UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY

Temperatior s.r.o.

Improving Cold Flow Properties of Biodiesel: Effects of Feedstock Composition, Amides, and Blending Strategies

Hájek M.[1], Kuchyňka P.[2], Vagunda J.[1] , Hajek T.[1] , Dvořáková K.[1]

[1]**Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice,** Studentská 573, 532 10 Pardubice

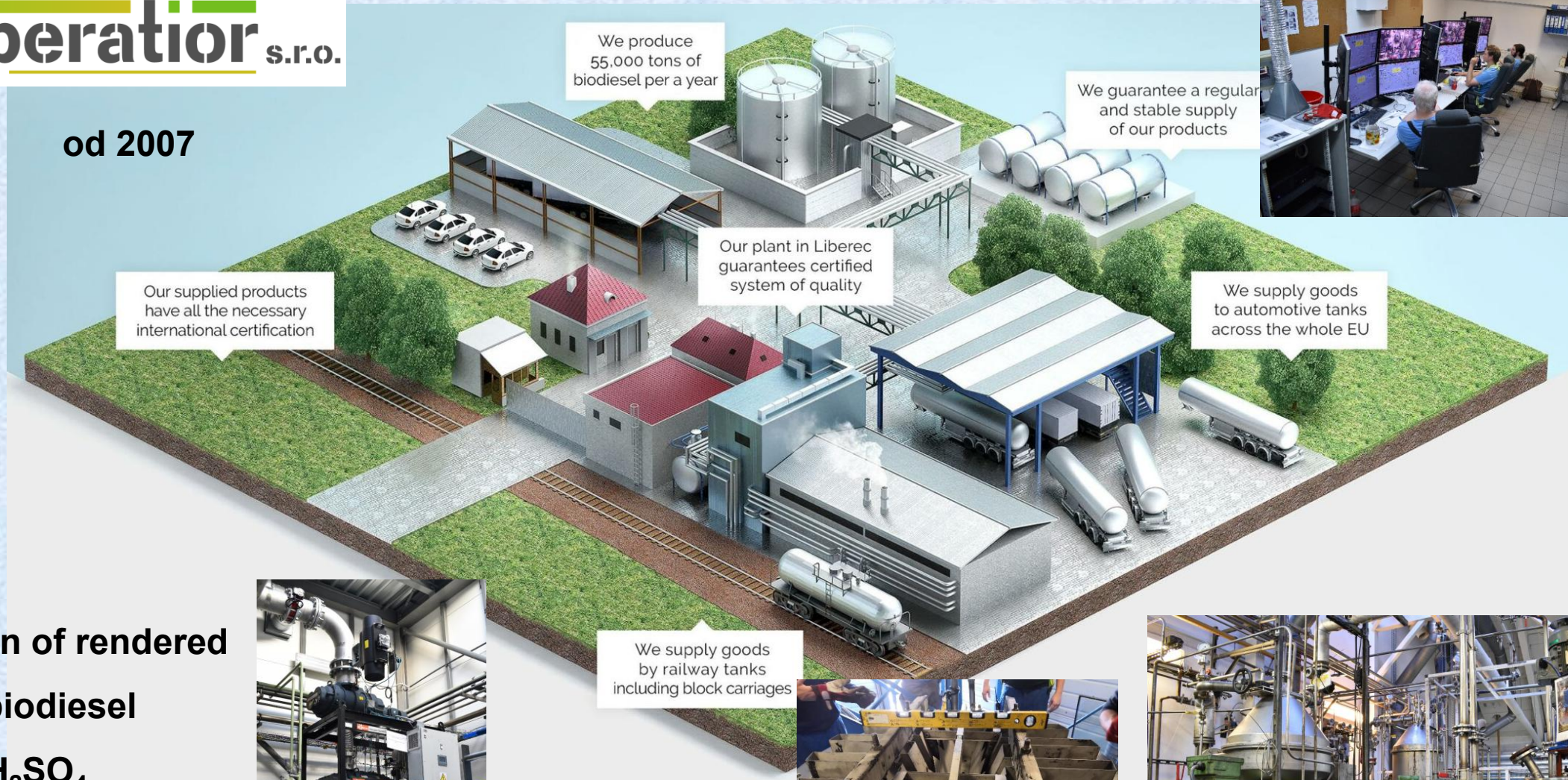
[2]**TEMPERATIOR s.r.o,** Liberec

e-mail: martin.hajek@upce.cz

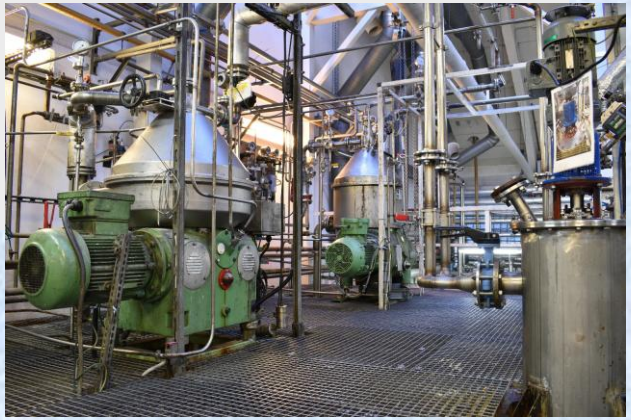
Biodiesel

Temperatior s.r.o.

Liberec **od 2007**



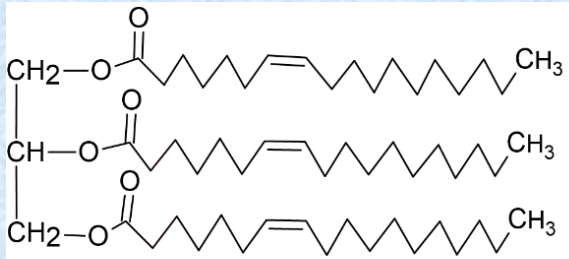
Transformation of rendered animal fat to biodiesel catalyzed by H_2SO_4



Transesterification

Chemical reaction between oil/fat (triglycerides) and alcohol – transesterification

Oils/fats

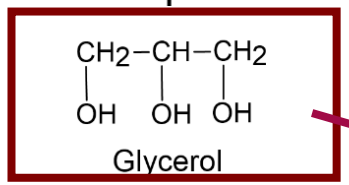


Triglycerides

Transesterification
(alcohol and base catalysts)

Methyl esters

\+



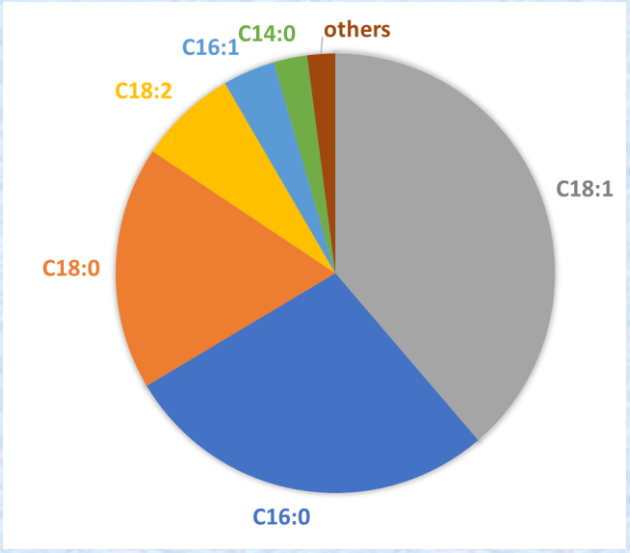
Glycerol

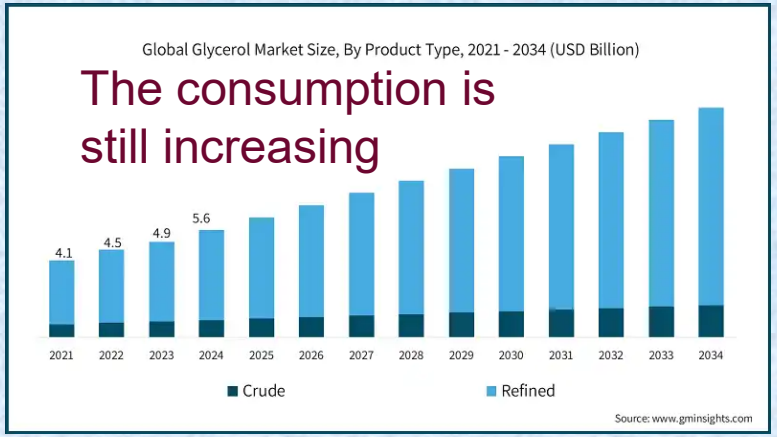
Transesterification have to be catalyzed (H_2SO_4)

Lighter ester phase

Fuel (biodiesel)

Rendered animal fat





Heavier glycerol phase

many applications in chemistry, food, pharmaceutical industries, tobacco, explosives

Biodiesel turbidity

turbidity of biodiesel at room temperature

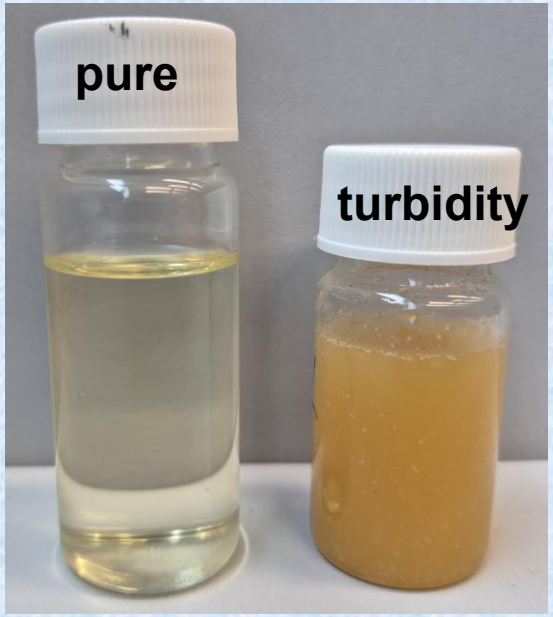
At low temperatures, diesel has poor properties

higher viscosity, solids release,

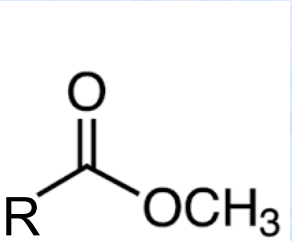
Negative influence Cloud point (CP) cloud point,

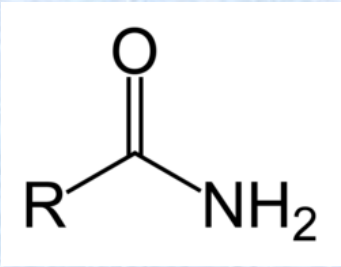
Cold filter plugging point (CFPP)

Pour point (PP) = fuel solidification point



According to Infrared spectroscopy – **amides of fatty acid**



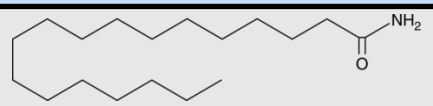
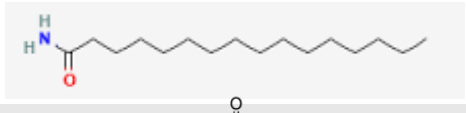
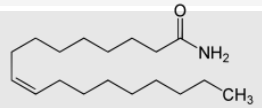
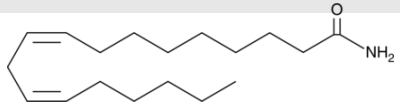


Amides are white/colorless waxy solids that are used as a **lubricant and corrosion inhibitor**.
Amides can occur from all higher fatty acids

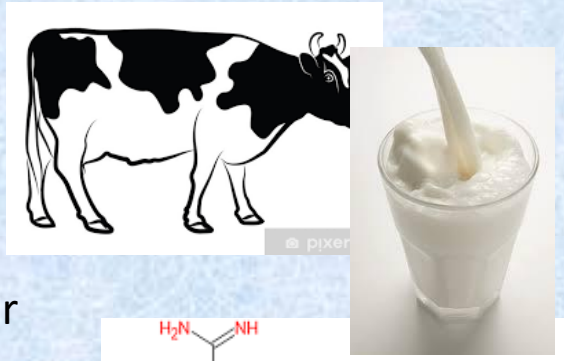
Amides generally have

(i) tendency to association (formation of hydrogen bonds).
(ii) NOx is produced during combustion.
(iii) a higher melting point than esters and are thus solid even at room temperature, which affects CFPP and CP

Amides - properties

Amide of fatty acids	Structural formula	Melting point, °C	CAS	M, g/mol
Palmitic (C16:0)		**107**	629-54-9	255.5
Stearic (C18:0)		**102-104**	124-26-5	283.5
Oleic (C18:1)		**70**	301-02-0	281.5
Linoleic (C18:2)		**52-56**	3072-13-7	279.5

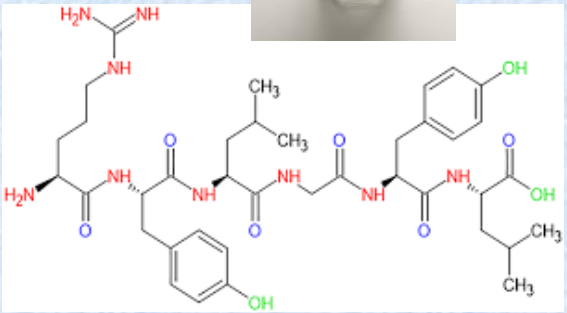
70-80 °C more than the corresponding methyl esters



Amides formation

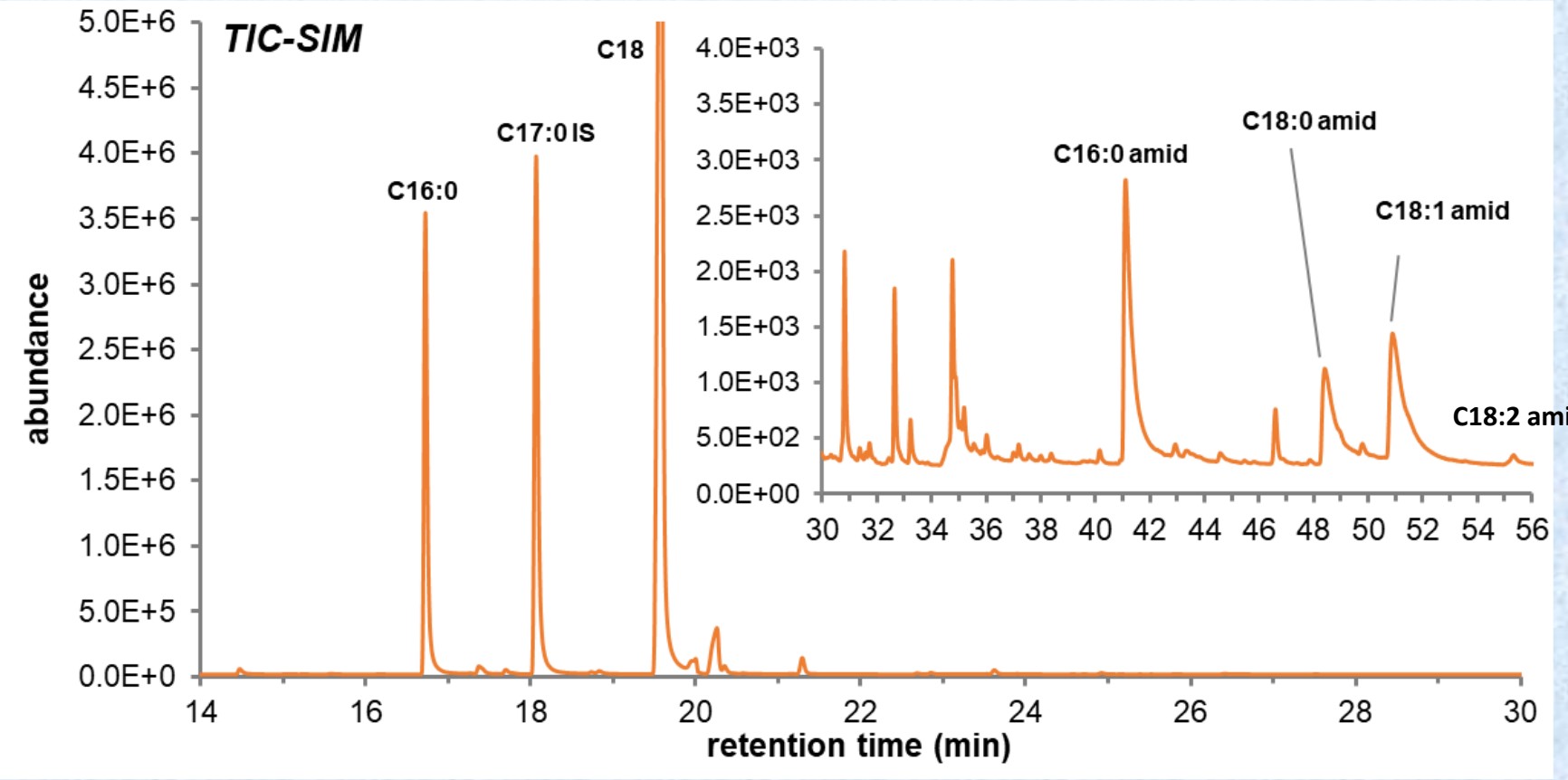
Biochemically are formed from free fatty acids with ammonia by (trans)amidation in the liver using enzymatic catalysis (amidotransferase).

more nitrogen-containing substances (in the form of proteins or urea) are added to **cow feed, due to the greater production of milk containing proteins** (**casein** and whey proteins).



Amides - determination

Determinination various types of amides by GC-MS



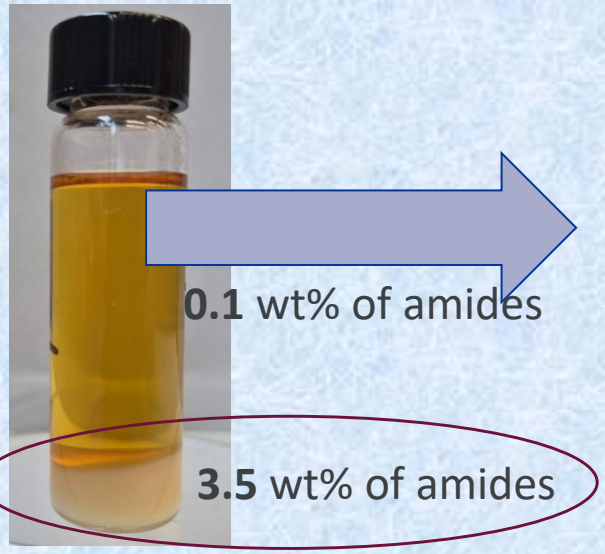
Agilent (7890B/5977A Series GC/MSD) equipped with autosampler operating in the electron ionization: 70 eV, 300 °C, the quadrupole temperature 150 °C

A TRACE™ TR-FAME capillary column, 60 m 0.25 mm I.D., film thickness

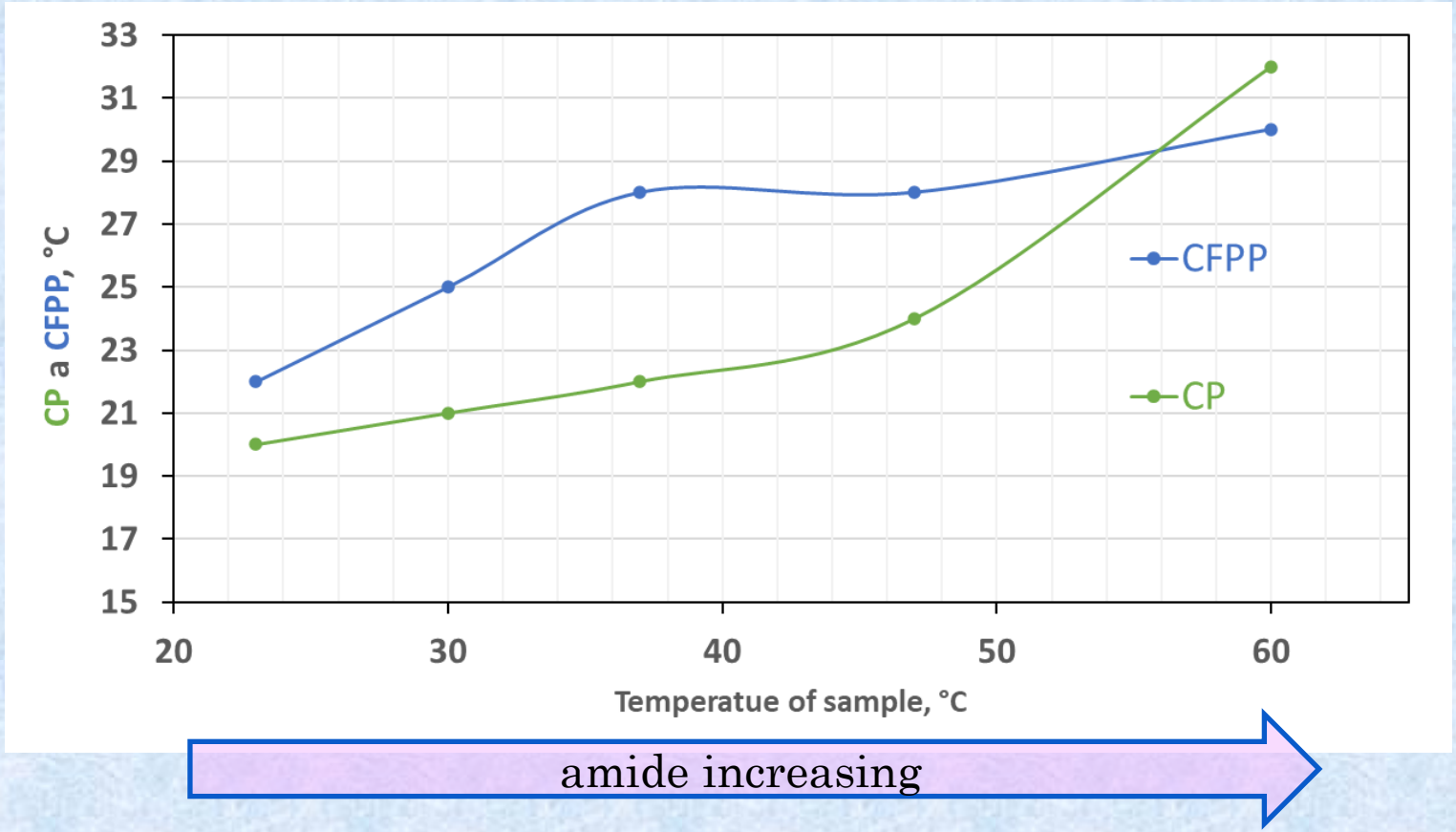
The presentation of amides in the formed biodiesel (FAME) formation

Amides - CFPP

Use of higher melting points with subsequent filtration - affecting solubility by temperature



Amide of fatty acids	Melting point, °C
Palmitic (C16:0)	107
Stearic (C18:0)	102-104
Oleic (C18:1)	70
Linoleic (C18:2)	52-56

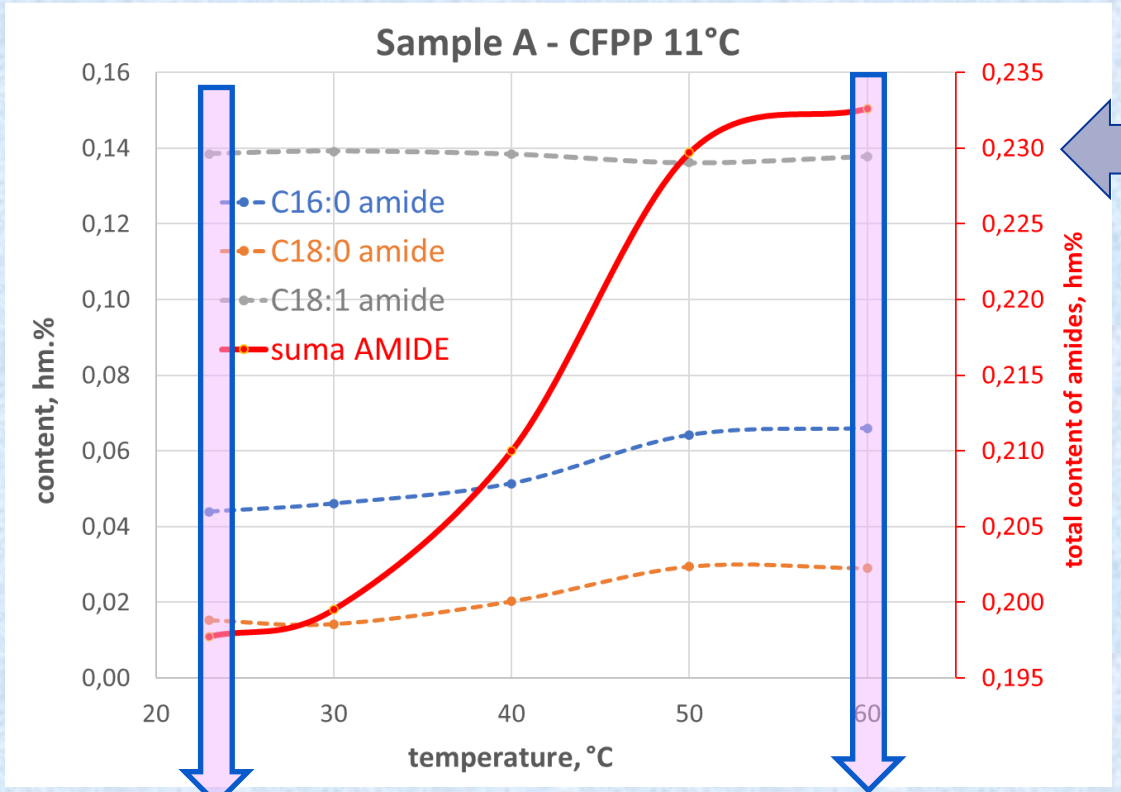


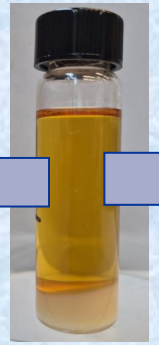
Inreasing temperature – increasing CP a CFPP due to increasing content of amides

Removing of amides - solubility

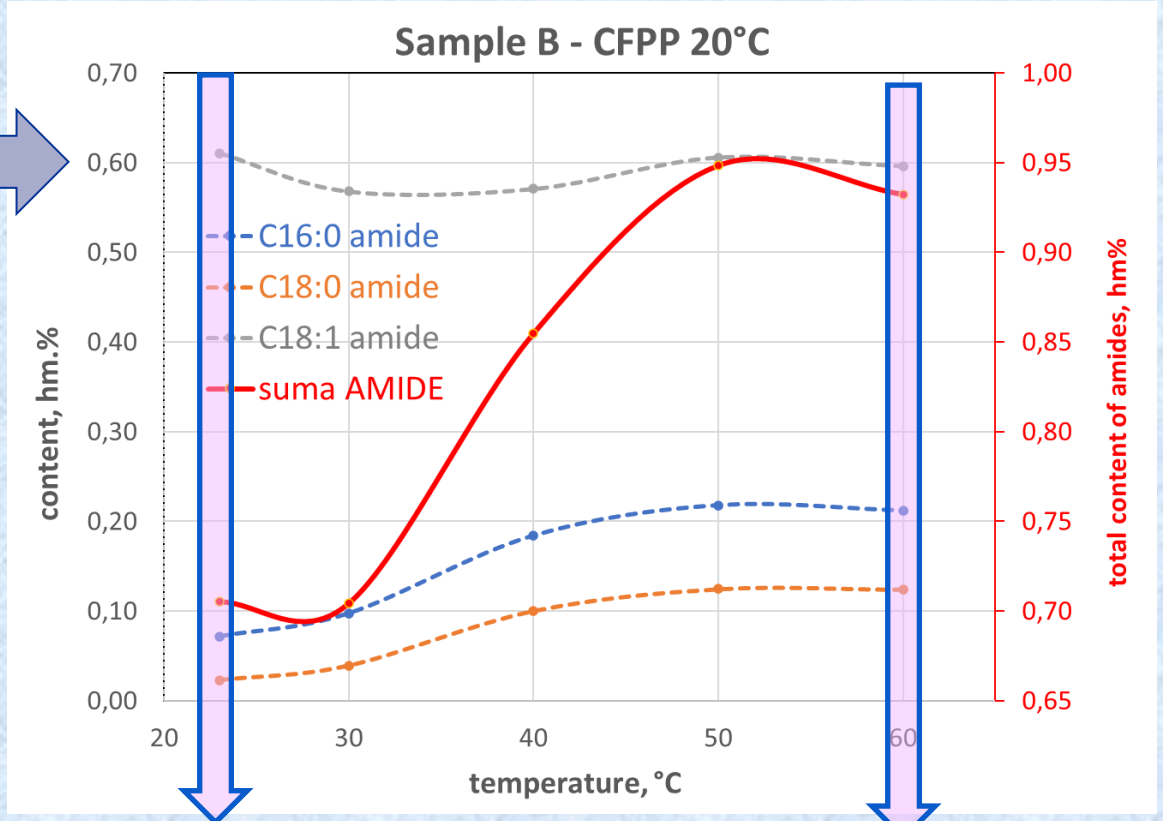
Use of higher melting points with subsequent filtration - affecting solubility by temperature

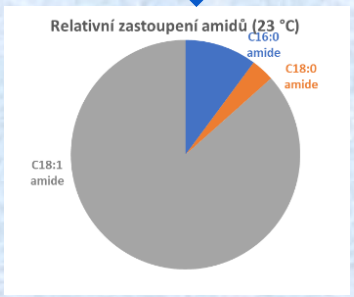
Lower content of amides (0.24 wt.%)

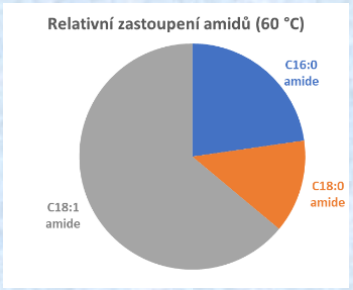


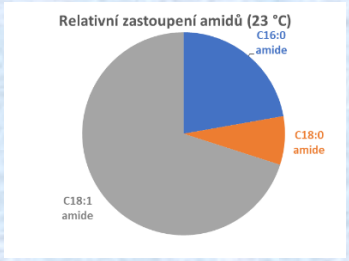


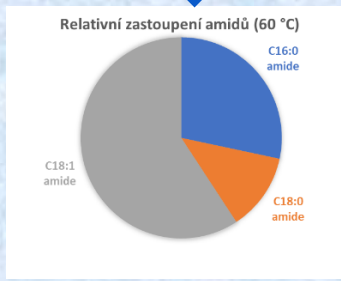
Higher content of amides (almost 1 wt.%)







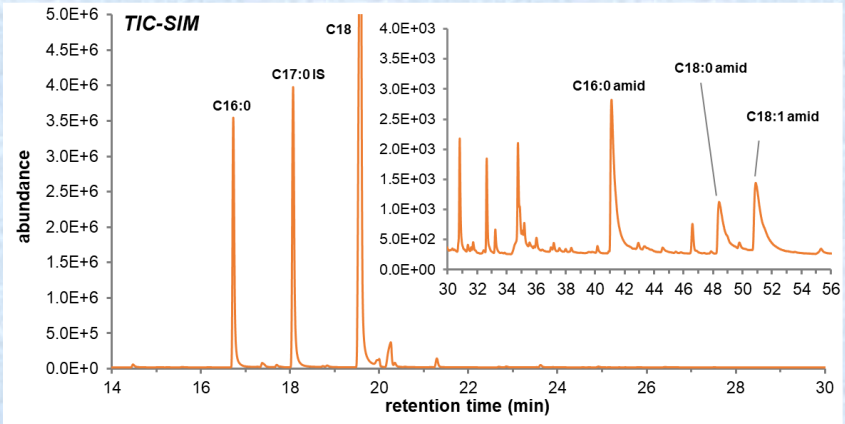




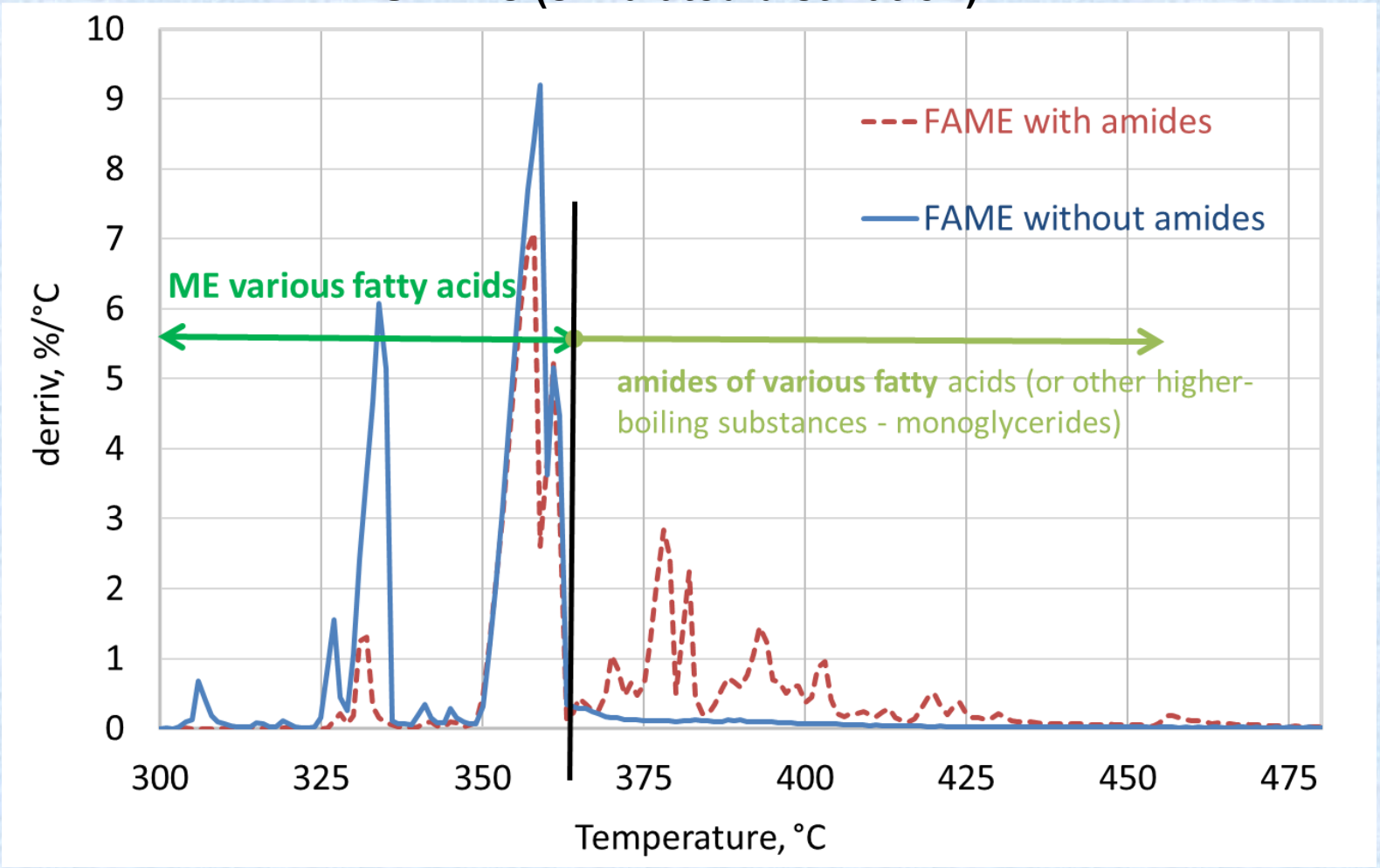
Removing of amides - distillation

Use of higher boiling points of amides than esters - distillation

at standard pressure: amides have a **boiling point about 20-25 °C higher** than methyl esters (an estimate according to Jaback metody)



SimDis (simulated distillation)

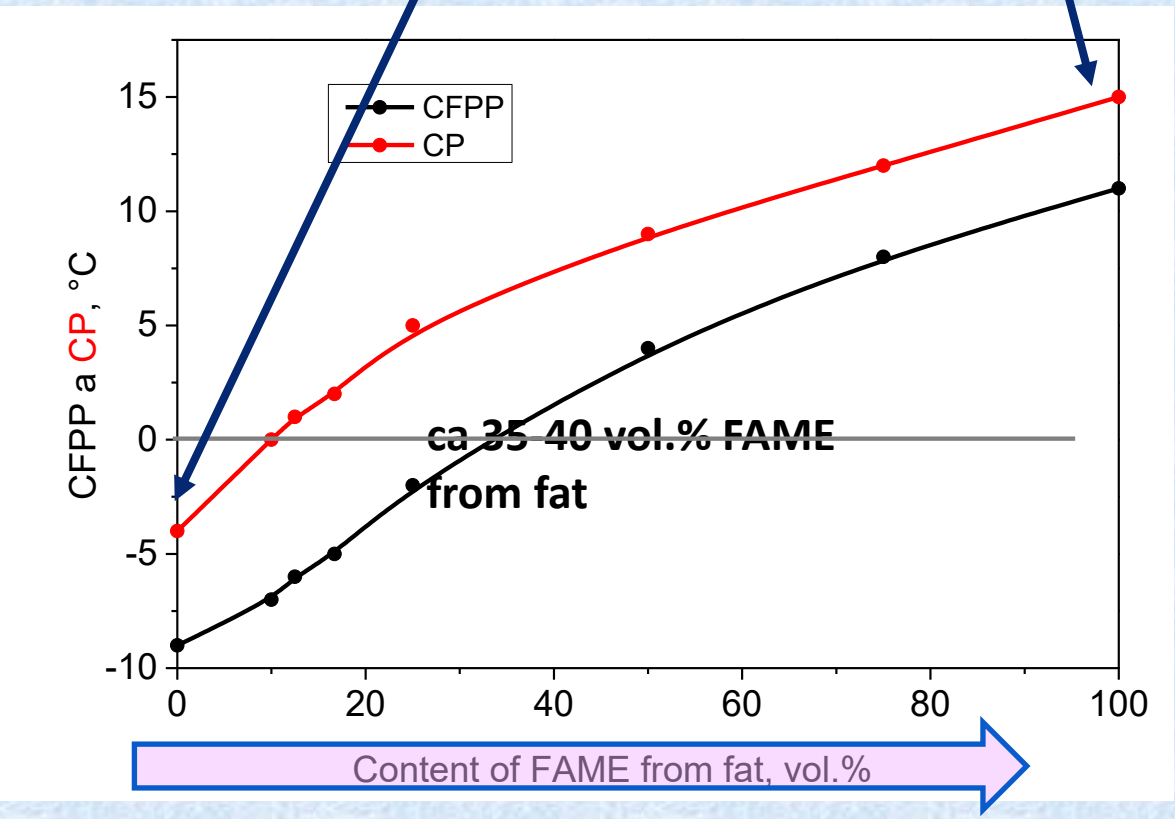


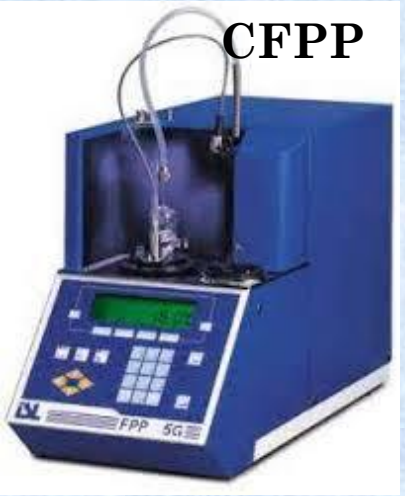
Blending FAME

No CFPP or CP in the biodiesel standard (EN14214)

Type of diesel	Season	CFPP, °C
Summer	15.4. – 30.9.	**0**
Intermediate	1.3. – 14.4. 1.10. – 15.11.	**-10**
Winter	16.11. – 28.2.	**-20**
Arktic	For high mountain areas	**-32**

Blending FAME from rapeseed oil and rendering fat





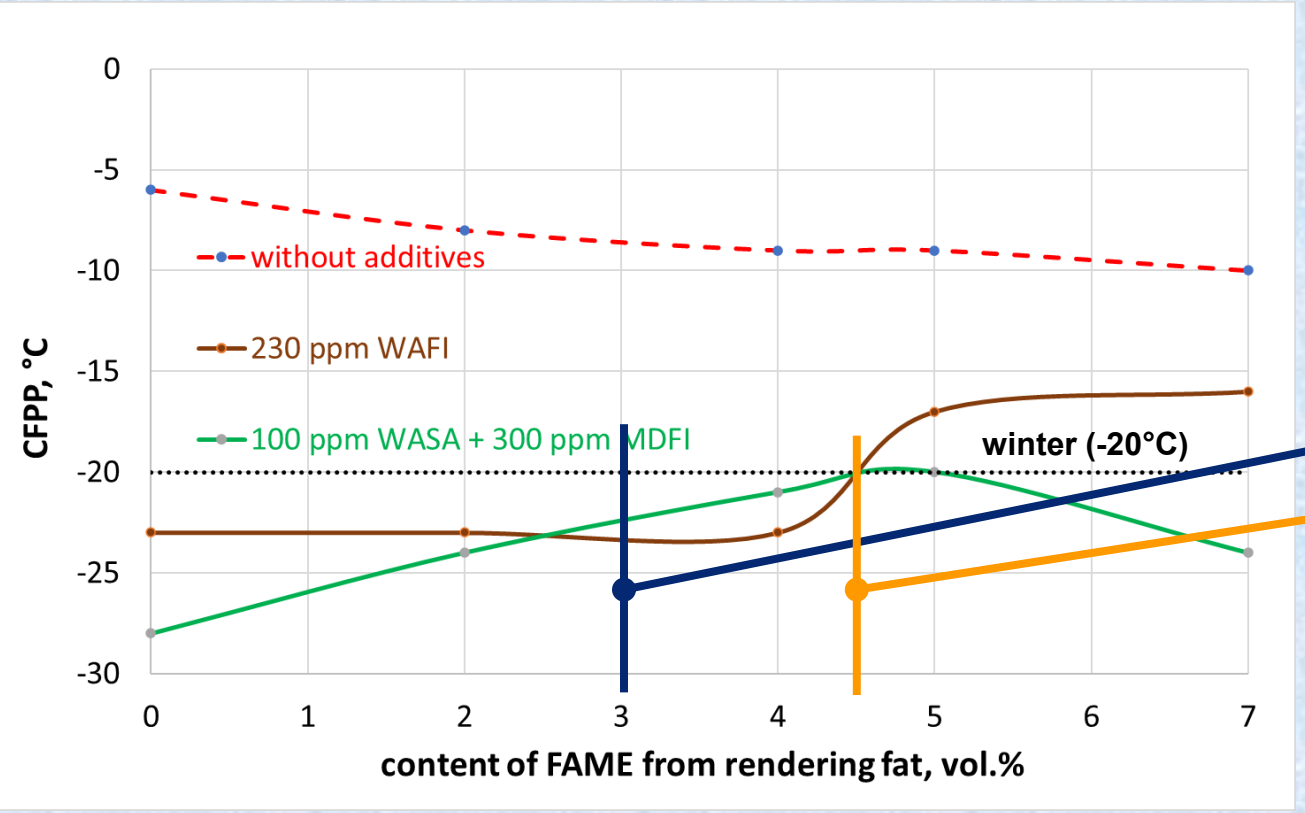
Blending FAME with diesel

Blending FAME from rendering fat (0-7 vol%) and rapeseed oil (7-0 vol%) with winter fossil diesel (93 vol.%)

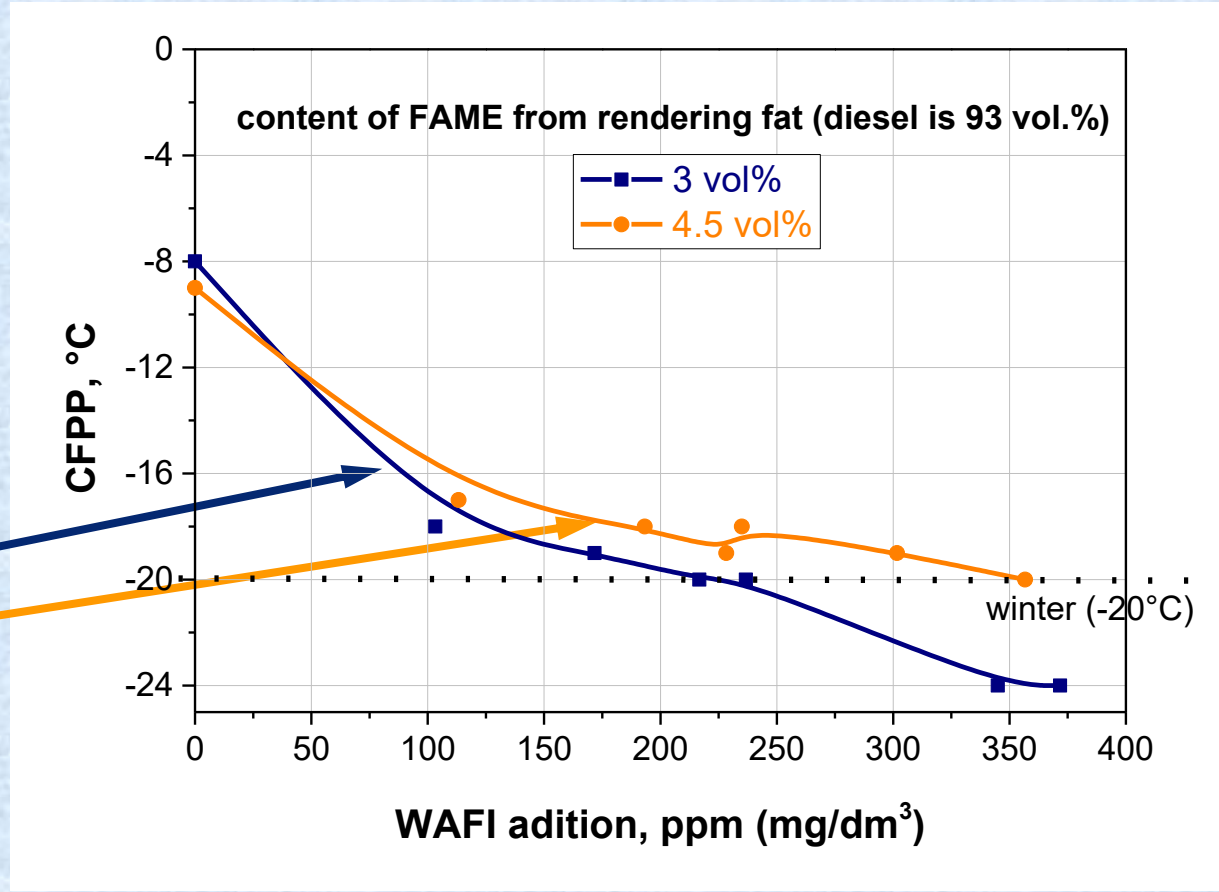
Two types of **additives with constant content**

WAFI (Wax Anti-Settling + Flow Improver)

WASA (Wax Anti-Settling Additives) and
MDFI (Middle Distillate Flow Improver)



Two mixtures with **various content of WAFI additives** (0-380 ppm)



Conclusion

- **The amides in methyl esters from animal/rendering fats were found**
- The amides negatively influence the low temperature properties (CP, CFPP)
- The content was determined by GC-MG
- Methods of removal were outlined (cooling with filtration or distillation)
- Dependence of CFPP to FAME from rendering fat and rapeseed oil with (i) various content and two types of additives and (ii) two FAME mixtures with various additive content

Thank you for your attention.