PROCESSING OF LIPIDS AND FREE FATTY ACIDS IN BIODIESEL RAW MATERIALS TO HYDROCARBON BASED FUELS

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Agenda

- Objectives
- Sodium salt of hexadecanoic acid as model compound for conversion of FFA & lipids
- Analysis of products and mechanisms
- Pilot scale results from conversion of FFA & lipids
- Markets for Products
- Conclusions

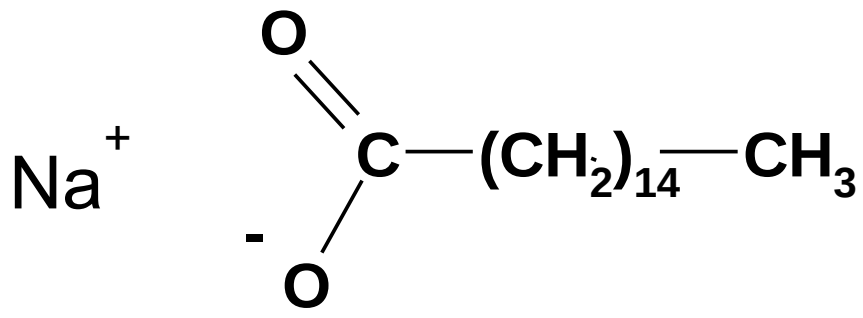
Primary Objectives

- **Feasibility study to find new markets both for lipids derived from organic residues and free fatty acids (FFA) removed from vegetable oils:**

  Approach: Explore on site production of hydrocarbons:

  - Thermal decarboxylation of sodium salt of hexadecanoic acid and FFA in the presence of sodium carbonate (Na_2CO_3)
  - Thermal decarboxylation of waste lipids in the presence of ashes from fire wood or sodium carbonate (Na_2CO_3)
  - Characterize and process products formed in view of suitability for hydrocarbon based fuels or feedstock in chemical industry.

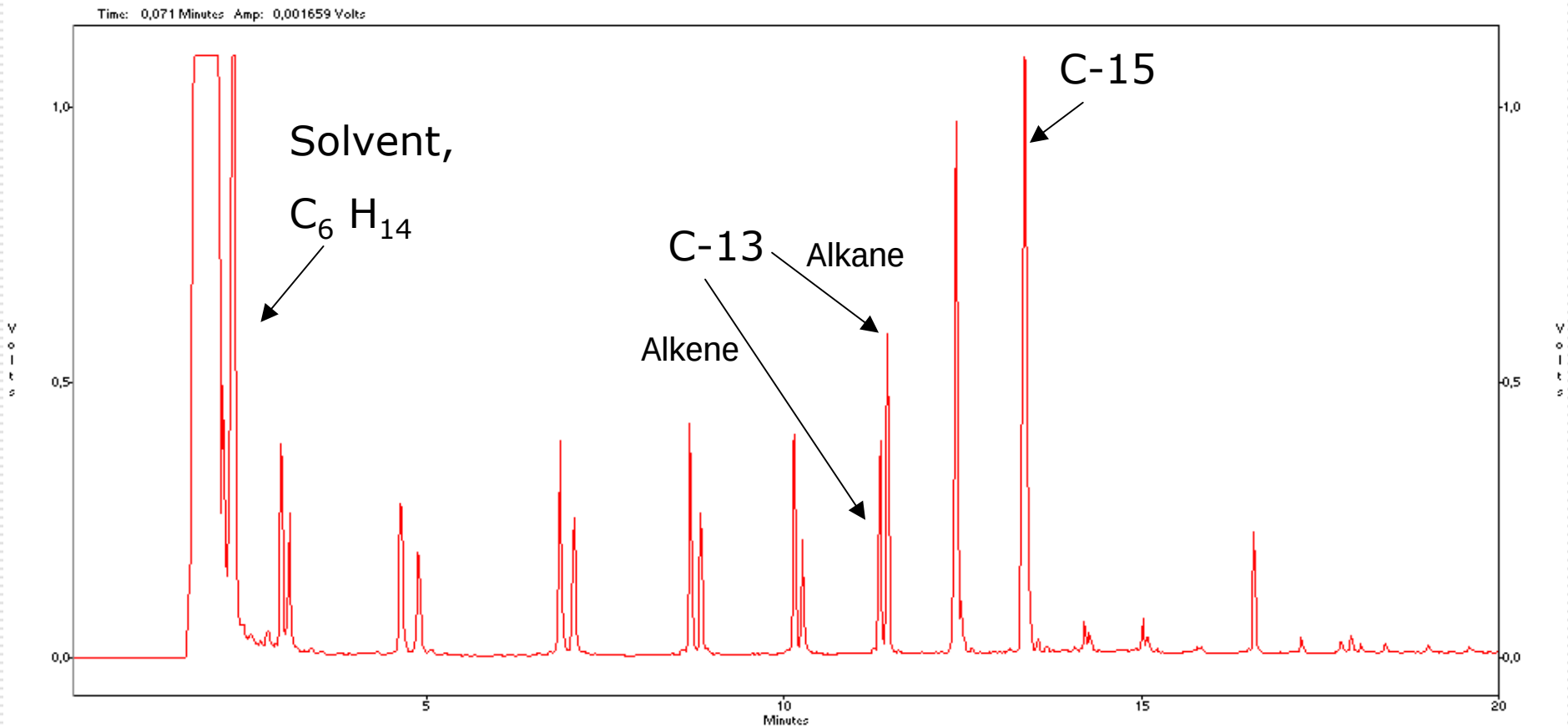
Sodium Salt of Hexadecanoic Acid as Model Compound for Thermal Conversion of FFA & Lipids



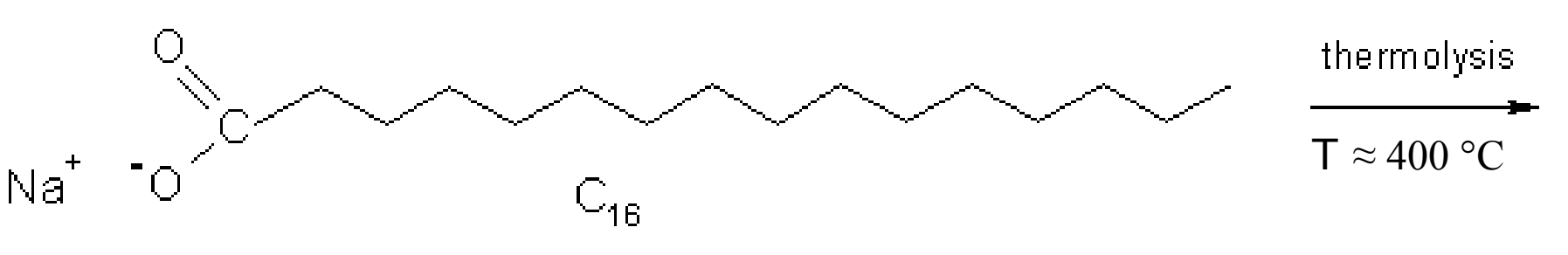
[C_{16}]

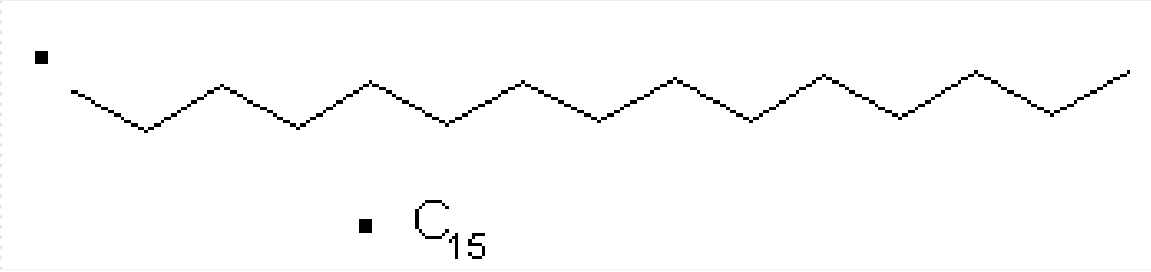
Bond energy: C - H (≈ 413 kJ/mol); C – O (≈ 358 kJ/mol); C – C (≈ 347 kJ/mol)

Thermal Decomposition of Sodium Salt of Hexadecanoic Acid at T ≈ 400°C [C-16]



Radical Formation Through Homolysis of the Weakest Bond by Heat Energy



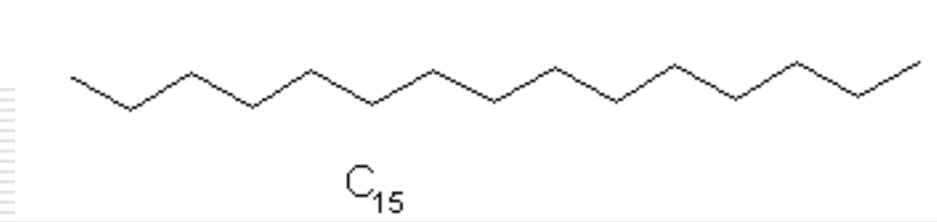


Reactions of Free Radicals (I)

Several types of reactions with transfer or loss of radical properties take place simultaneously:

a) Chain propagation reaction:

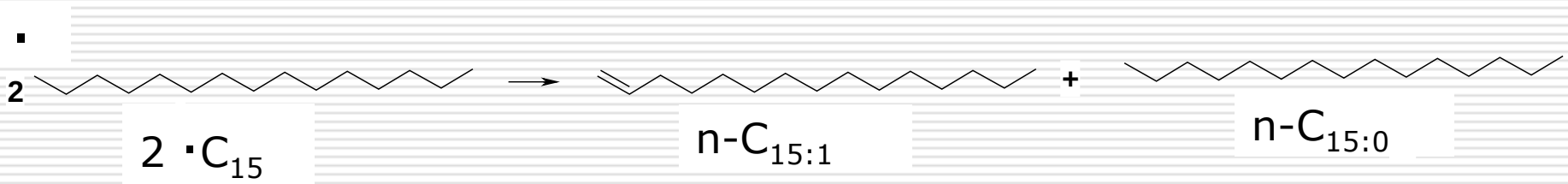
R-H **+**



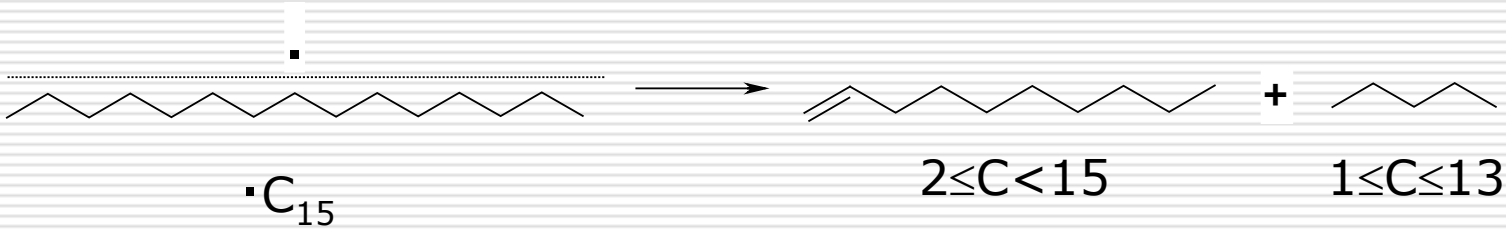
+ **R·**

Reactions of Free Radicals (II)

b) Disproportionation:



c) Intramolecular radical transfer & disproportionation:



d) Combination of two radicals:

$$R_1\cdot \quad + \quad R_2\cdot \quad \rightarrow \quad R_1 - R_2$$

Thermal Decomposition of Hexadecanoic Acid via Sodium Salt as Intermediate at T ≈ 400°C [C-16]

Basic reactions:

a) On-site production of sodium salt of hexadecanoic acid:

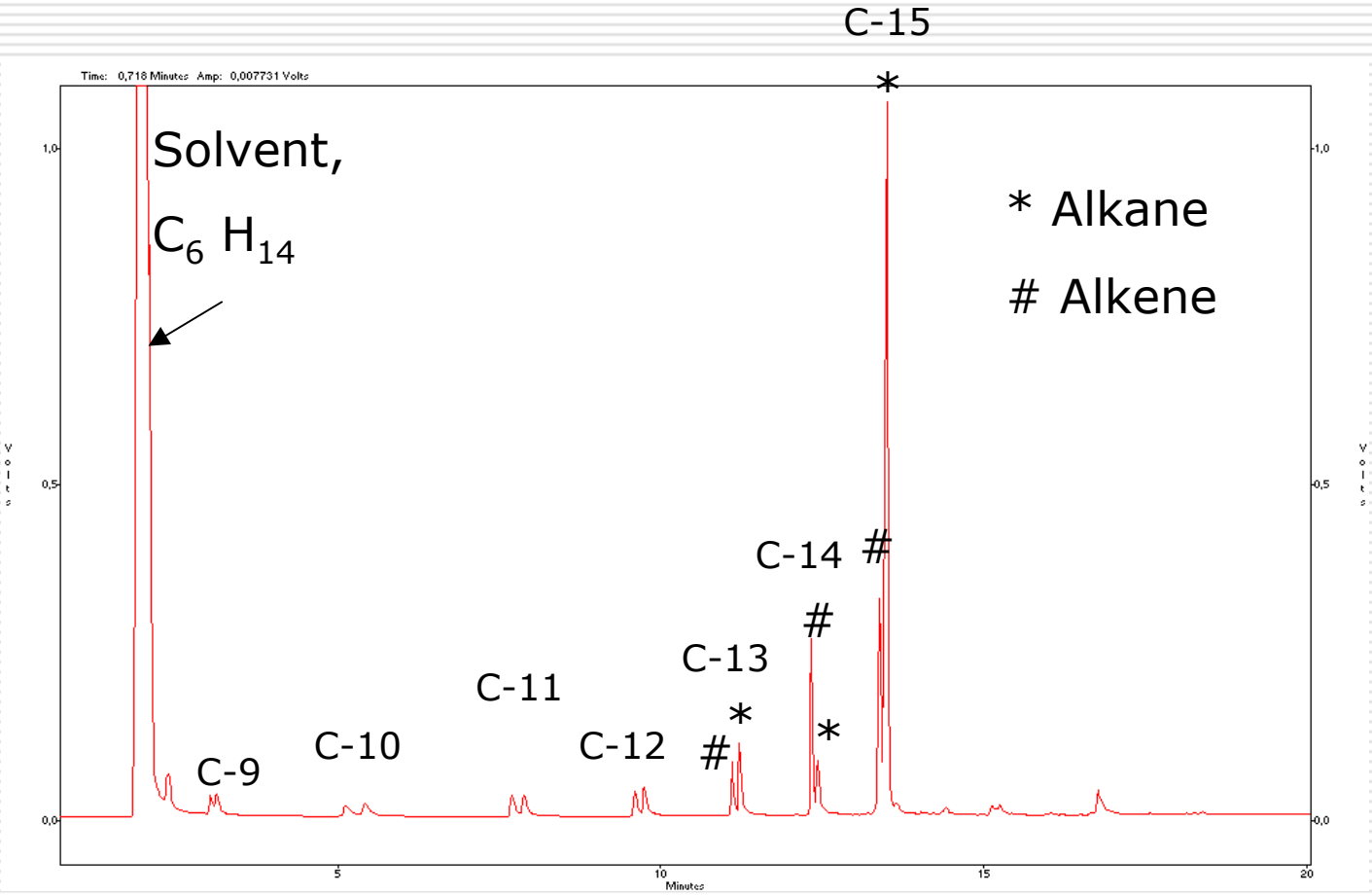
$$Na_2CO_3 + H_2O \rightarrow NaOH + NaHCO_3$$

$$R\text{-}COOH + NaOH \rightarrow R\text{-}COONa + H\text{-}OH$$

b) On-line decomposition of sodium palmitate formed at T ≈ 400°C

Vapours of hexadecanoic acid and water pass over pellets of ashes from fire wood or Na_2CO_3

GC of Products Formed by Distillation of Hexdecanoic Acid [$CH_3(CH_2)_{14}COOH$] over Pellets of Na_2CO_3 in the Presence of Water



FFA and Waste Lipids as Feedstock in Pilot Scale

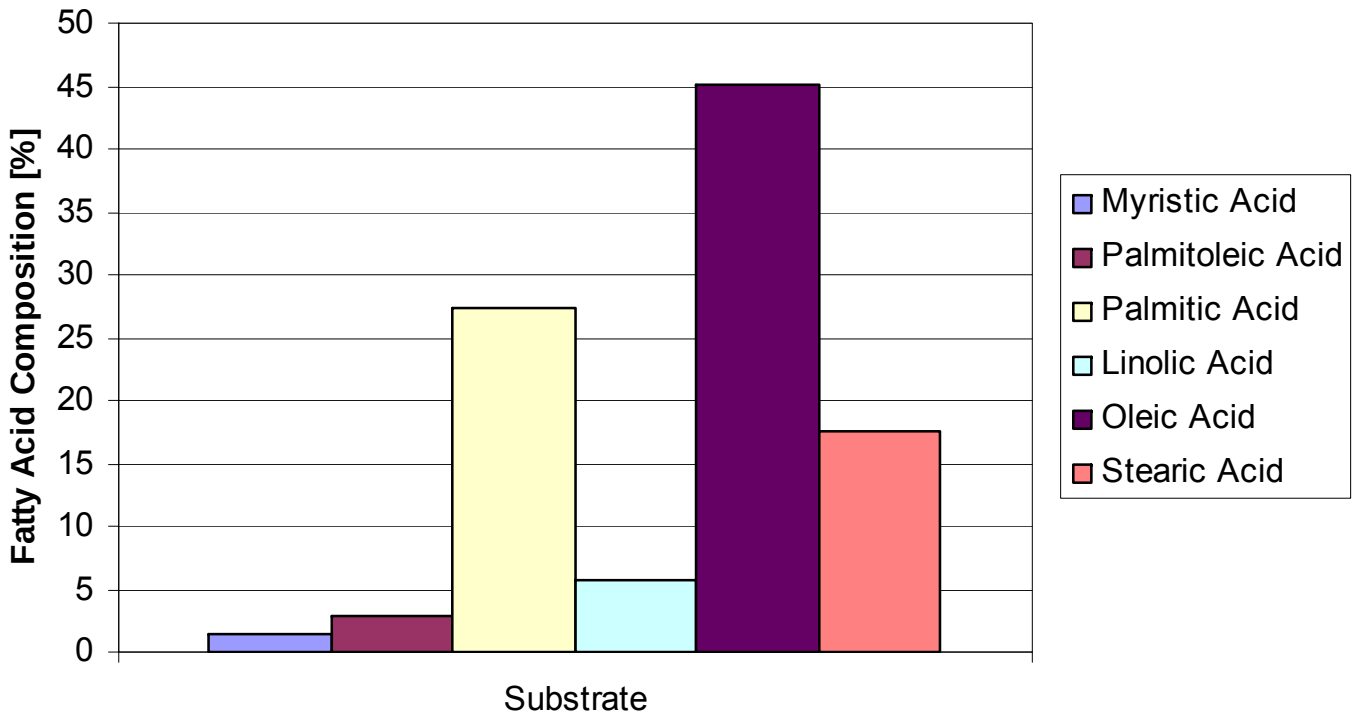
Feedstock	FFA [%]
FFA removed from refined oils , e.g. residue from processing of high priced Rapeseed Oil, Sunflower Oil, Soybean Oil, Palm Oil, Camelina Oil from Food or Biodiesel Industry	<99
Used Cooking Oil & Yellow Grease	<15
Animal Fat (Cat. 1,2,3)	<30
Trap / Brown Grease	70 - 90
Jatropha	<20
Corn oil	<15

Pilot plant: Continuous input of FFA & lipids in the presence of Na_2CO_3 or ashes from fire wood

Profile of Fatty Acids in Animal Fat from Rendering Plant

(determinded as methylesters after transesterification)

Total Fatty Acid Content: 95 %

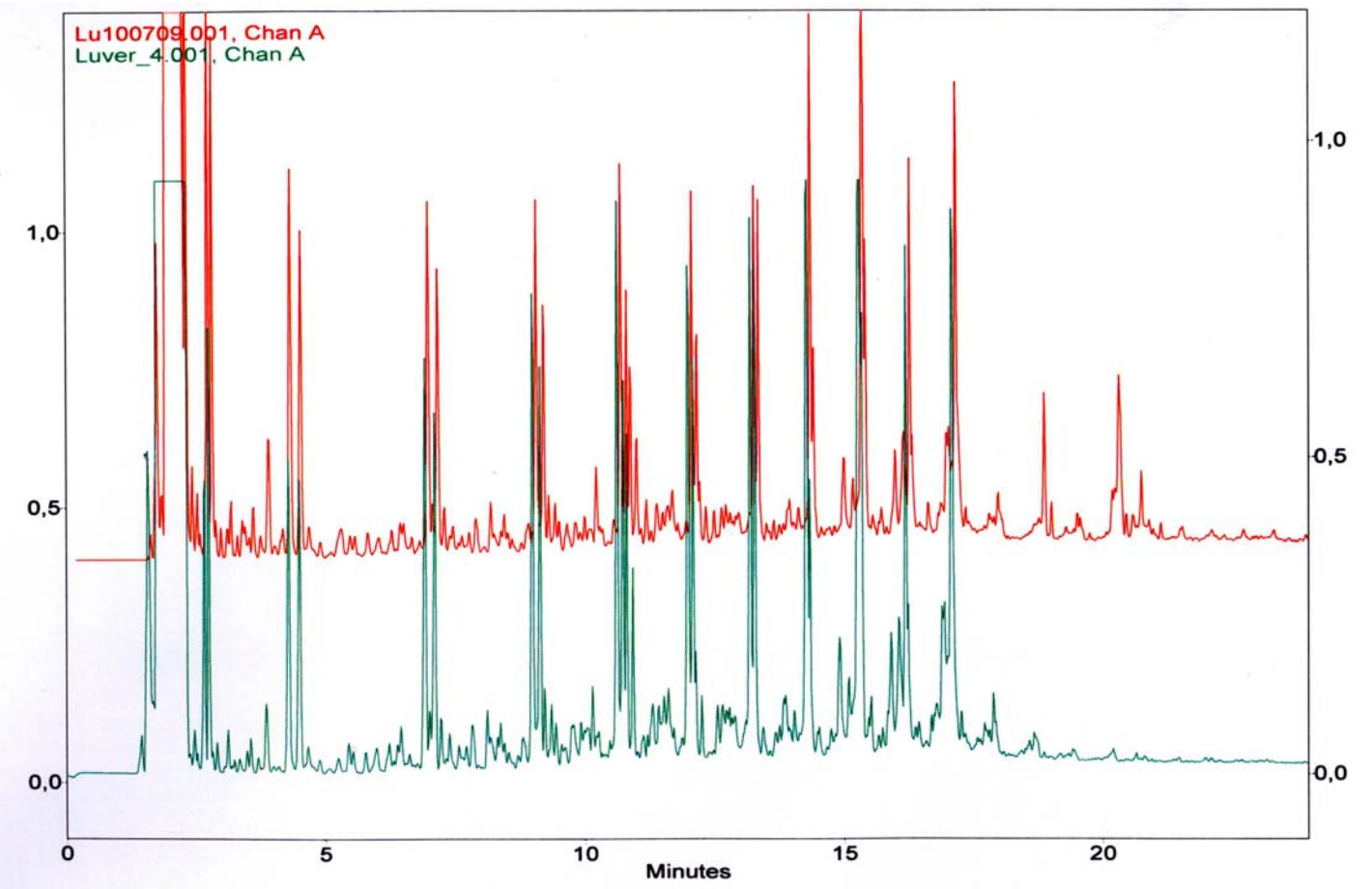


Converting Animal Fat to Hydrocarbons in Pilot Scale

(T = 400°C ±20°C; ashes from fire wood, Na_2CO_3, 5% Water)

GC of Crude Oil from Animal Fat

(Pilot plant; T = 400°C ±20 °C / Na_2CO_3)



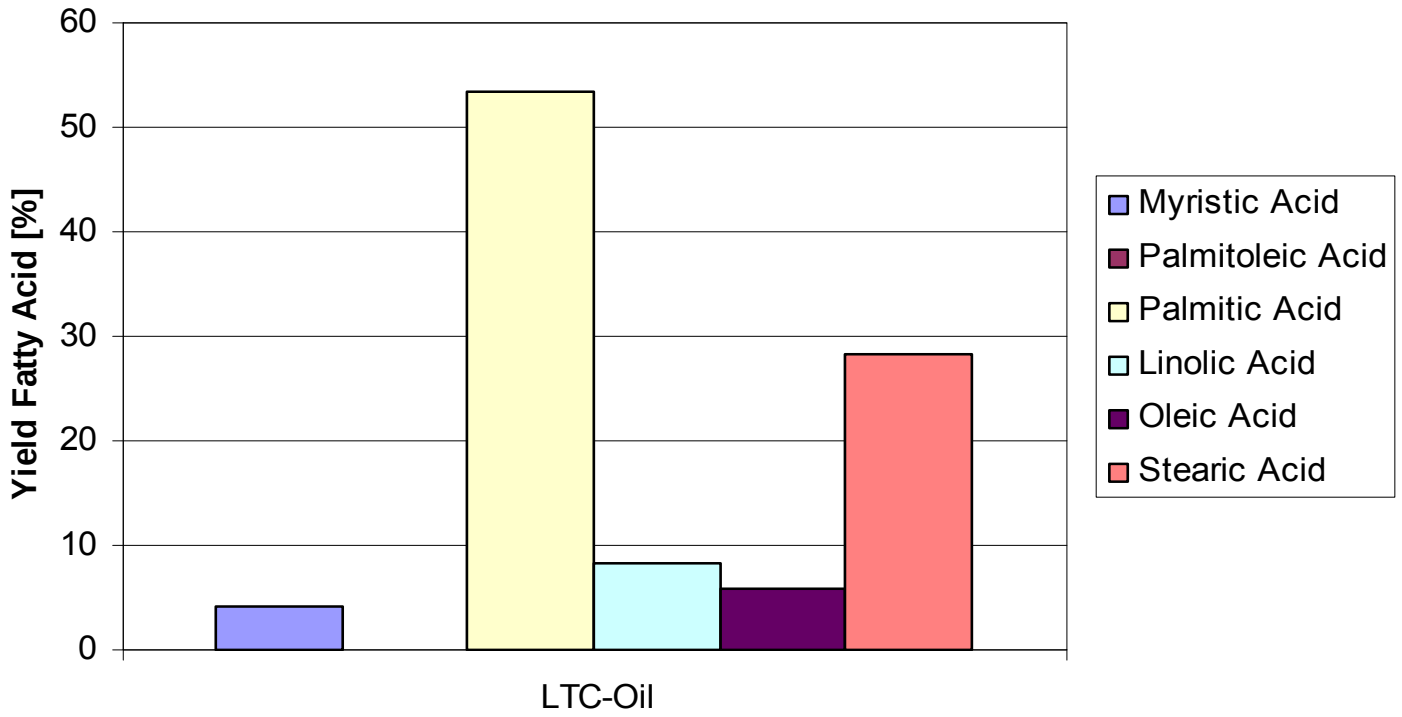
Upper red GC pattern: Original oil

Lower green GC pattern:

Oil after SPE: Removal of polar compounds

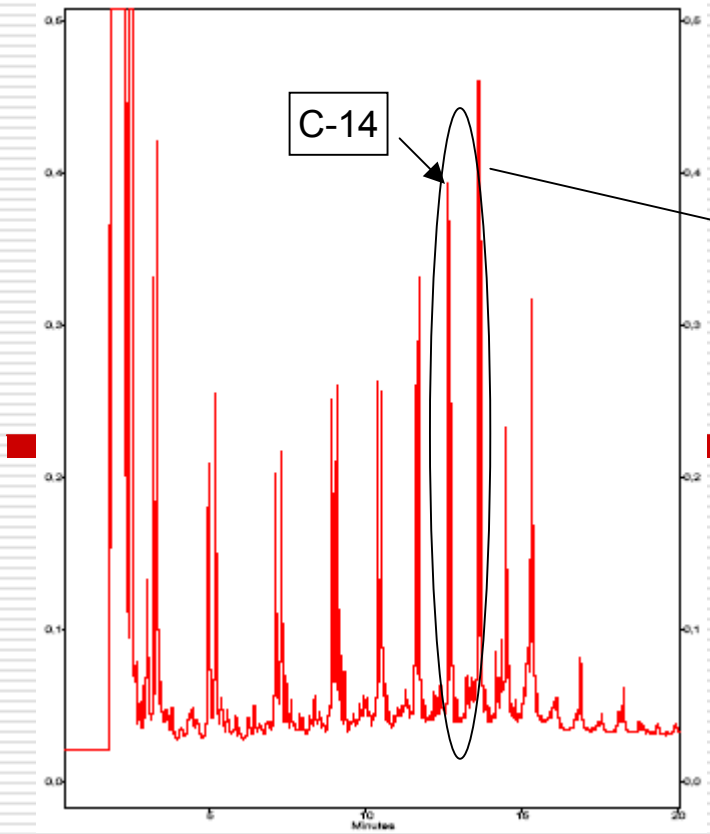
Fatty Acids in Oil

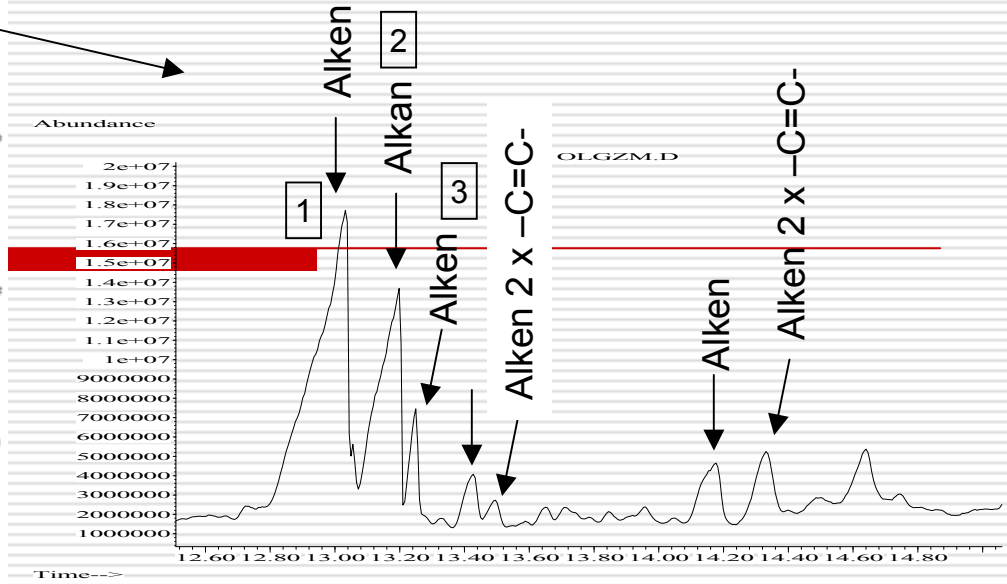
Fatty Acid Content : 0,2 % giving rise to an acid number of 0,5 mg KOH/g

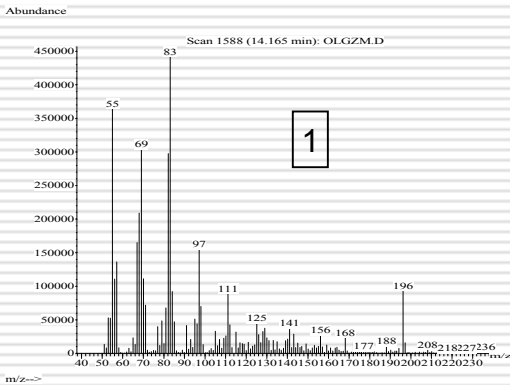


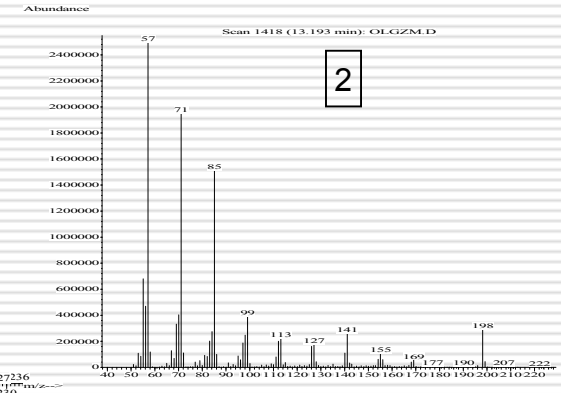
Identification of Products by GC-MS:

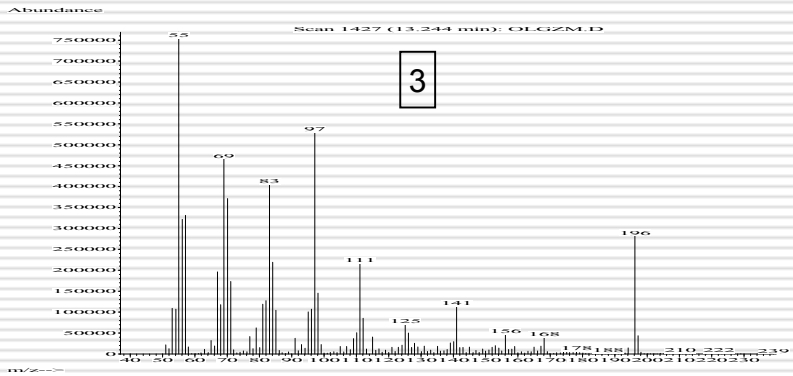
Mass Numbers: 1 (196 g/mol); 2 (198 g/mol); 3 (196 g/mol)





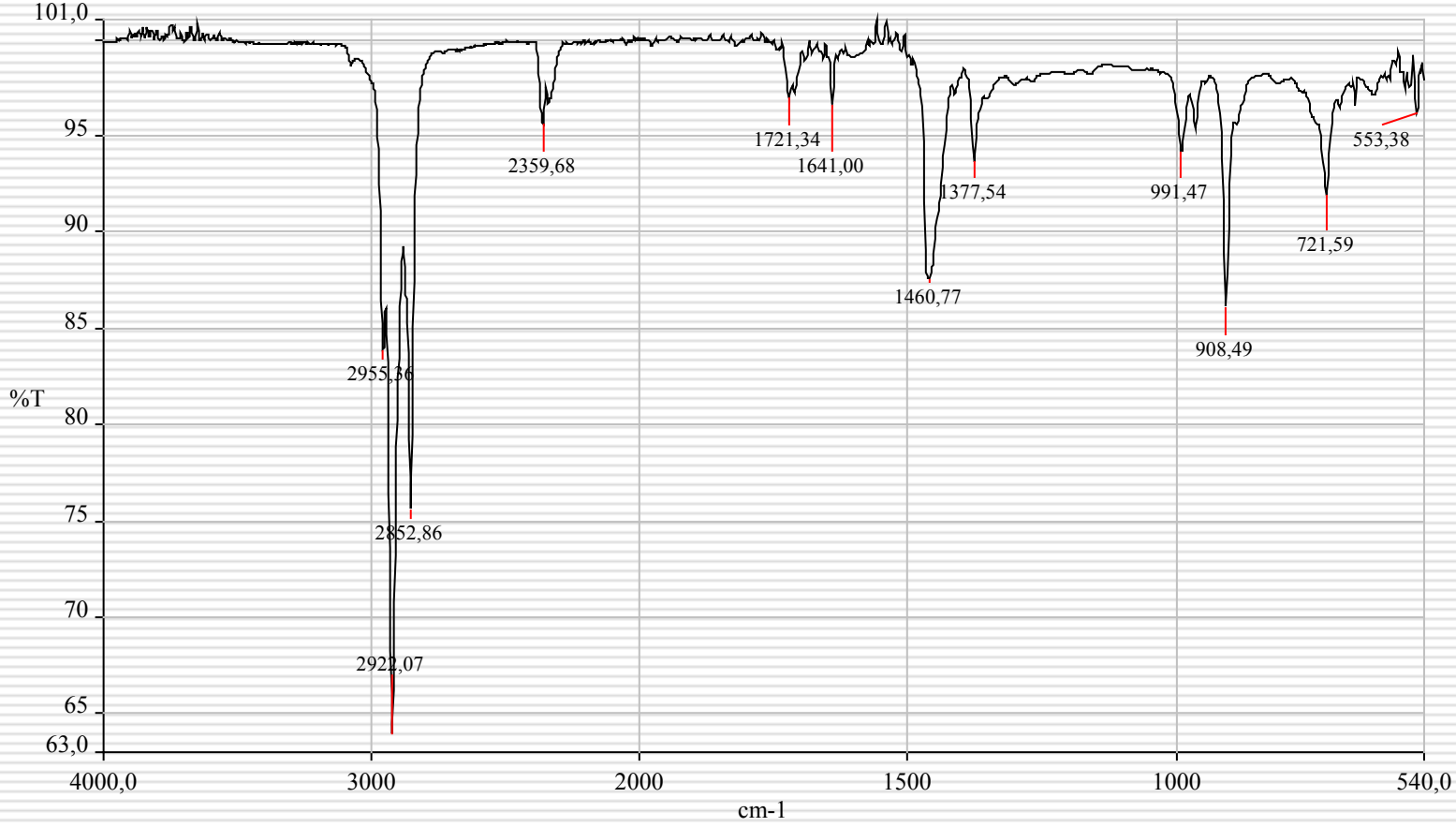






IR of Crude Oil from Animal Fat

(Pilot plant; T = 400°C ± 20°C / Na_2CO_3)



NMR of Crude Oil from Animal Fat

(Pilot plant; T = 400°C ± 20°C / Na_2CO_3)

^{1}H

	CH_2 =	CH -	CH_2 -	$(CH_2)_n$ -	CH_3
δ [ppm]	4,77	5,62	1,89	1,13	0,74

^{13}C

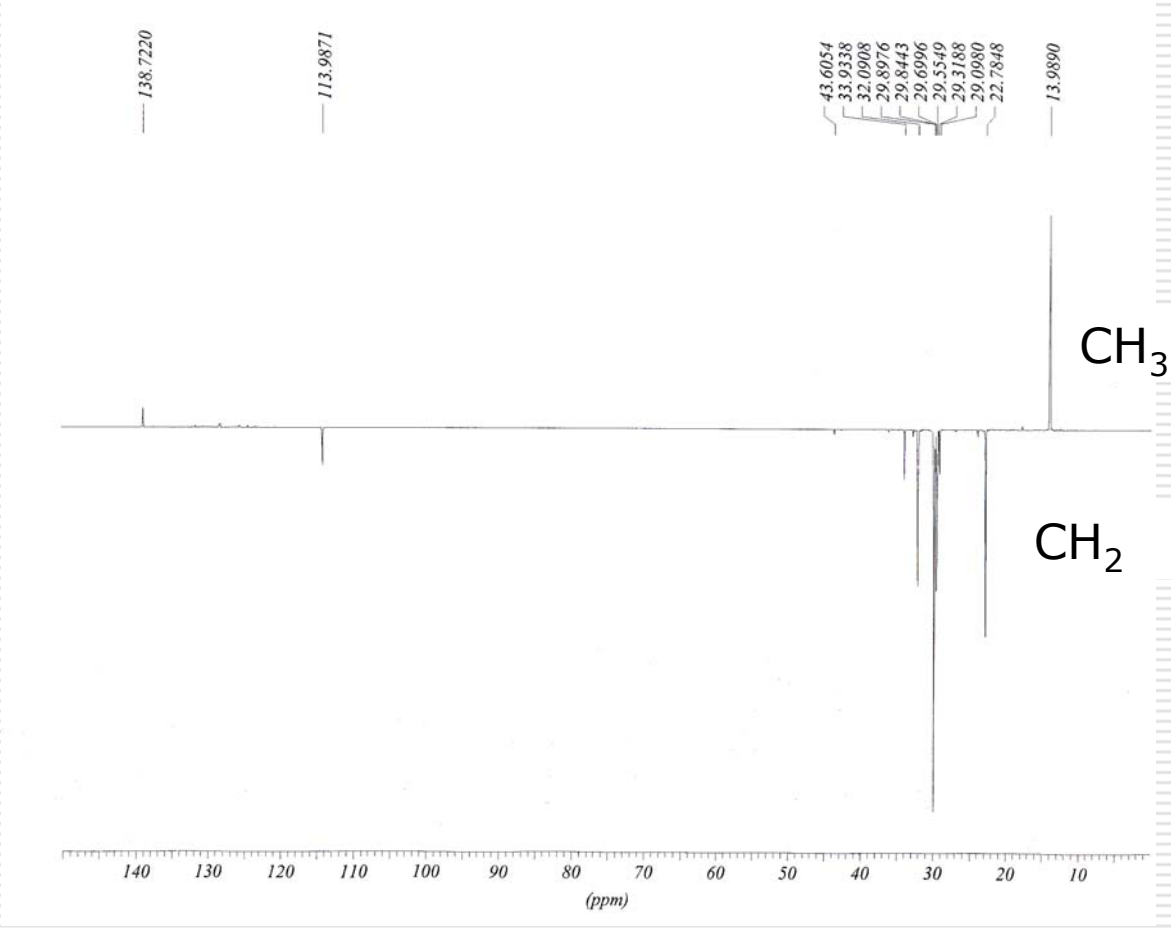
	CH_2 =	CH -	CH_2 -	$(CH_2)_n$ -	CH_3
δ [ppm]	114,09	138,83	31,86	22,07	14,09

These profiles reflect nmr data for 1-pentene from literature

	CH_2 =	CH -	CH_2 -	$(CH2)_n$ -	CH_3
^{1}H δ [ppm]	≈5.0	≈5.8	2.03	1,42	0,91
^{13}C δ [ppm]	114,26	138,96	35,89	22,07	13,59

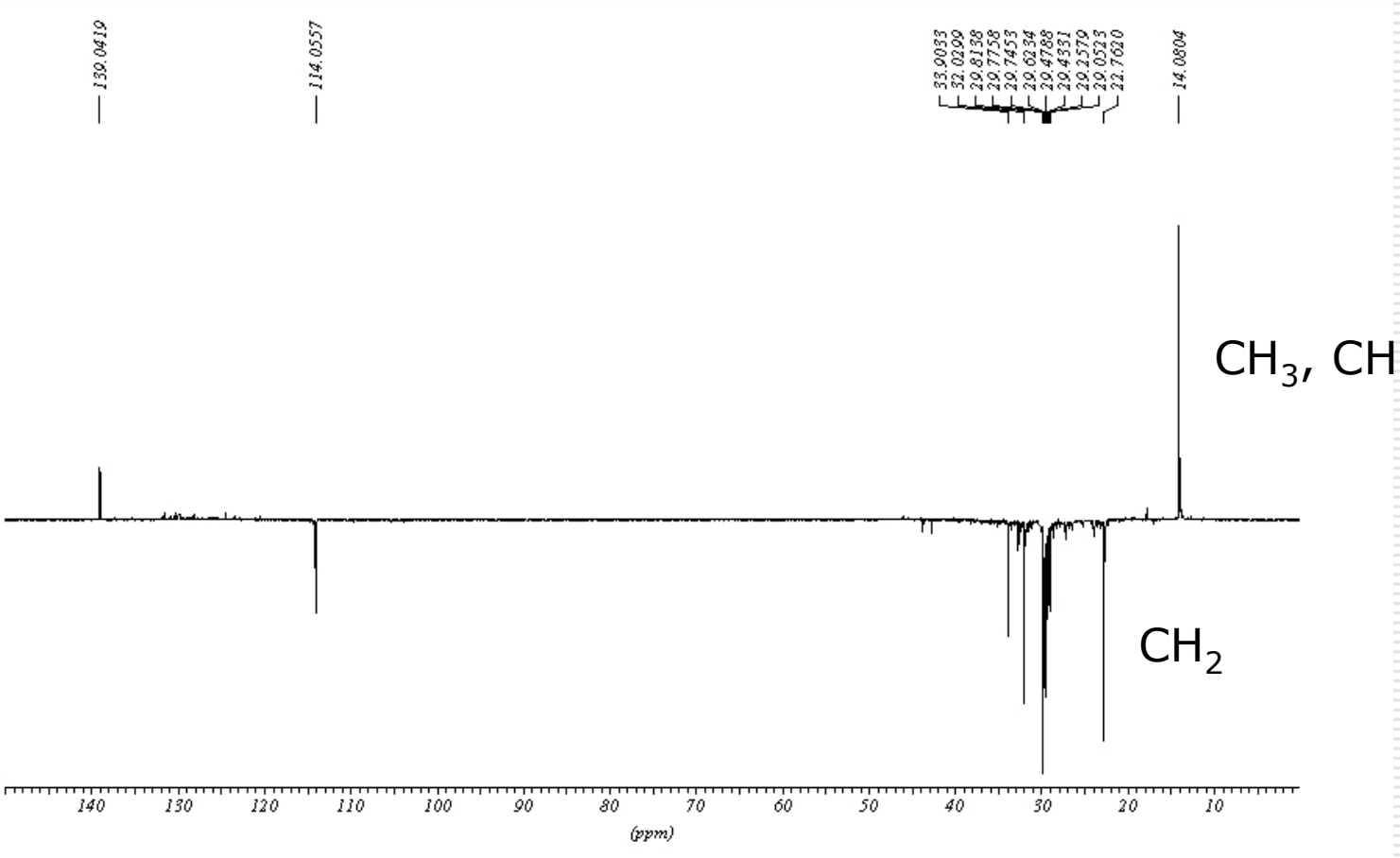
^{13}C-Dept-135 NMR of Crude Oil from Animal Fat Confirms:

$CH_2 = CH - CH_2 - (CH_2)_n - CH_3$ and $CH_3 - CH_2 - CH_2 - (CH_2)_n - CH_3$;
with variable chain length n



^{13}C-Dept-135 NMR of Crude Oil from Animal Fat Confirms:

$CH_2 = CH - CH_2 - (CH_2)_n - CH_3$ and $CH_3 - CH_2 - CH_2 - (CH_2)_n - CH_3$;
with variable chain length n

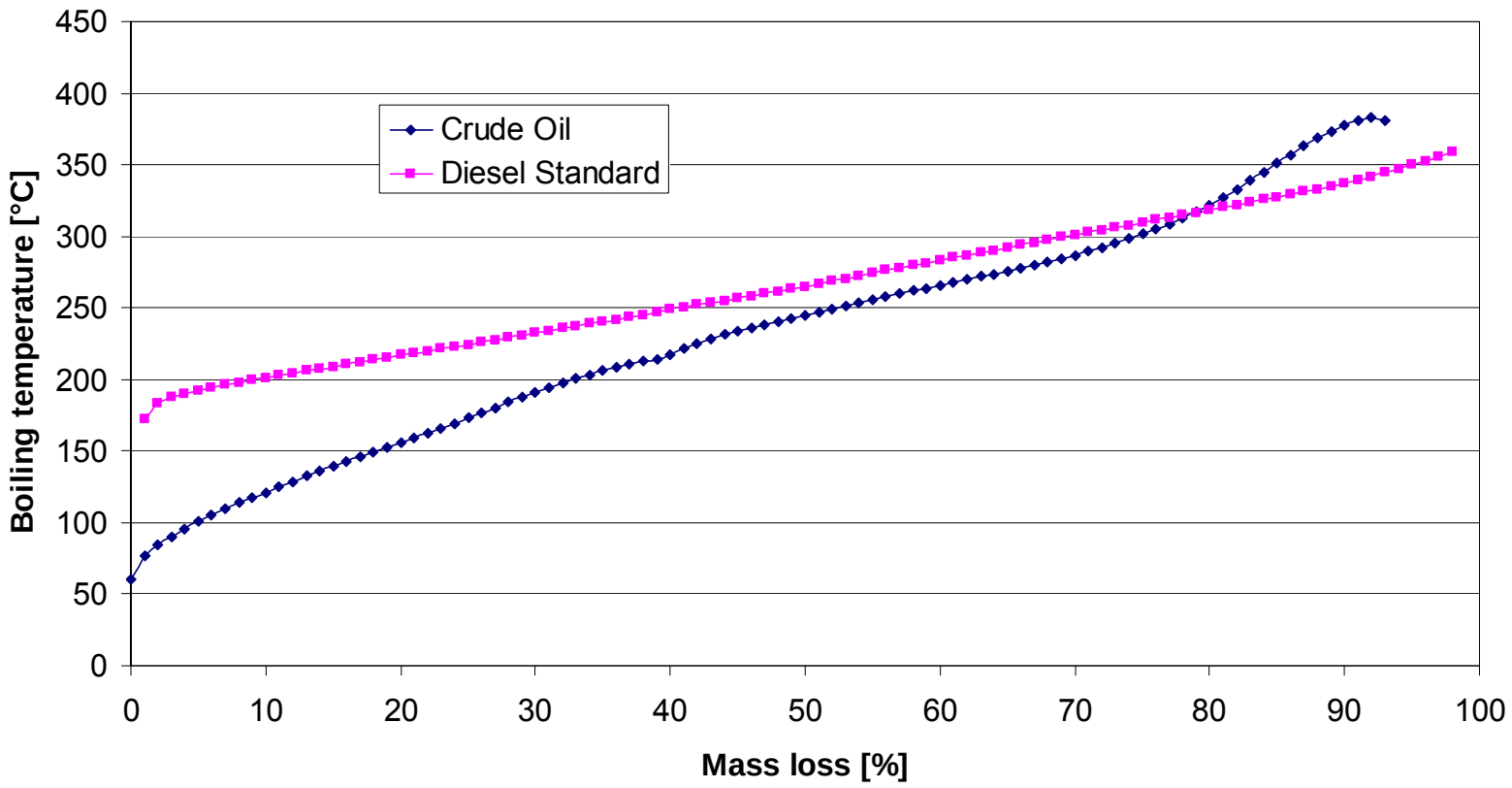


Characteristics of Oils from Decarboxylation of Lipids

(Pilot plant; T = 400°C ± 20°C / Na_2CO_3 or ashes and 5 % Water)

Parameter	Unit	DIN EN 590	Pilot Plant 1
Density at 15°C	kg/m³	820 - 845	815
Viscosity 40°C	mm²/s	2,0 - 4,5	1.78
Flash Point	°C	min. 55	< 30
Cetane number	-	min. 51	57
NCV	MJ/kg	≈42	41.6
Water Content	mg/kg	max. 200	400
Total Sulphur	mg/kg	max. 350	50
Na and K	mg/kg	max. 5	0.1
Ca and Mg	mg/kg	max. 5	0.5
Phosphorus	mg/kg	max. 10	0.5

Distillation Characteristics of Crude Oil Obtained from Animal Fat at Atmospheric Pressure (EN 3405)



Conclusion

- Decomposition of both FFA and lipids in the presence of sodium carbonate or ashes from fire wood mainly produces a spectrum of alkanes and alkenes (crude oil). The relative abundances depend on radical stabilization either by intermolecular hydrogen radical transfer or random ß-scission of delocalized radicals along the carbon chain.

- Flash-point criterion shows the importance of rectification for post treatment to fulfill industrial standards in bio-fuel production. Use crude oils for raw material in production of detergents is of interest, too.

Intelligent Biofuels from Organic Residues are today's challenge and tomorrow's reward.

Thank you for your attention