obj. Function
90	5.22	9.92	0.0141
100	11.36	13.15	0.0249
110	24.36	21.96	0.0456
120	43.36	36.15	0.0391

MeOH/FFAs : 2.89:1 mol·mol^{-1}





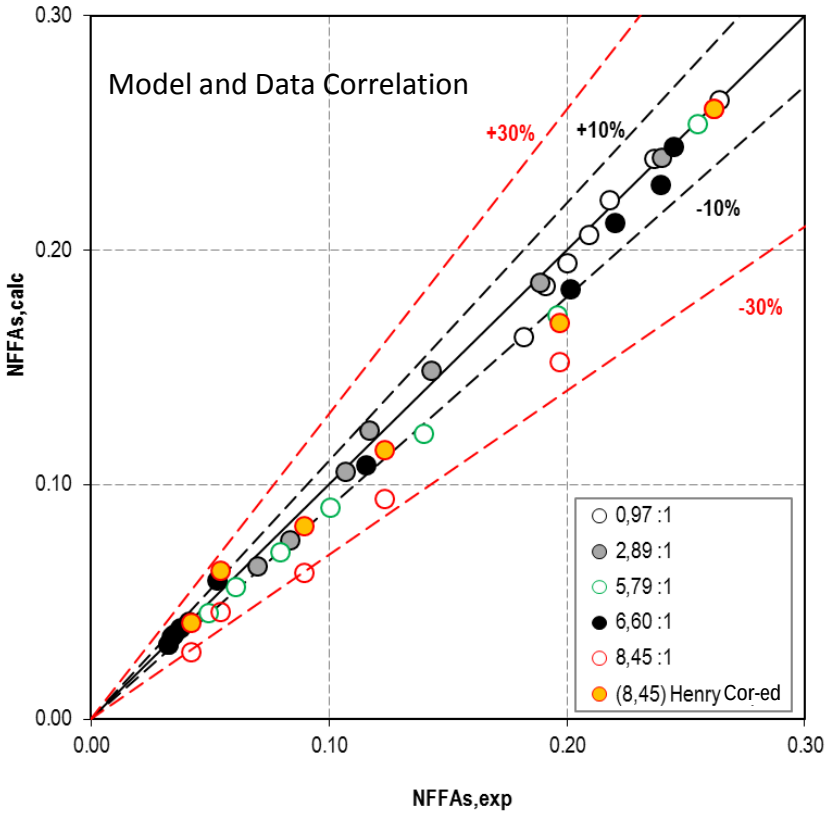


Esterification reaction rate, k_{FFA}

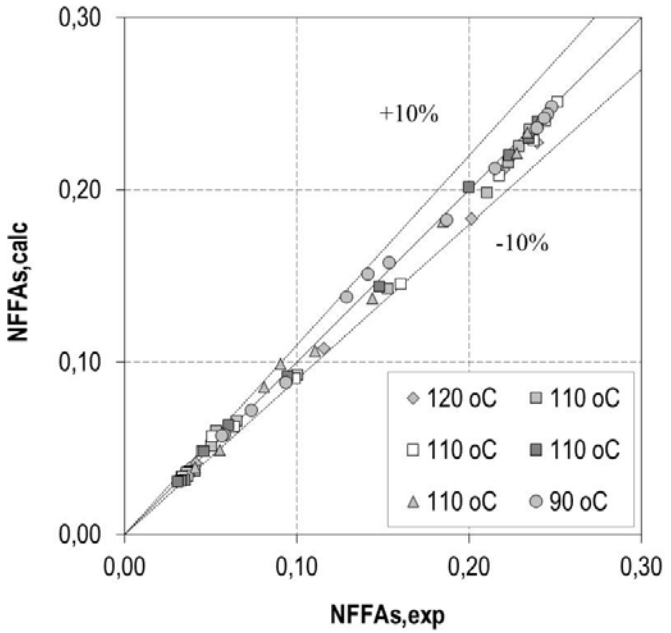
$$g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$$

T (°C)	k_{ffas}	k_{-ffas}	Obj. Function
90	9.12	17.31	0.0029
100	9.55	11.06	0.0426
110	27.60	24.89	0.0471
120	40.95	34.14	0.0375

All Methanol to Free Fatty Acids molar ratios

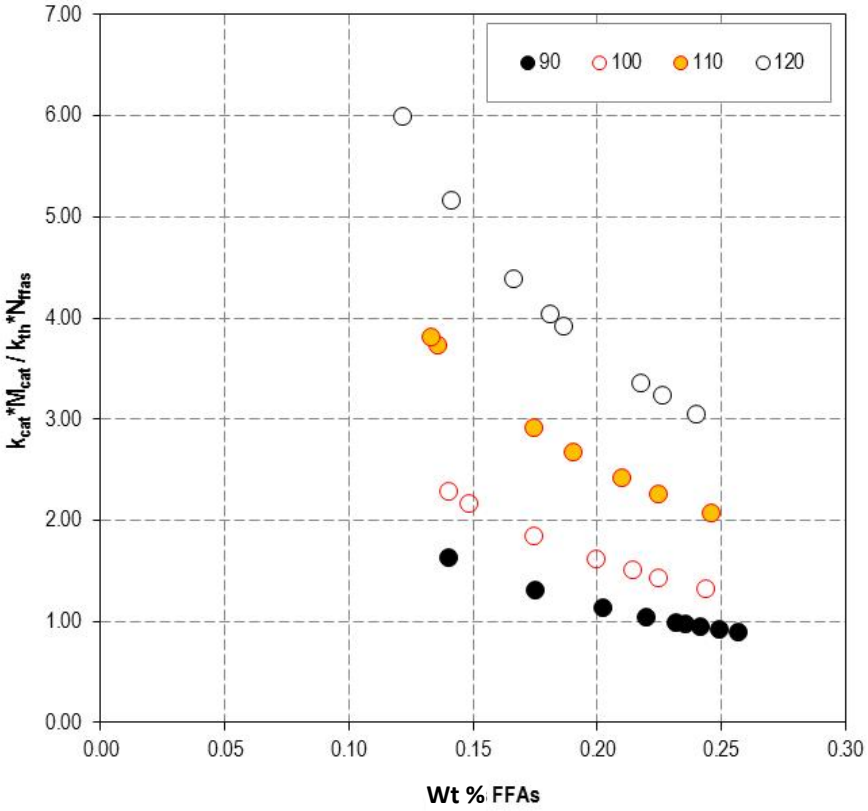


All temperatures tested



Critical point for the study of the system is the dissolved methanol

Comparison of the Catalytic and Thermal Rates



$$\frac{\text{Catalytic Rate}}{\text{Thermal Rate}} = \frac{k_{cat}\, M_{cat}}{k_{ther}\, N_{FFAs}}$$

- The lower the concentrations of Fatty Acids, the higher the catalytic rates as compared with the thermal ones
- The higher the temperature, the higher the catalytic rates as compared with the thermal ones

- Verification of the model in the case of vegetable oils with **very high FFA content**
- Two equilibrium experiments were conducted with different feedstocks and methanol-to-oil molar ratios.
- After the **1st equilibrium** step the methanol and the produced water were stripped off the mixture. Then, a measured quantity of methanol was added to the mixture (FFAs, MEs and TGs) and esterification proceeded to the **2nd equilibrium** step

Feedstock I

58 wt.% Acidity

T = 120 °C

6/1 molar ratio

	Experimental	Model Prediction	
K_e=1.1994	Acidity (wt. %)	Acidity (wt. %)	Esters (wt. %)
Initial	58.00	58.00	0.00
1º Equilibrium stage	6.13	7.62	51.40
2º Equilibrium stage	2.23	2.13	57.00
Final product	1.02	0.80	58.36

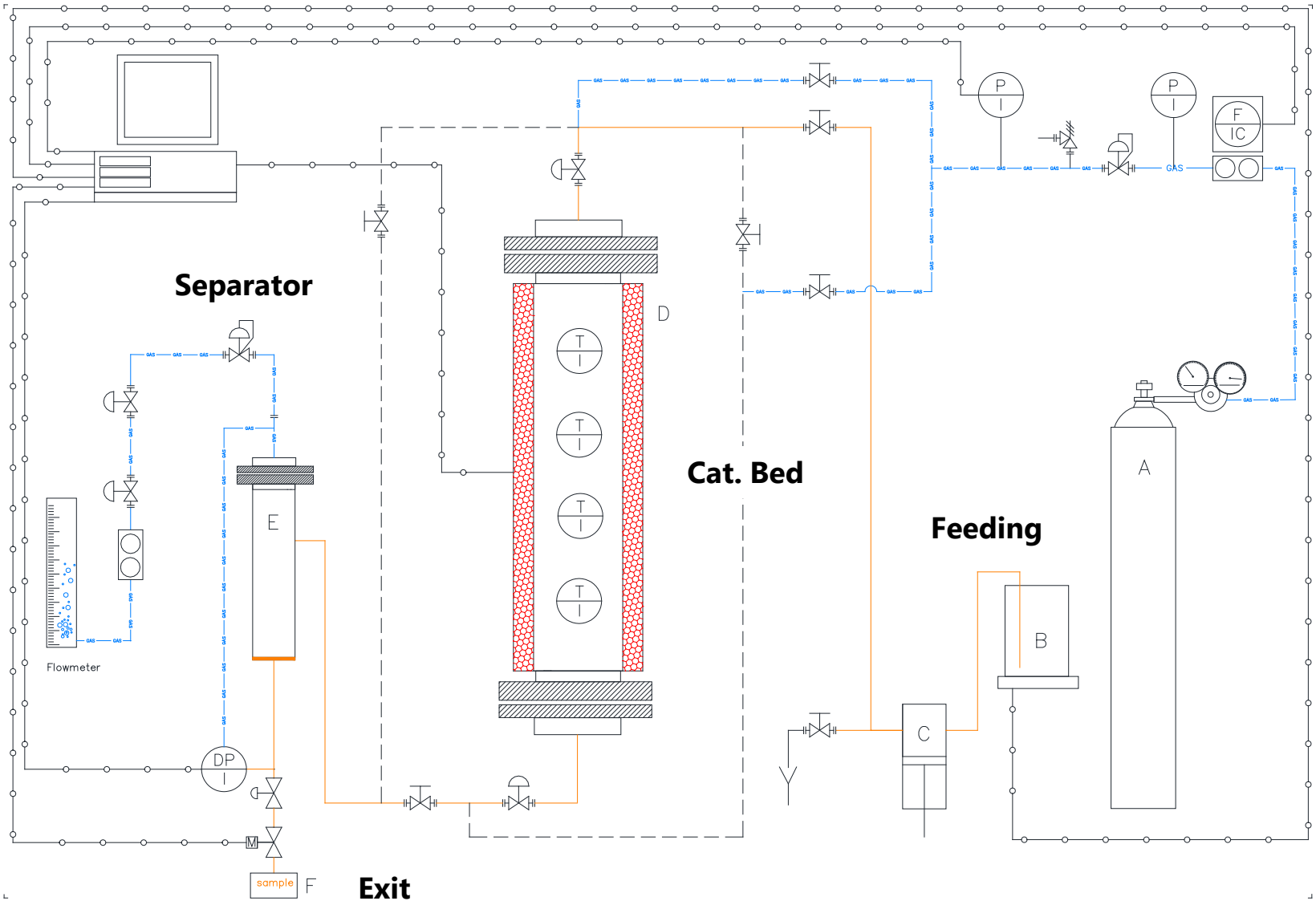
	Experimental	Model Prediction	
K_e=1.1994	Acidity (wt. %)	Acidity (wt. %)	Esters (wt. %)
Initial	100.00	100.00	0.00
1º Equilibrium stage	20.94	22.32	77.68
Final product	4.23	4.68	95.32

Feedstock II

100 wt.% Acidity

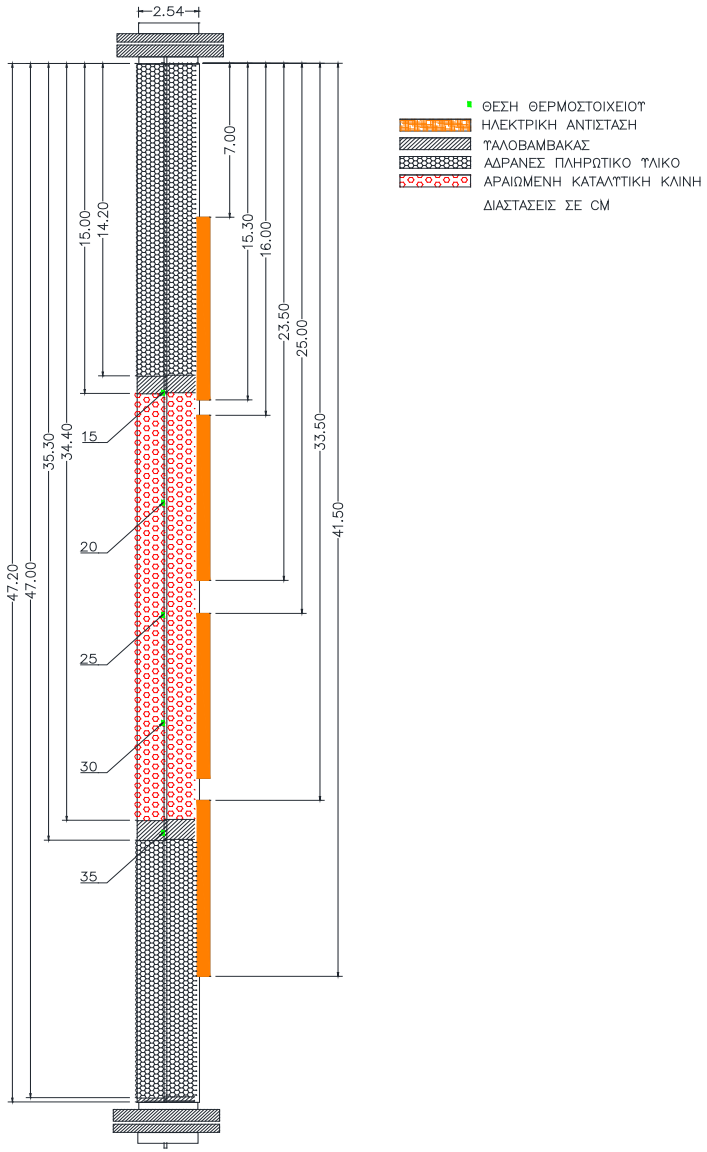
T = 120 °C

3/1 molar ratio


Separator
D
Cat. Bed
Feeding
E
A
B
C
Flowmeter
DP
P
P
F
IC
GAS
T
T
T
T
M
sample
F
Exit

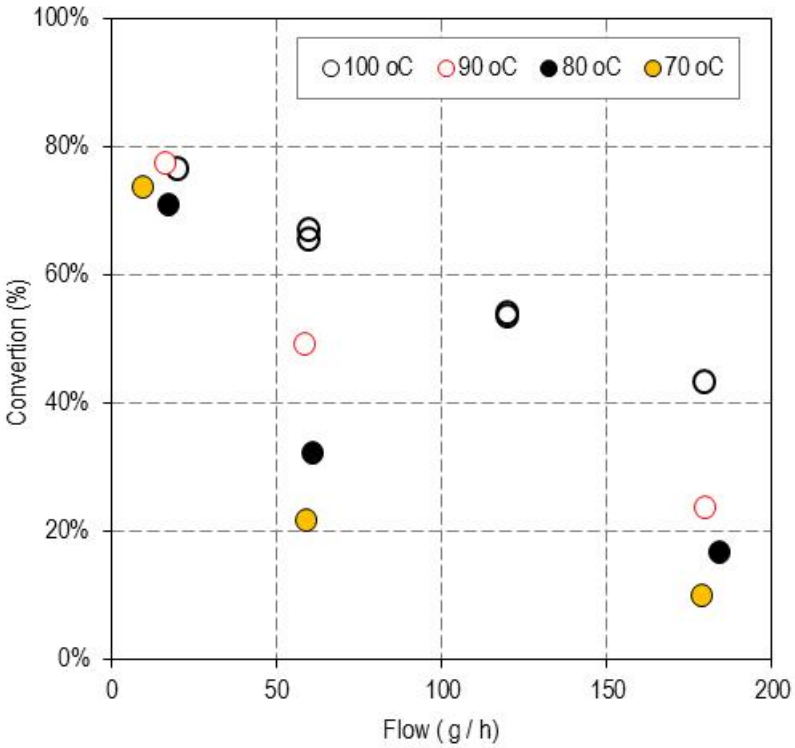
Macroporous Strong Acid Resin Catalyst Purolite CT-275

- Polystyrene Sulfonic Acid
- Polymer structure : Macroporous polystyrene crosslinked with divinylbenzene
- Total acid capacity : 5,2 eq H^+ / kg
- Particle Diameter range : 0,65 – 0,90mm
- Specific surface area : 20 - 40 m^2/g
- Specific gravity : 1.2 g/mL
- Pore volume : 0.4 - 0,6 (mL/g)
- Mean pore diameter : 400 - 700 Å
- Temperature limit : 140 ^oC



Catalytic Bed

- **Catalyst : 20 g**
- Carborundum (SiC) : 105 g
- Diluent diameter : 0.25 mm
- Bed length : 19.4 cm

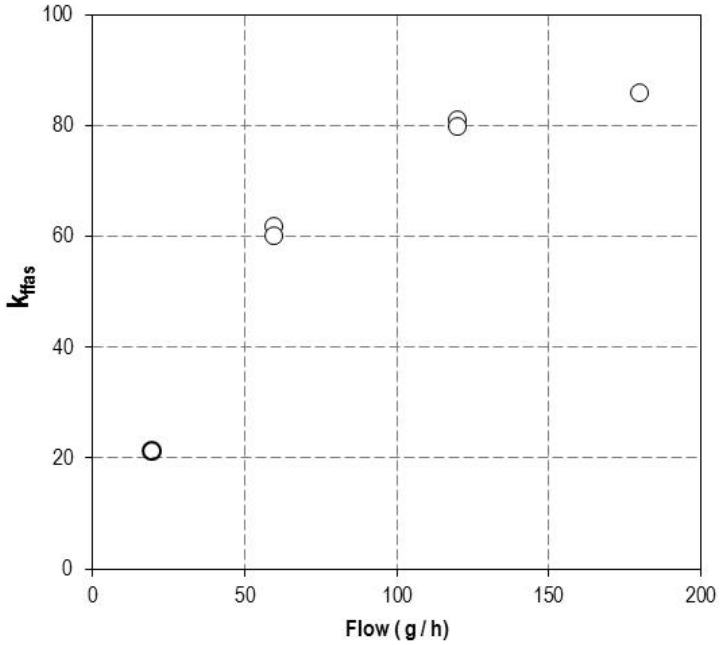


- Temperature range : 70 - 100 ^{o}C
- Feedstock : acid cotton seed oil FFAs = **2.98 wt. %**
  acid sunflower oil FFAs = **3.00 wt. %**
- Moral Ratio : MeOH / FFAs = 10:1 molmol^{-1}

- **Satisfactory catalytic resin activity**
- **Free Fatty Acids conversion from 15% to 80%**

- Model using **ONLY** the reversible Esterification reaction
  - Reactor flow model : Plug flow
  - Free Parameter for fitting : the Esterification Reaction rate Constant, k_{ffas}
  - Significant variation of the Reaction Rate Constant with flow rate

T = 100 °C
Specific reaction rates



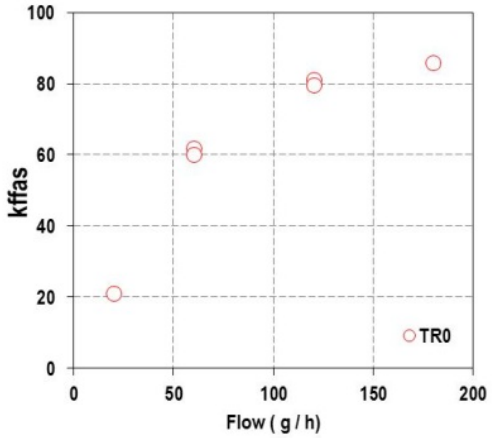
Check for equilibrium

No	Flow	Initial Acidity	Final acidity	$F_{MEs} \times F_{H_2O} / F_{FFAs} \times F_{MeOH}$
	g/h	(%)	(%)	K_{eq}=0,8638
6	120.0	2.912	1,34	0,09999
7	60.0	2.912	0,96	0,20377
8	60.0	2.912	1,01	0,19046
9	20.0	2.912	0,69	0,35779
10	120.0	2.912	1,36	0,09633
11	180.0	2.912	1,66	0,05478

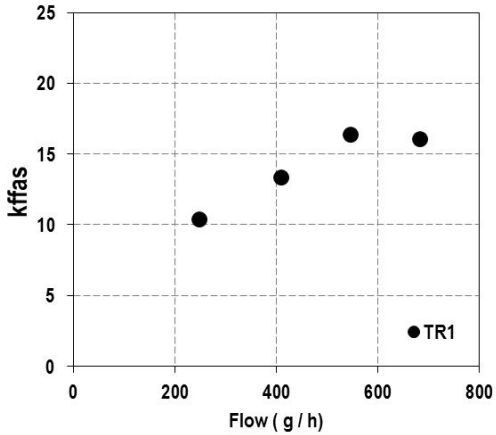
	This Study	LIT 1*	LIT 2*
Reactor Code	TR0	TR1	TR2
Catalyst	Purolite CT-275	Relite CFS	Relite CFS
Total acid capacity	5,2 meq H+ / g	3,6 meq H+ / g	3,6 meq H+ / g
Mean particles diameter	0,77 mm	0,7 mm	0,7 mm
Bed length - L	19,4 cm	18,0 cm	70,0 cm
Bed diameter D_R	2,5 cm	1,0 cm	2,5 cm
Ratio L/D_R	7,76 cm	18,0 cm	28,0 cm
Catalyst mass	20,0 g	5,0 g	196,0 g
Μάζα αραιωτικού	105,0 g	9,0 g	356,0 g
Flow	20 - 180 g / h	130 - 700 g / h	800 - 3.500 g / h
Free fatty acids Input	2,91 - 3,03 %	51,0 %	41,0 - 47,0 %
Molar ratio MeOH : FFAs	10:1	8:1	10:1
Space Velocity (WHSV)	1,0 - 9,0 h^{-1}	26,0 - 140,0 h^{-1}	4,1 - 17,9 h^{-1}

** Ind. Eng. Chem. Res. 2007, 46, 5113-5121*

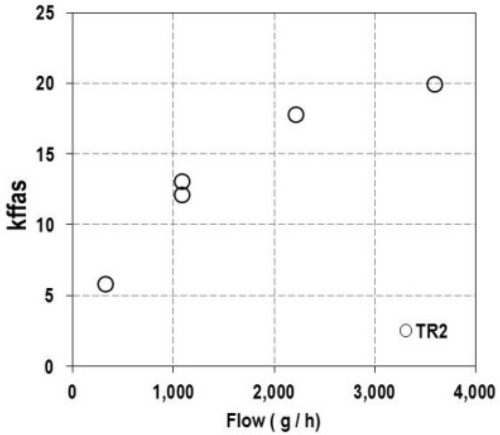
This Study



LIT 1/ TR1



LIT 2 / TR2



FIXED BED TUBULAR REACTOR

- Homogeneous mixture, methanol full dissolved to oil (d mixture = constant)
- Isothermal reactor – reaction in liquid phase
- Plug Flow Operation

TRIGLYCERIDES HYDROLYSIS REACTION

- The reaction was considered as single stage

$$TGs + 3H_2O \underset{H^+}{\overset{H^+}{\rightleftharpoons}} 3FFAs + GL$$

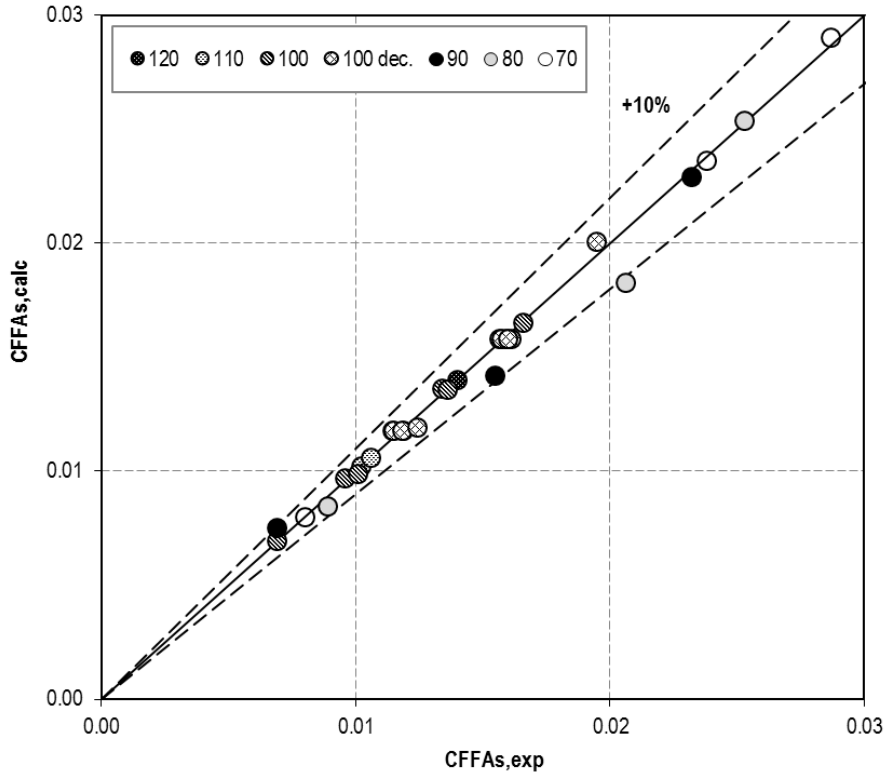
$$\left(-r_{TG}\right)_{cat} = \left(k_{tg,cat} C_{TG} C_{H_2O} - k_{-tg,cat} C_{FFA} C_{GL}\right)$$

SINGLE REACTION FIRST ORDER WITH RESPECT TO EACH REACTING COMPONENT

$$\frac{dF_{FFA}}{dz} = -\left(-r_{FFA}\right)_{th} \times A \times \varepsilon_L - \left(-r_{FFA}\right)_{cat} \times A \times \varepsilon_{cat} + \left(-r_{TG}\right)_{cat} \times A \times \varepsilon_{cat}$$

- Use of equilibrium constants from batch reactor
- A : reactor surface, ε_L: free reactor volume, ε_{cat} :catalytic bed porosity

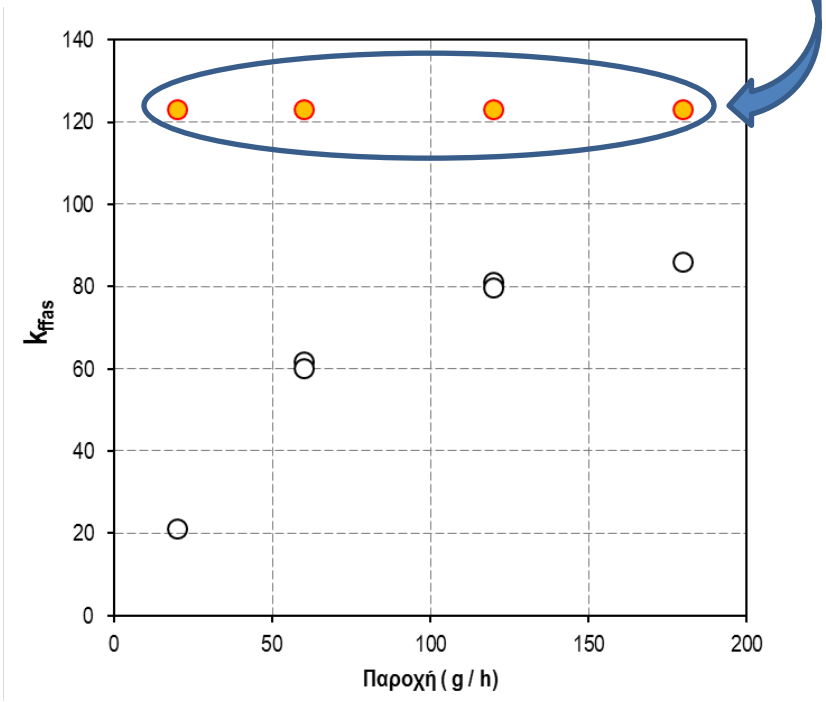
- Fitting with Mathematical model using both FFAs esterification and TGs hydrolysis reactions
  - Excellent fitting to experimental values



Temperature	k_{ffas}	k_{-ffas}	k_{tgs}	k_{-tgs}
°C				
120	611	510	1.165	32.509
110	305	275	196	14.826
100	123	142	35,5	6.660
90	62	118	1,3	678
80	38	90	0,3	207
70	27	88	0,2	185

All ks in : $g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$

Esterification and TG Hydrolysis



T = 100 C

k_{ffas} = 123, 6 $g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$ k_{-ffas} = 143,1 $g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$

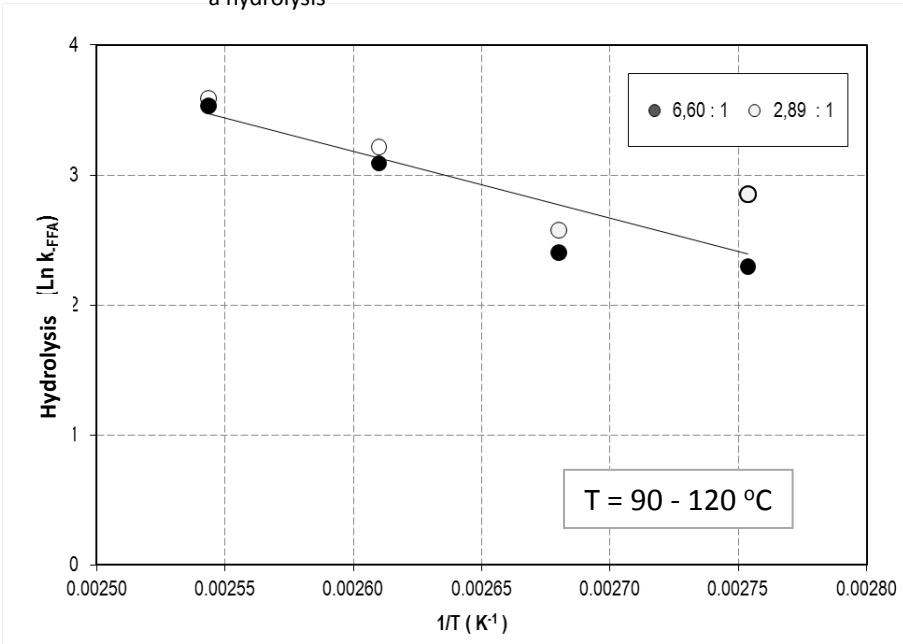
K_{tgs} = 35,5 $g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$ k_{-tgs} = 6660 $g^2 \times g_{cat}^{-1} \times mol^{-1} \times min^{-1}$

Esterification and TG Hydrolysis
Model Predictions

Flow	Initial acidity	Experiment acidity	Predicted acidity
g/h	(%)	(%)	(%)
120.0	2.912	1,34	1,3599
60.0	2.912	0,96	0,9685
60.0	2.912	1,01	0,9857
20.0	2.912	0,69	0,6939
120.0	2.912	1,36	1,3595
180.0	2.912	1,66	1,6523

ESTERIFICATION MODEL

- $E_{a\ esterification}$: 75 kJ×mol^{-1}
- $E_{a\ hydrolysis}$: 43 kJ×mol^{-1}



Literature data :

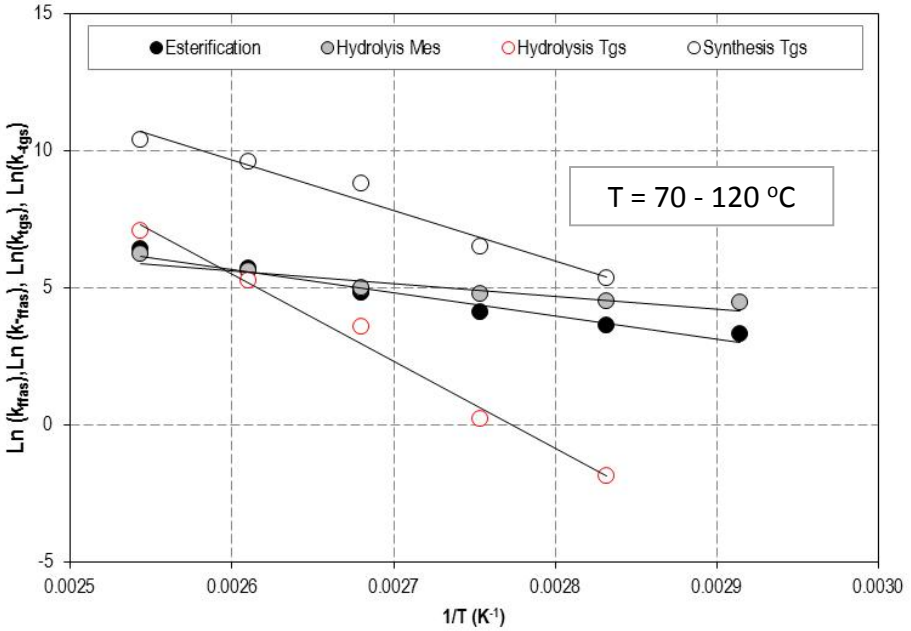
- $E_{a,ester.=}$ 73,11 kJ×mol^{-1}, $E_{a,hydrol.}$ = 36,70 kJ×mol^{-1}
  Tesser, et al., 2005* (Relite CFS)

- $E_{a,ester.}$ = 72,23 kJ×mol^{-1}
  Steinigeweg & Gmehling, 2003** (Amberlyst 15)

** Ind. Eng. Chem. Res. 2007, 46, 5113-5121*
***CEP: Process Intensification, 2004, 43(3), 447-456*

ESTERIFICATION + TG HYDROLYSIS MODEL

- $E_{a\ esterification}$: 71 kJ×mol^{-1}
- $E_{a\ hydrolysis}$: 38 kJ×mol^{-1}
- $E_{a\ glycerides\ hydrolysis}$ $^{\#}$: 264 kJ×mol^{-1}
- $E_{a\ glycerides\ synthesis}$: 153 kJ×mol^{-1}

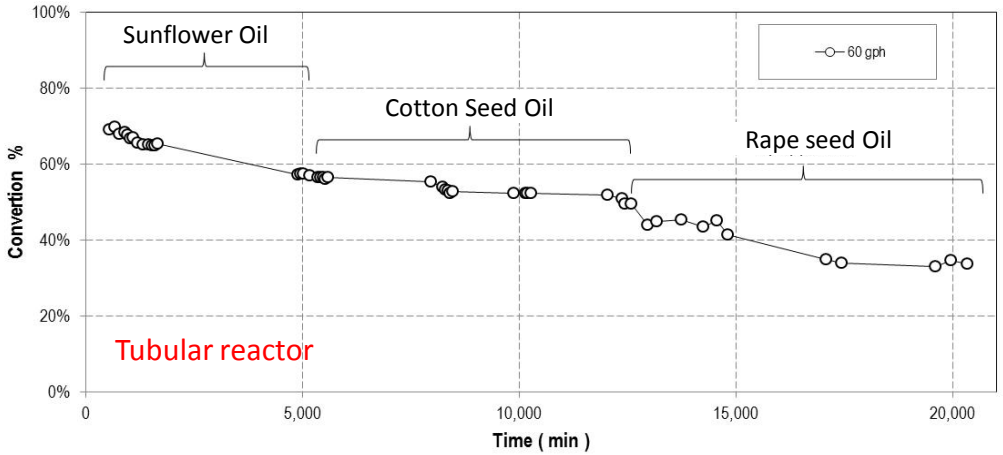


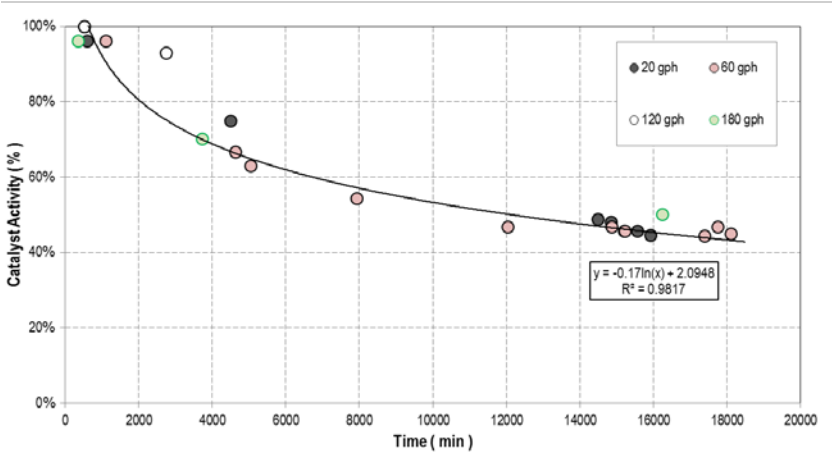
Literature data :

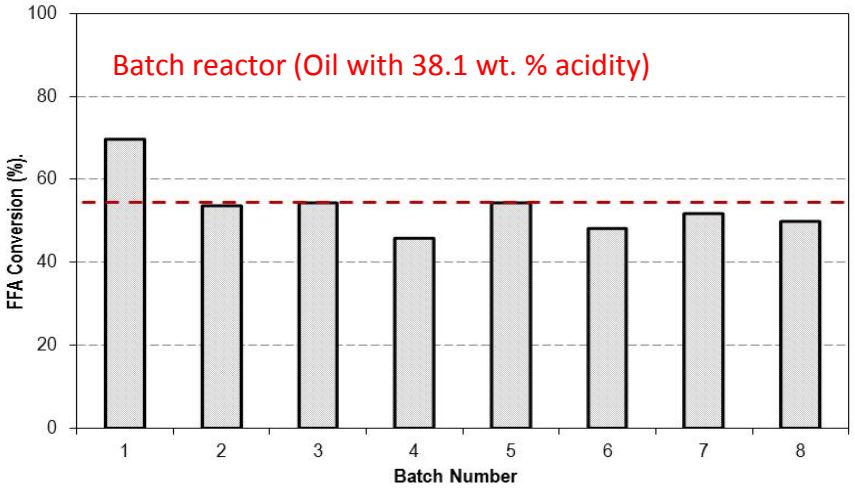
- $^{\#}$ $E_{a,glyc.\ hydrol}$ = 250 kJ×mol^{-1}
  Yow & Liew, 1999*** (Purolites)

***JAOCS, Vol. 76, no. 4 (1999)

Catalyst activity β : $\beta(t) = \frac{k_{t,exp}}{k_{t=0}}$







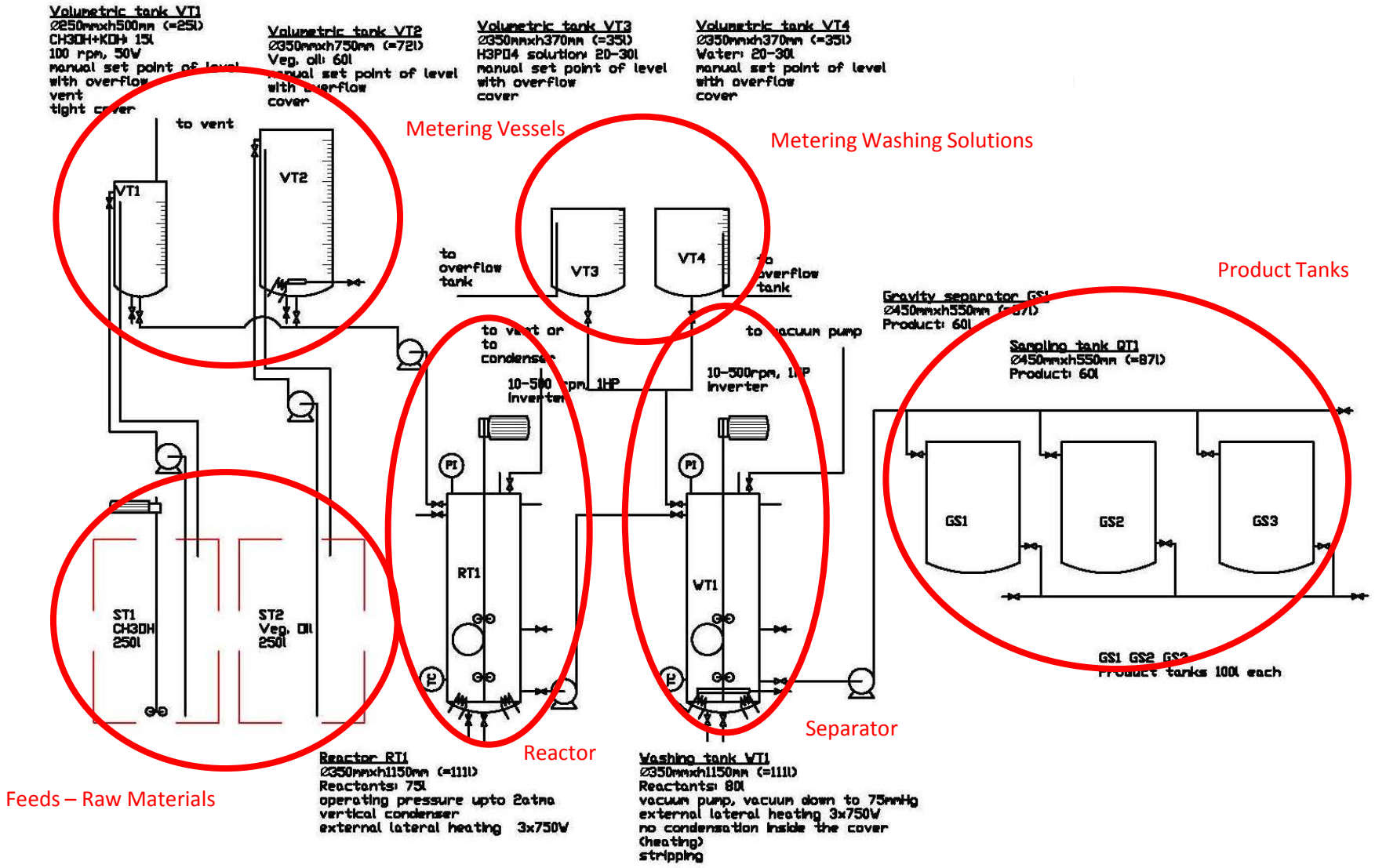
Reactor Volume: 20lt
Temperature: 62 – 64 ^{o}C
Catalyst: 1 wt.% KOH
Alcohol: 6/1 MeOH

FEED STOCKS

Refined Soybean oil
Neutralized Cottonseed oil

Glycerol Removal

Biodiesel Collection


Volumetric tank VT1
Ø250mmxh500mm (=25l)
CH3OH+KOH 15l
100 rpm, 50W
manual set point of level
with overflow
vent
tight cover
Volumetric tank VT2
Ø350mmxh750mm (=72l)
Veg. oil: 60l
manual set point of level
with overflow
cover
Volumetric tank VT3
Ø350mmxh370mm (=35l)
H3PO4 solution: 20-30l
manual set point of level
with overflow
cover
Volumetric tank VT4
Ø350mmxh370mm (=35l)
Water: 20-30l
manual set point of level
with overflow
cover
Metering Vessels
Metering Washing Solutions
Product Tanks
to vent
VT1
VT2
VT3
VT4
to overflow tank
to overflow tank
to vent or to condenser
to vacuum pump
10-500rpm, 1HP inverter
10-500rpm, 1HP inverter
PI
PI
RT1
WT1
Gravity separator GS1
Ø450mmxh550mm (=87l)
Product: 60l
Sampling tank ST1
Ø450mmxh550mm (=87l)
Product: 60l
GS1
GS2
GS3
GS1 GS2 GS3
Product tanks 100l each
ST1
CH3OH
250l
ST2
Veg. Oil
250l
Reactor RT1
Ø350mmxh1150mm (=111l)
Reactants: 75l
operating pressure upto 2atma
vertical condenser
external lateral heating 3x750W
Washing tank WT1
Ø350mmxh1150mm (=111l)
Reactants: 80l
vacuum pump, vacuum down to 75mmHg
external lateral heating 3x750W
no condensation inside the cover
(heating)
stripping
Reactor
Separator
Feeds – Raw Materials

- Operation since February 2005
- Capacity : 70 kg Biodiesel/Batch or 1 barrel/shift
- Oils Processed :
  Cottonseed oil, sunflower oil, soybean oil, palm oil, rapeseed oil
- Biodiesel according to **EN**-14214
- Easily adapted to new biodiesel technologies

Conclusions

- Esterification of FFAs in the Oil matrix appear to be a viable solution for the treatment of acidic oils with FFAs > 1.5 wt %
- Homogeneous Acid Esterification is an effective process for simultaneous Esterification and Transesterification but the use and consumption of the catalyst is a serious drawback
- Esterification processes catalyzed by solid super acid catalysts appear to be the most promising and sustainable processes
- Esterification reactions produce water that hydrolyzes also the Triglyceride Molecules of the matrix oil
- High FFAs conversions can be achieved with removal of the produced water

Acknowledgements

Contributors for this presentation :

Collaborators

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GF Energy