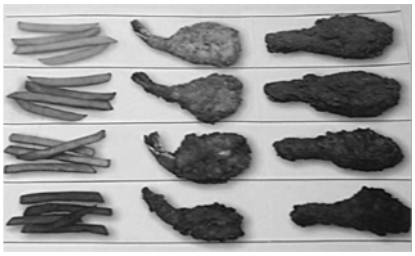
Natural and Synthetic Additives for an Optimized Frying Process

Christian Gertz, Hagen (Germany)
Official Institute of Chemical and Food Analysis
cgertz@cua-hagen.de



Criteria for Good Frying Oils

- **Appealing appearance** of the fried food
- Aroma and **flavor**
- **Texture**
- **Mouth feel** (no a waxy taste of palm oil and hardened fats)
- **Aftertaste**
- **Shelf life** (loss of texture or development of rancidity during storage)

Technical criteria:
High oxidative stability
High thermal stability

Economic Criteria
availability
costs

Nutritional Aspects
low trans (<2 %)
low in saturated fats
low in linolenic acid (<3%)

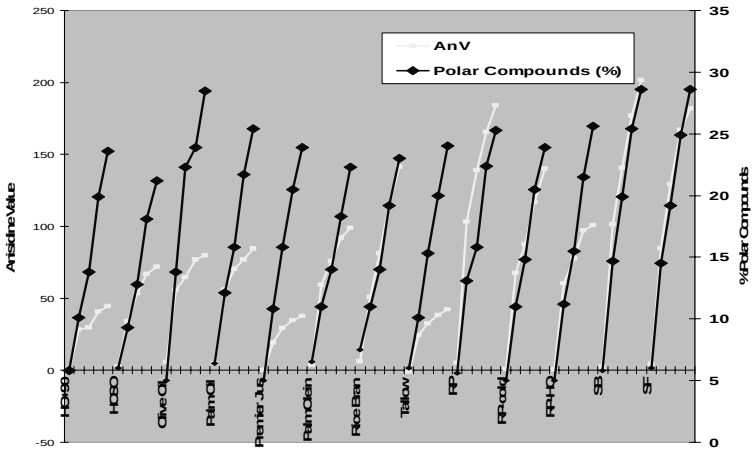
Legislative Aspects

Analytical Specifications for Frying Fats

• Taste, Flavor	Bland
• Free fatty acids (wt%)	<0.05
• Monoglyceride (wt%)	<0.4
• Peroxide value (wt%)	<1.0
• Anisidine Value	<4.0
• Phosphorus (mg/kg)	<0.5
• Iron/Copper (mg/kg)	<0.5
• **Oxidative Stability**	**high**
• **Heat Stability**	**high**
• Linolenic Fatty Acids	<2-3 %

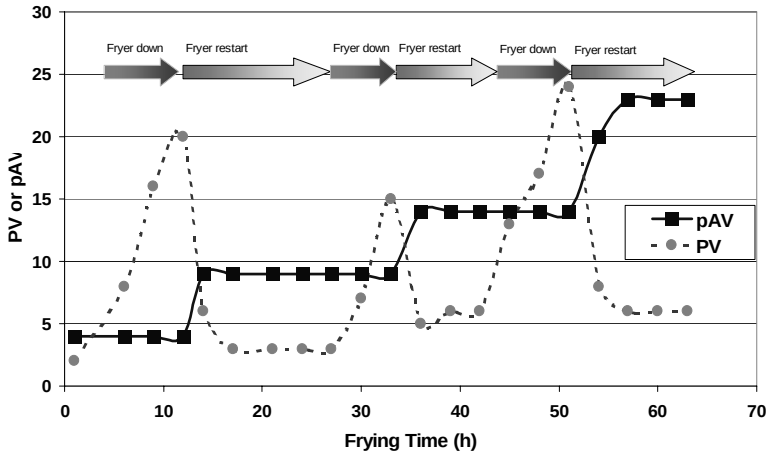
Variations of AnV and Polar Compounds during Discontinous Frying

(16hrs, 180 °C)

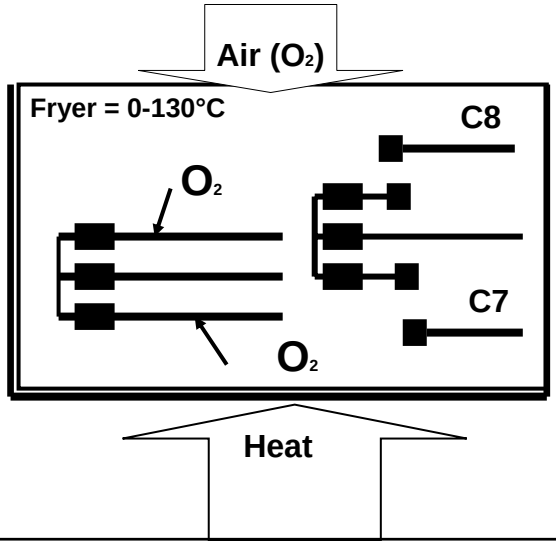


Peroxide value(PV) and *para*-andisidine value(pAV) in fryer oil during frequent shutdowns

(Data Source: M.Gupta Frying Technology and Practices(2004) page 74



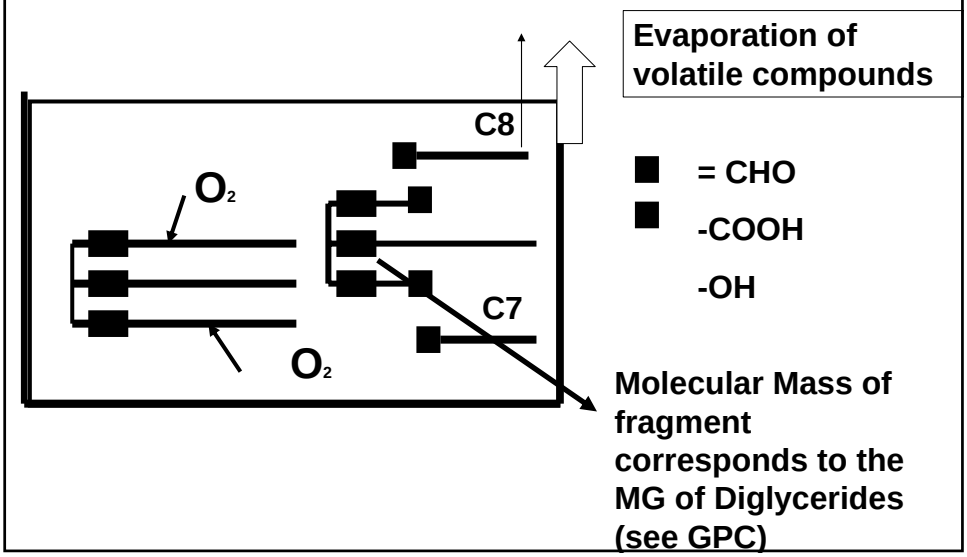
Autoxidation/Oxidation during Deep Frying



Boiling point of fatty acids

C4:0	**165 °C**
C5:0	**186 °C**
C6:0	**203 °C**
C7:0	**223 °C**
C8:0	240 °C
C9:0	253 °C
C10:0	270 °C
C18:0	383 °C
C18:1	>290 °C

Autoxidation / Oxidation during Frying Process



Oxidative stability tests

- **Based on Oxygen Consumption**

  Oxygen Bomb (Oxipress™)

  Oxidograph™

  Sylvester Test

- **Generation of Oxidation Products**

  Schaal Oven Test

  Swift Test

  (Active Oxygen Method (AOM))

  Rancimat (Conductivity)

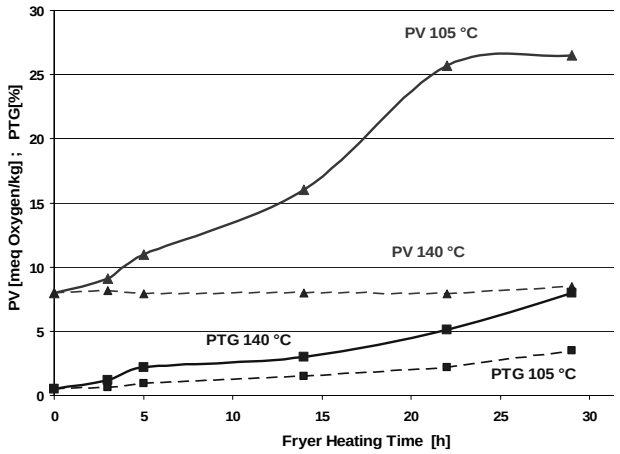
  Oxidative Stability Index (OSI)

Practical Arguments for Two Different Routes of Fat Degradation during Deep Frying

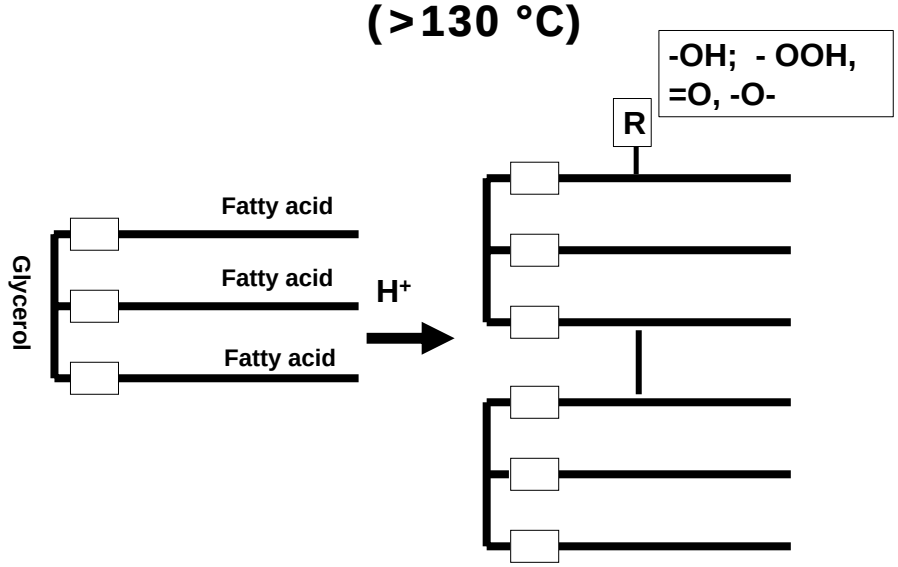
- Frying of food prolonges shelf life of frying fats and oils
- The stability of frying fats does not correlate with their fatty acid composition
- Dilution with fresh oil do not reduce heating time of frying fats
- Different oxidative stability effects of some natural antioxidants and AP at ambient temperature and frying temperature
- Antiradical power (ARP) decreased faster when oil was heated

Changing of PV and PTG during heating of sunflower oil

at 105 and 140 °C



Polymerisation during Deep Frying (>130 °C)



Analytical Procedure of OSET-Test

(Gertz, Kochhar 2000)

20 g sample (oil) into a 100ml-glass vessel (40 mm diameter)

1.0 g silica gel (conditioned with 10 % water)

2 h at ambient temperature

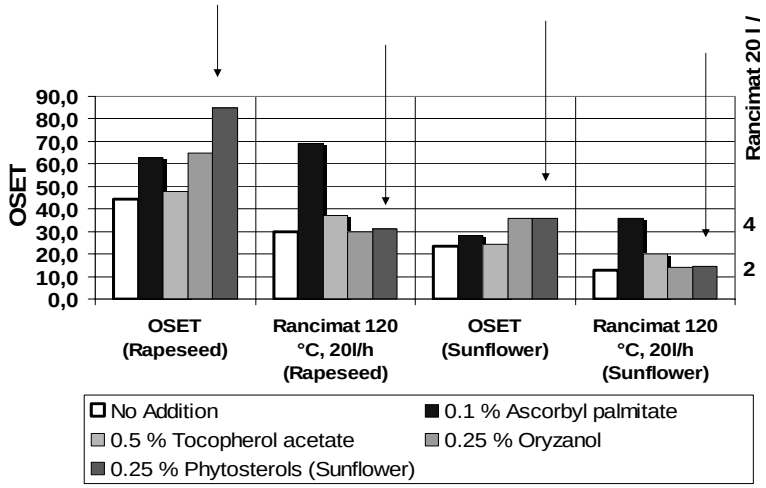
1 min treatment in a ultrasonic bath

2 h heating in an aluminium box at 170 °C

50 mg in 1 ml THF; **SEC (HPLC**) of polymerised triacylglycerols

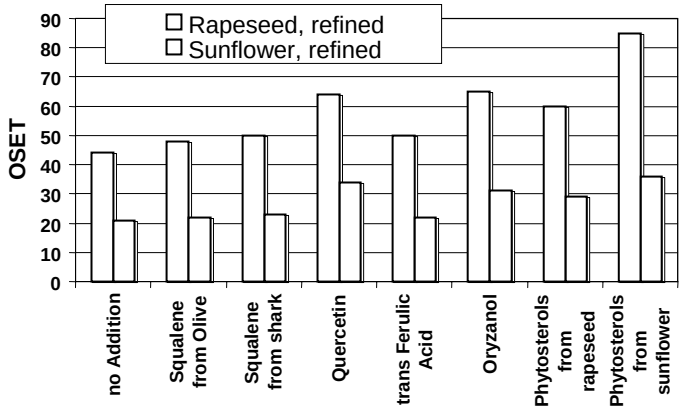
OSET= 100/ PTG (%)

Comparison OSET / Rancimat



Effectiveness of Natural antioxidants on Stability of Refined Vegetable oils

(50 mg/20 g)



Heat stability effects of sterols

(OSET-Values)

Sterolfraction (Sample no)	OSET (Rapeseed)	OSET (Sunflower)	Chole-sterol	Brassica-sterol	Campe-sterol	Stigma-sterol	beta-Sitosterol	D5-Avena-sterol	D7-Stigma-sterol	D7-Avena-sterol
St1	83,3	37,0	0,1	3,3	17,9	5,4	55	1,8	9,3	2,3
St2	62,5	33,3	0,2	10,5	36,6	0,8	46,6	1,9	0,2	0,07
St3	62,5	32,3	0,03	0	7,7	1,4	80,1	0,6	0,7	0,3
St4	55,6	31,3	0,5	2,3	27,3	18,1	46,8	0,9	0,4	0,1
St5	55,6	30,3	0,4	2,1	25,3	19,6	46,8	1,3	0,4	0,2
St6	52,6	29,4	0,6	2,2	26,4	17,8	47,6	1,4	0,4	0,2
St7	52,6	28,6	0,4	2,4	27,3	19,4	46,4	0,1	0,3	0,2
St8	50,0	28,6	0,4	1,8	26,8	20,7	45,5	1,1	0,4	0,2
St9	47,6	28,6	0,5	1,5	26,5	20,7	44,9	1,3	0,4	0,2
no Addition	47,6	27,8								

Antipolymerising agents

Substance	Reaction product	Temperature (°C)
Tocopherols	Dimeric tocopheryl reaction products (C-O-C linked)	80 °C
Phytosterols	Steroloxides	100 °C
Squalene	Squalene hydroperoxides, squalene hydroxide	100 °C
Sesamolin	Sesamol, Sesamin, Sesaminol isomers	120-130 °C
Ascorbic palmitate	Dehydro-Ascorbic Palmitate Ascorbic acid	130 °C
Phytosterols	Steradienes	150 °C
Ascorbic palmitate	Dehydro-Ascorbic Palmitate	130 °C
Alpha Tocopherol	Tocopherol-Trimer (C-C linked)	160 °C
Squalene	Tetracyclo-squalene	170 °C

Stabilizing agents for deep frying fats and oils

- **< 130 °C**
  - **Antioxidants as radical scavengers**
    - Phenolic compounds forming quinones
      - (BHT, BHA, TBHQ, gamma-and delta tocopherols)
  - **Water**
- **> 130 °C**
  - **Antipolymerising agents:**
    - Compounds, forming dimeric products by proton catalysed reactions (dehydratisation)

Natural antioxidants / agents

- **Unsaponifiables isolated from**:
  - olive
  - corn
  - wheat germ
- **Extract (ethanolic, petrolether) from:**
  - rosemary
  - oregano
  - sage
  - savory
  - oat

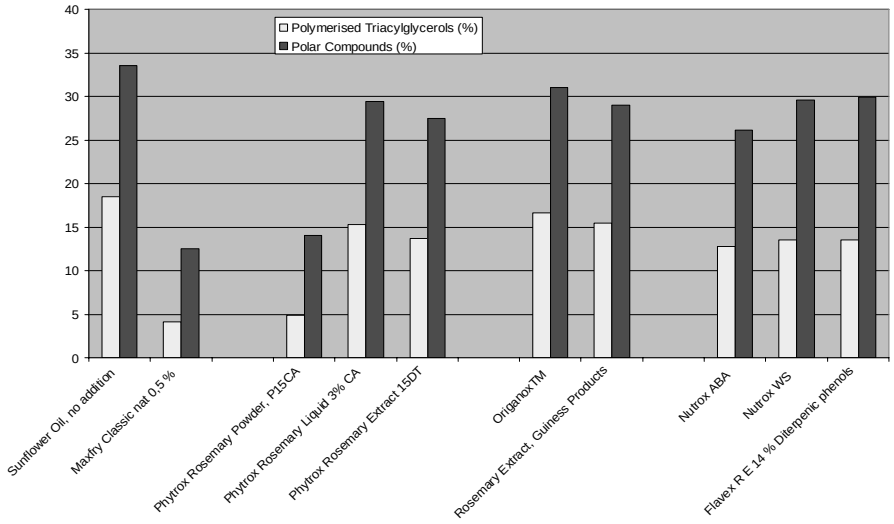
Commercially Available Frying Oil Stabilising Formulations

Guardian RE 08	Rosemary extract, E472c, E471
Guardian RE 09	Rosemary extract, Polyoxy-ethylene sorbitan monooleate, E472c, E471
Grindox 1021	ACP, Tocopherol extract, E472c, E471
Grindox 1029	ACP, E472e, E471
Oilmaster	ACP, TOC, E471, E472c, Citric acid, Water
Miroil Fryliquid	**Citric Acid, Water, Ascorbic Acid, Plant Extract**
Maxfry Classic nat	**Tocopherols, Rice bran oil, Plant Extract, E471, E472c, Citric Acid**
E900	**Dimethylpolysiloxanes**

Frying Oil Stabilising Formulations with Rosemary and Oregano

(Discontinous Frying at 180°C,16h)

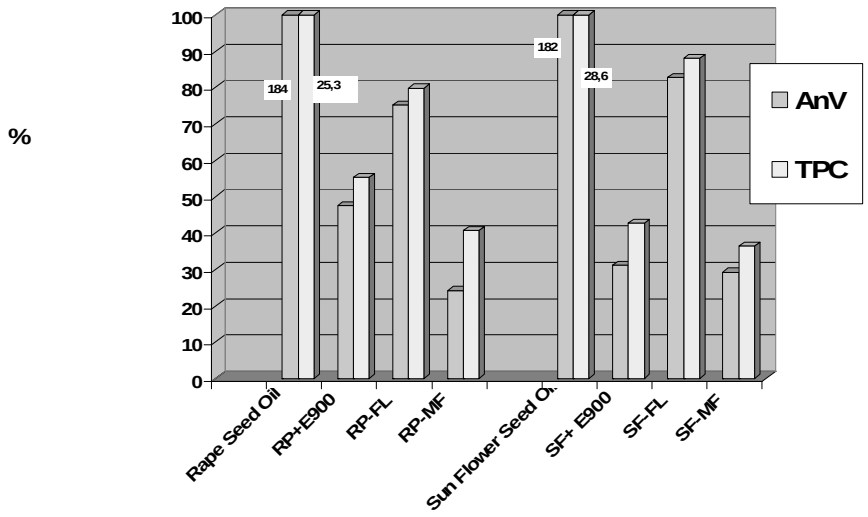
(Addition 500 mg/kg, Oil: Sunflower oil, Reference MFnat)



Reduced oil Degradation in Presence of Additives

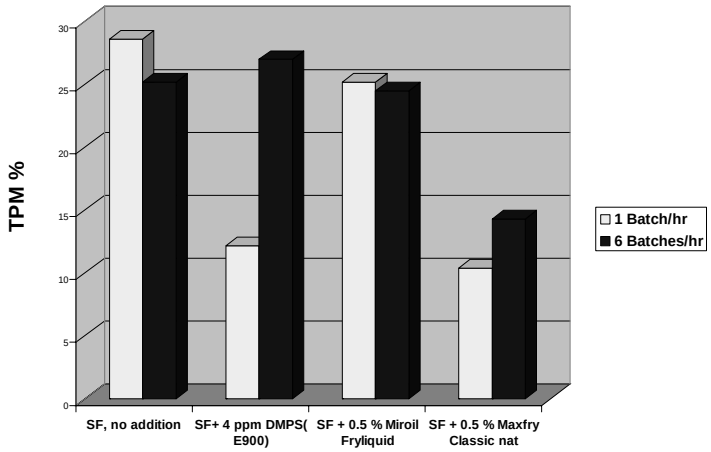
(16 hrs Discontinous Frying at 180 °C)

(DMPS=E900, FL=Miroil Fry Liquid, MF=Maxfry Classic nat)



Different effectiveness of DMPS during continous and discontinous Frying

(Sunflower Seed Oil,180 °C,16h)



Effectiveness of Additives on Heat Stability and Smoke point

	Smoke Point (°C)	OSET (180 °C), %PTAG	Ranzimat, 120 °C, hrs
Rape Seed Oil (RP)	170	2,85	2,4
RP+ 4 ppm E900	174	1,95	2,6
RP+0,5 % Mroil FryLiquid	172	2,8	2,7
RP+ 0,5 %Maxfry Classic	180	1,8	2,9
Sunflower Seed Oil (SF)	176	4,6	2,2
SF + 4 ppm E900	191	1,8	2,1
SF+ 0,5 % Fryliquid	190	4	2,3
SF+ 0,5 % Maxfry Classic	196	1,75	2,5

Conclusions

- Oxidative and heat stability are different properties
- OSET Test is a good tool to estimate the oxidative and heat stability of vegetable oils.
- Rancimat gives a good information on oxidative stability
- Peroxid value and FFA are no appropiate analytical criteria to monitor the fat degradation at elevated temperature.
- Anisidine Value should be used as quality criteria of fried products with longer shelf life.
- Addition of DMPS has a certain effect only in discontinous frying. It causes an off-flavor due to agglomeration of short fatty acids in the frying oil
- Frying oils with better fatty acid profiles and a better combination of natural agents help to stabilise deep frying oils and to produce high quality fried products