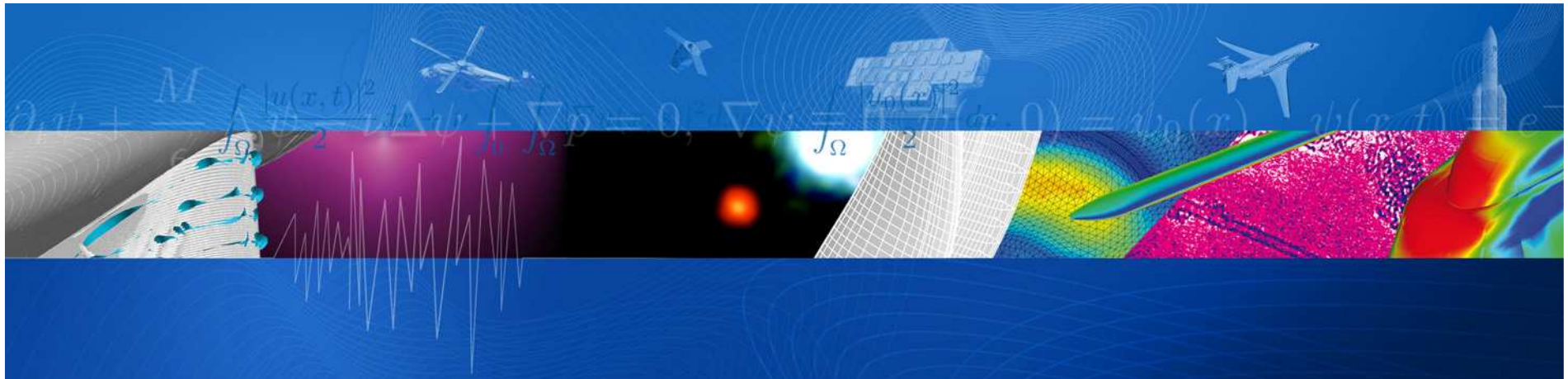

8th Workshop of the Biofuels FlightPath Initiative

Investigation of the relations between jet fuel chemical composition and properties

Cases of conventional and alternative jet fuels

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(ONERA)

Brussels, 25 April 2013

ONERA
THE FRENCH AEROSPACE LAB

retour sur innovation

Context - Requirements for jet fuels

- **Requirements imposed by:**
  - The conditions met by the planes on the ground and at high altitude
  - Besides providing a source of energy, fuel is used as a hydraulic fluid and as a coolant

    ⇒ Broad temperature range of use: -47 to 150 °C
  - Reliability/safety criteria: altitude relight, cold start, flash point…
  - Compatibility criteria between materials and jet fuel
  - Range

⇒ *Energy content* and *combustion quality* are key fuel performance properties

⇒ Other significant performance properties are *thermal stability, lubricity, viscosity, volatility, corrosion, cleanliness, density*…

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Context - Jet fuel specifications

♦ Standards

ASTM and MOD (DEF Stan) leading roles in setting and maintaining specifications for civil aviation turbine fuel (*jet fuel*)

- ➢ ASTM D 1655
- ➢ DEF STAN 91-91

⇒ Standards very similar but not identical

Jet fuel specifications and requirements defined in terms of required performance rather than in terms of target composition

Fuel	Jet A or Jet A-1*	Jet A-1
Specification	*ASTM D1655*	*DEF STAN 91-91*
Acidity, mg KOH/g	0.10	0.15
Aromatics, % vol, max	25	25.0
Sulfur, mass%	0.30	0.30
Sulfur, mercaptan, mass%	0.003	0.003
Distillation, °C:		
Initial boiling point	-	Report
10% recovered, max	205	205
50% recovered, max	Report	Report
90% recovered, max	Report	Report
End point	300	300
Flash point, °C, min	38	38
Density, 15°C, kg/m^3	775-840	775-840
Freezing Point, °C, max	-40 or -47*	-47.0
Viscosity, –20°C, mm2/sec, max	8	8.0
Net Heat of combustion, MJ/kg, min	42.8	42.8
Smoke point, mm, min	18	19.0
Naphthalenes, % vol, max	3.0	3.00
Copper corrosion, 2 hr @ 100°C, max rating	No. 1	No. 1
Thermal stability		
Filter pressure drop, mm Hg, max	25	25
Visual tube rating, max	< 3	< 3
Existent gum, mg/100 ml, max	7	7

[1]

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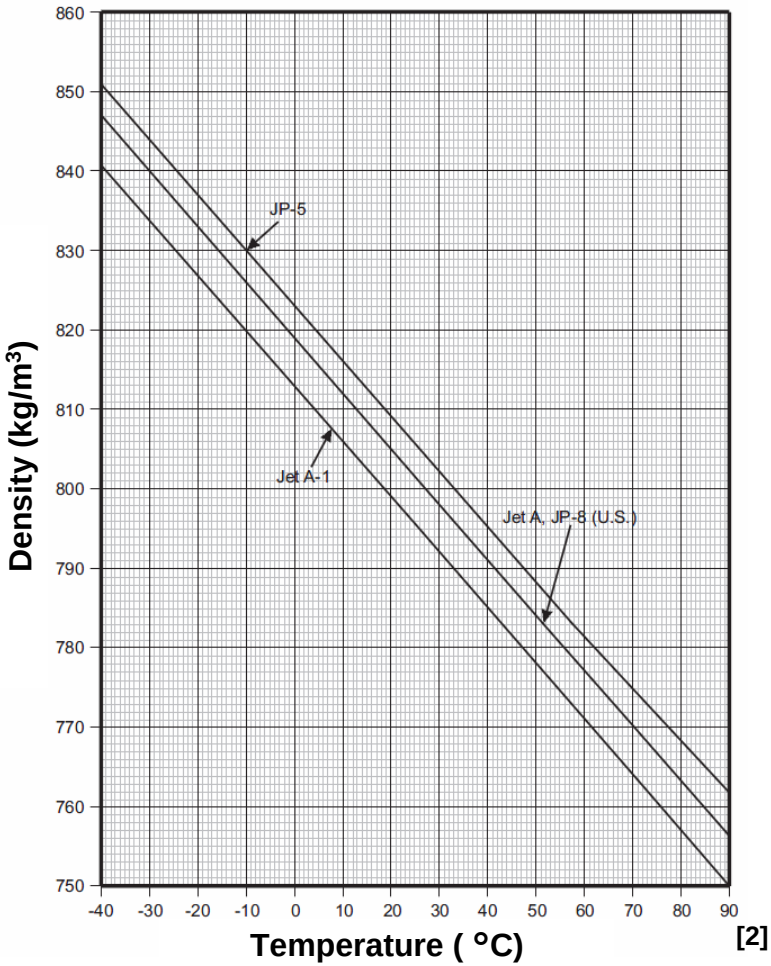
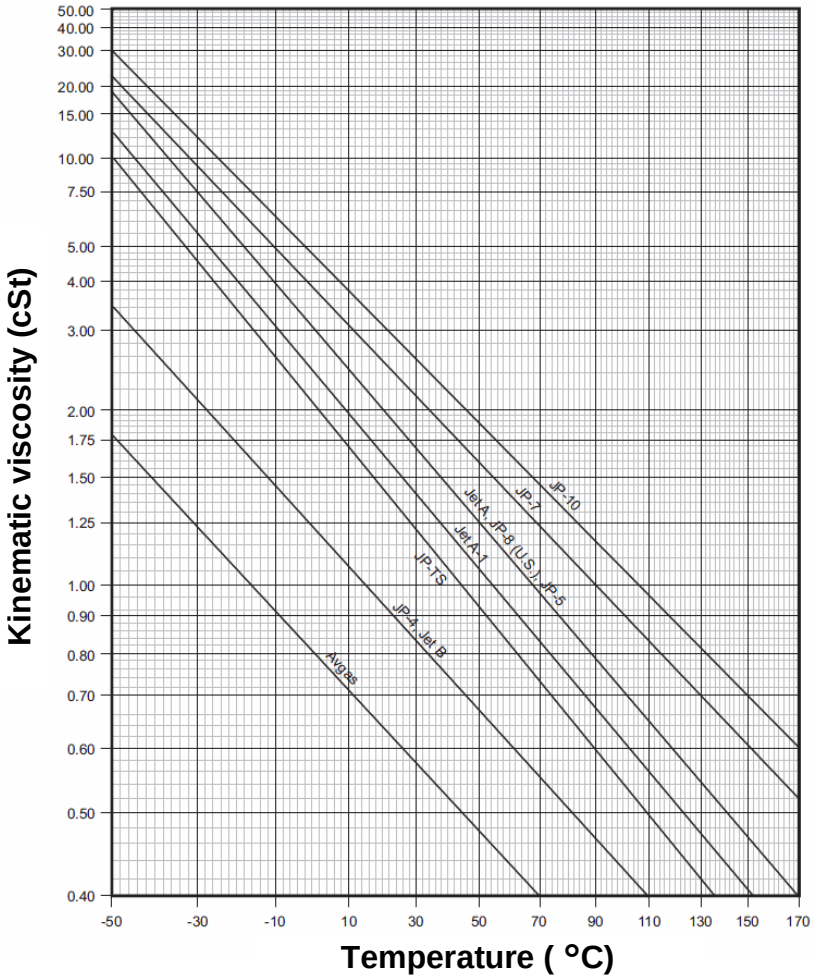
Context - Jet fuel specifications

♦ Specifications



[2]



[2]

⇒ Numerous data on fuel performances are available

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Context - Jet fuel chemical composition

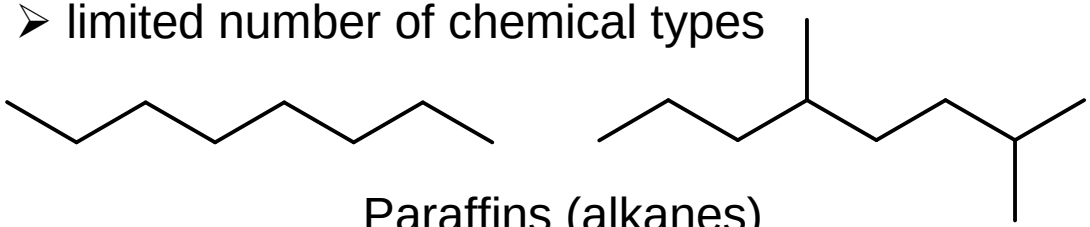
♦ Jet fuel or jet fuels?

All crude oils are unique blends of many different chemical compounds, that directly influence jet fuel composition due to production process

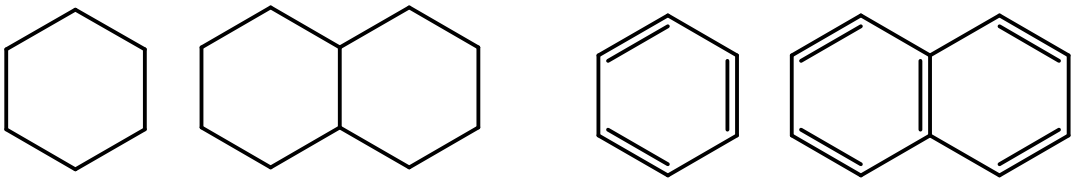
⇒ Variability of the jet fuel chemical composition

Nevertheless:

- carbon number distribution between 8 and 16 (typical boiling range: 150 to 260 °C)
- limited number of chemical types



Paraffins (alkanes)



Naphthenes (cycloparaffins) Aromatics

	World survey average, vol %
Paraffins (normal + iso)	58.8
Monocycloparaffins	10.9
Dicycloparaffins	9.3
Tricycloparaffins	1.1
Alkyl benzenes	13.4
Indans + tetralins	4.9
Naphthalene	0.1
Substitued naphthalenes	1.6

[3]

- compounds with heteroatoms (S, O and N)

~ Jet fuel: 20% n-paraffins, 40% iso-paraffins, 20% naphthenes, 20% aromatics

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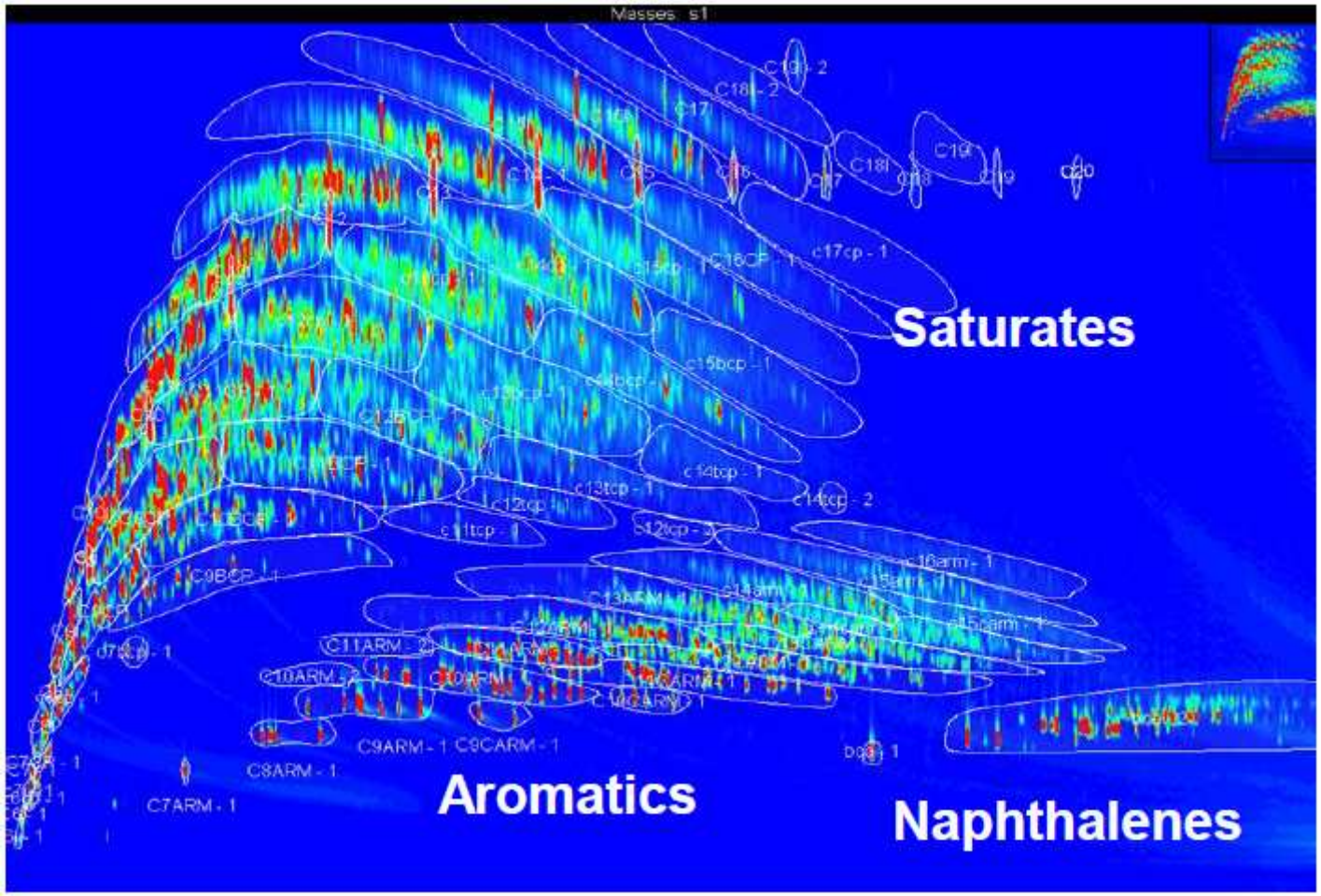
Context - Jet fuel chemical composition

GCxGC Plot for a Jet A-1



[4]

⇒ Jet fuel is a mixture of a large number - as many as a thousand or more - of different hydrocarbons

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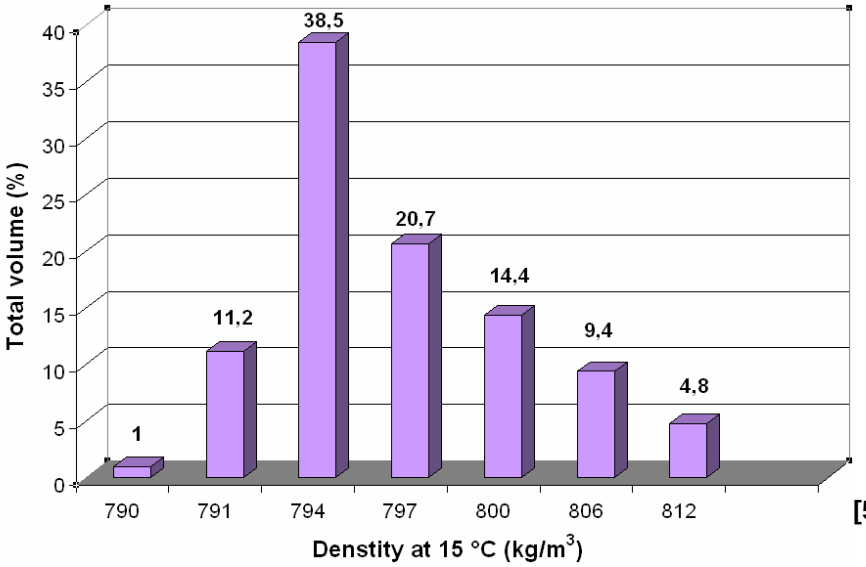
Context - Jet fuel chemical composition

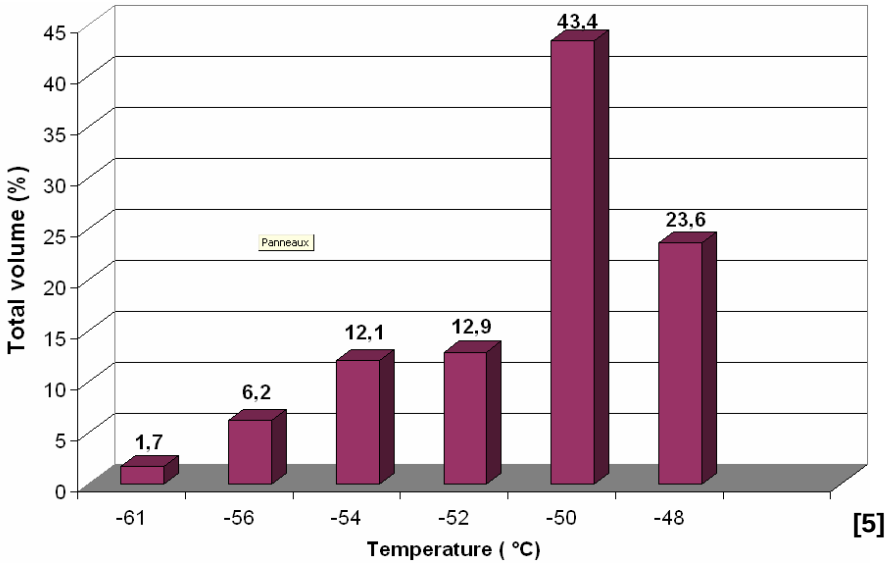
♦ Impact of the chemical composition variability on the jet fuel properties

Density



[5]

Freezing point



[5]

Jet fuel specifications provide minimum acceptable properties but the actual properties are governed by a statistical distribution that is attributable to:

- the underlying variability in petroleum
- the various processes used by refineries

Is it possible to establish a link between properties and chemical composition?

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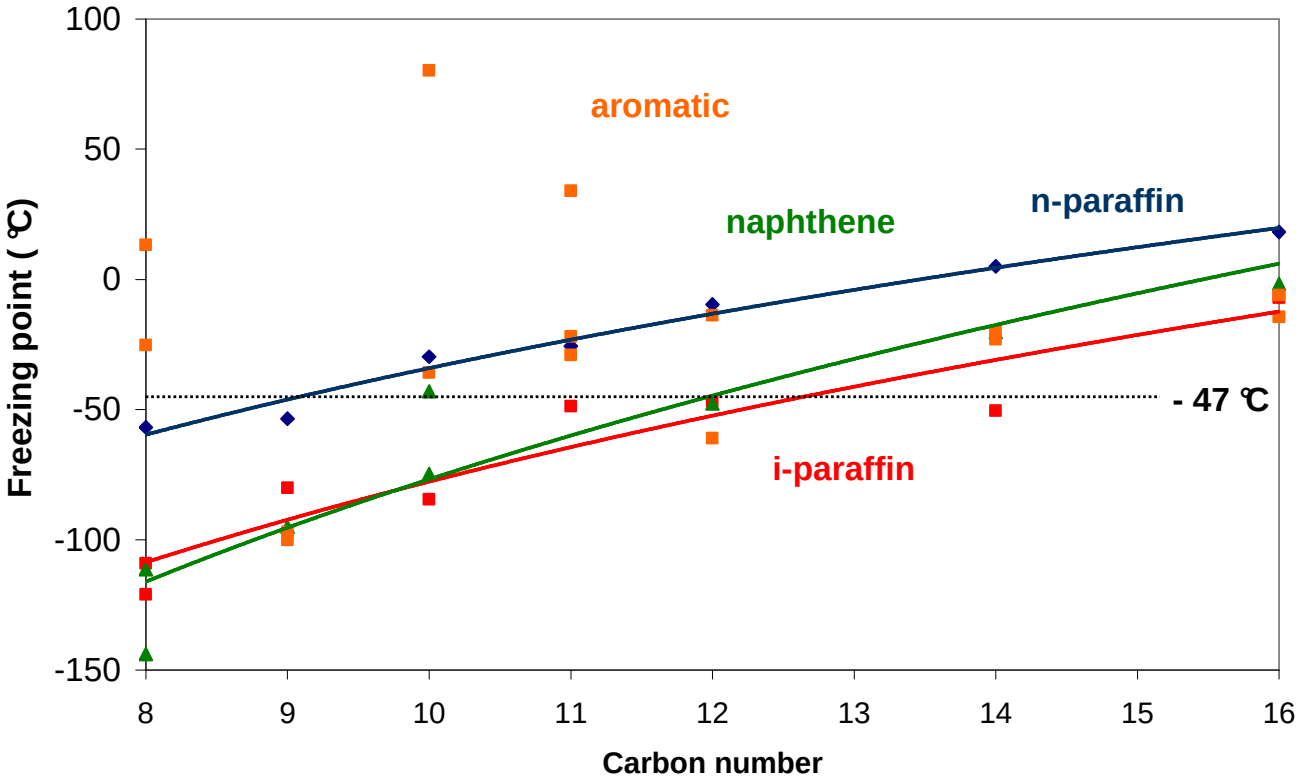
Properties of neat hydrocarbons

♦ Freezing point



⇒ FP ↑ with CN within each class but strongly influenced by molecular shape

⇒ n-paraffins and unsubstituted aromatics freeze at much higher temperatures due to easiness to pack together into a crystalline structure

⇒ i-paraffins and naphthenes: lowest freezing points

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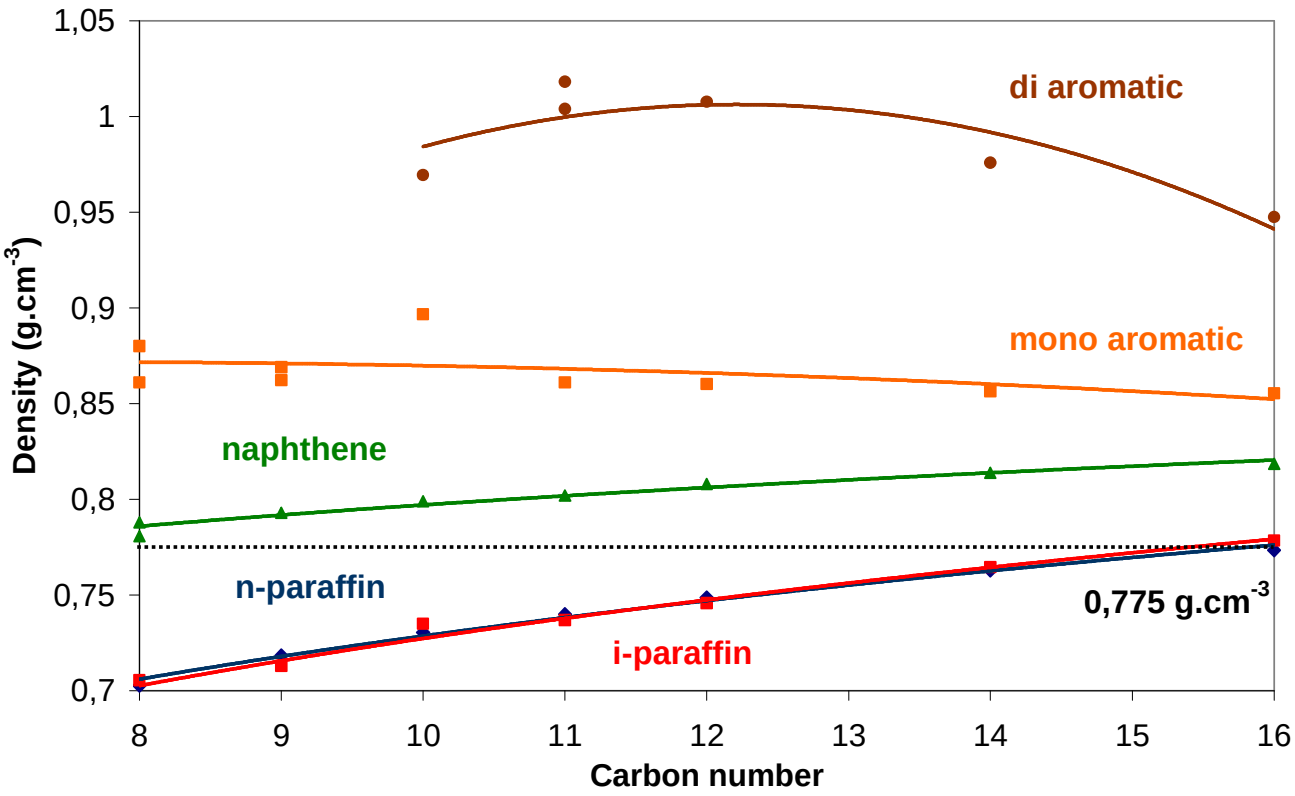
Properties of neat hydrocarbons

♦ Density



⇒ Density ↑ with CN for compounds in the same class except for aromatic

⇒ For the same CN, increasing density: paraffin < naphthene < aromatic

⇒ Paraffin density below jet specification

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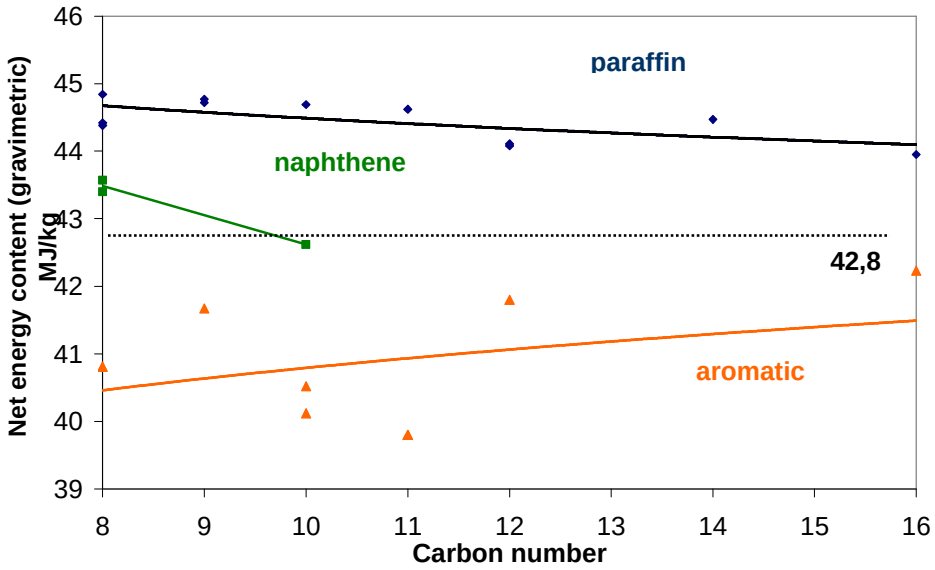
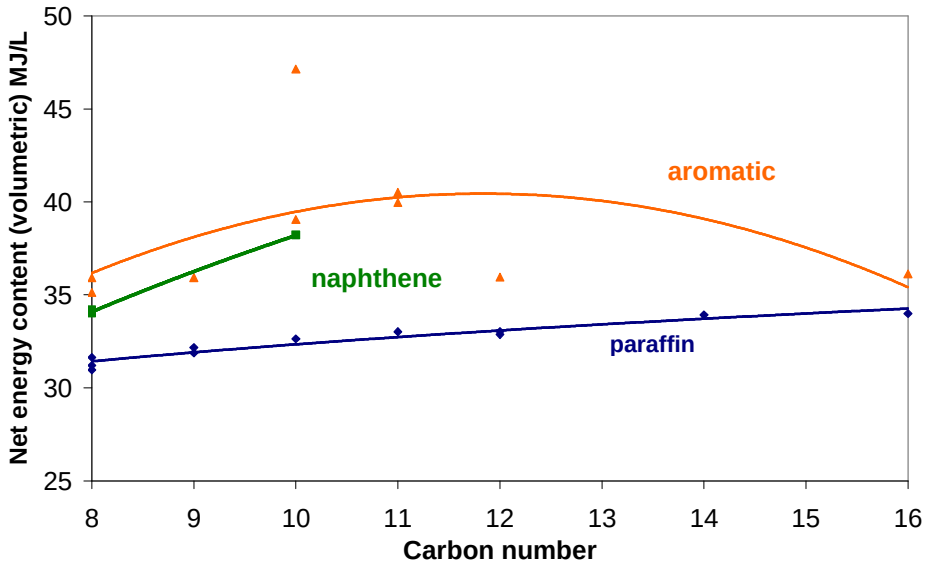
Properties of neat hydrocarbons

♦ Energy content

Gravimetric



Volumetric



For compounds with the same CN:

- ➢ Per unit weight: aromatic < naphthene < paraffin
- ➢ Volume basis: paraffin < naphthene < aromatic

Order is reversed

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Properties of neat hydrocarbons

♦ Viscosity

⇒ more related to CN than to hydrocarbon class

For a given CN: naphthenes > paraffins ~ aromatics

♦ Relationships between hydrocarbon class and jet fuel properties

Jet Fuel Property	Hydrocarbon Class			
	n-Paraffin	Isoparaffin	Naphthene	Aromatic
Energy content:				
Gravimetric	+	+	0	–
Volumetric	–	–	0	+
Combustion quality	+	+	+	–
Low-temperature fluidity	– –	0/+	+	0/–

[1]

- Normal paraffins: poor volumetric energy contents and very poor low-temperature flow properties
- Isoparaffins : high gravimetric energy contents, good low-temperature flow properties
- Aromatics: very good volumetric energy contents but poor combustion quality and low-temperature flow properties
- Naphthenes have intermediate properties

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Relationships between jet fuel chemical composition and properties

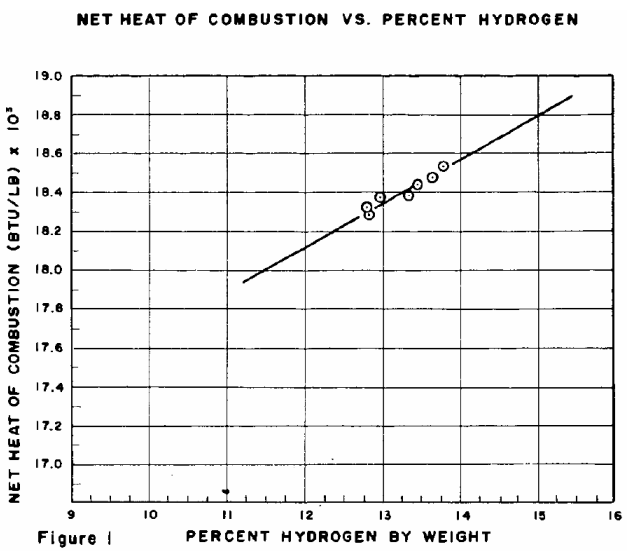
♦ 2 cases

⇒ Values are weight averages of the property values of each individual component

⇒ Values determined by the hydrocarbon class or by individual components present in small, or trace amounts

♦ Values linked to the chemical composition

- Density
- Elemental analysis
- Flash point
- Dynamic viscosity
- Energy content
- …



[6]

Density:

$$\rho(T) = \frac{m}{V(T)} = \frac{m/m}{\sum_{i=1}^{N} \frac{m_i}{\rho_i(T)} / m} = \frac{1}{\sum_{i=1}^{N} \frac{\omega_i}{\rho_i(T)}},$$

Flash point:

$$1 = \sum_{i=1}^{N} \frac{x_i \gamma_i p^*_{i,FP_{mix}}}{p^*_{i,FP_i}}$$

Dynamic viscosity:

$$\ln(\eta_{mix}) = \sum_{i=1}^{N} x_i \ln(\eta_i)$$

[7]

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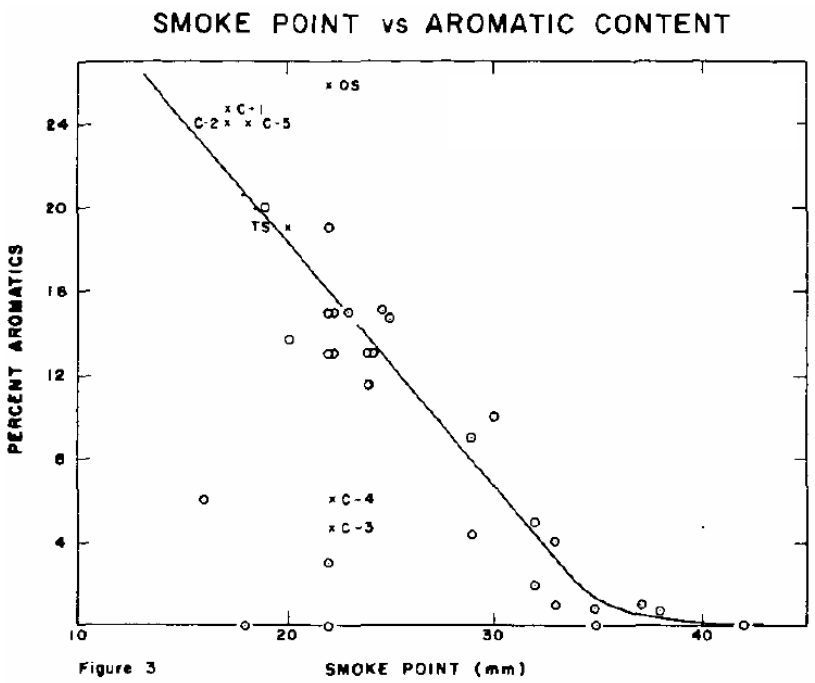
Relationships between jet fuel chemical composition and properties

♦ Values linked to the presence of specific compounds

- Electrical conductivity
- Total acidity
- Thermal stability
- Freezing point
- …



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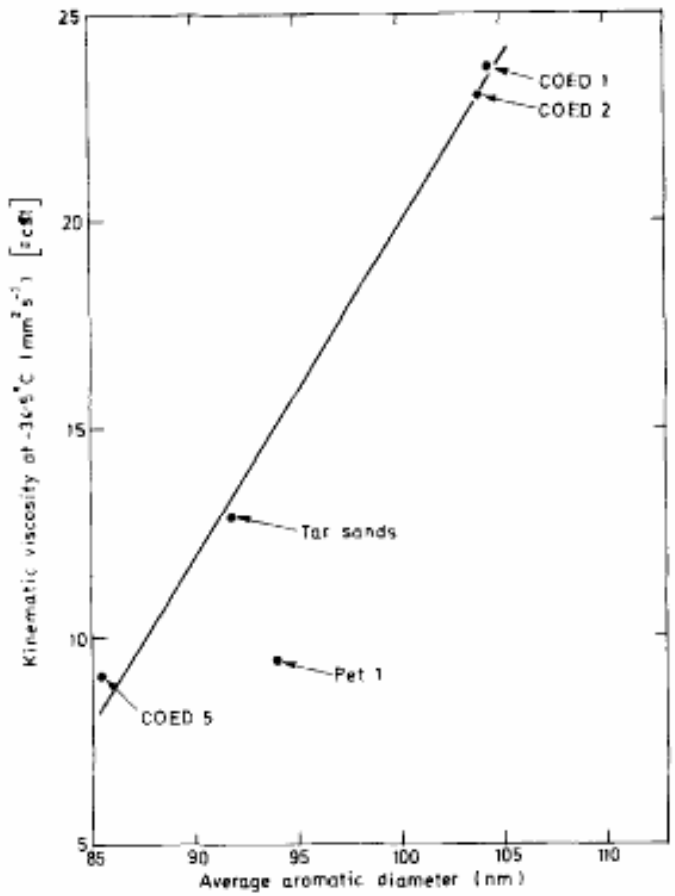

[8]

➡ Identification of the key parameters

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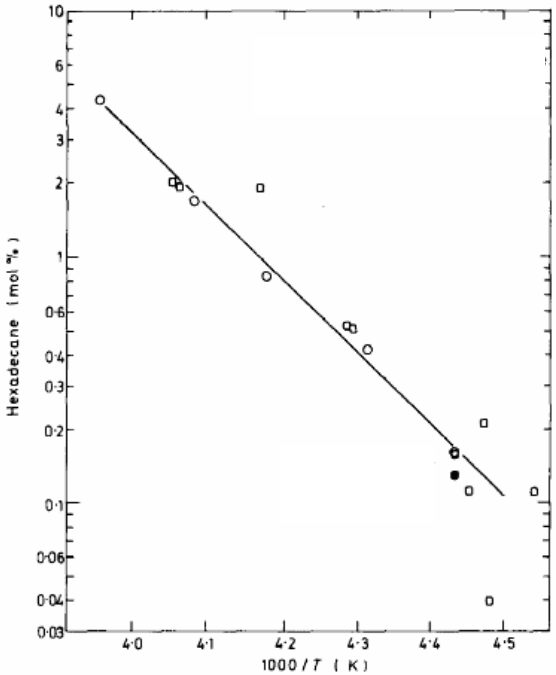
Relationships between jet fuel chemical composition and properties

♦ Values linked to the presence of specific compounds

⇒ Difficulties to understand the correlation between the composition and the value of the evaluated property



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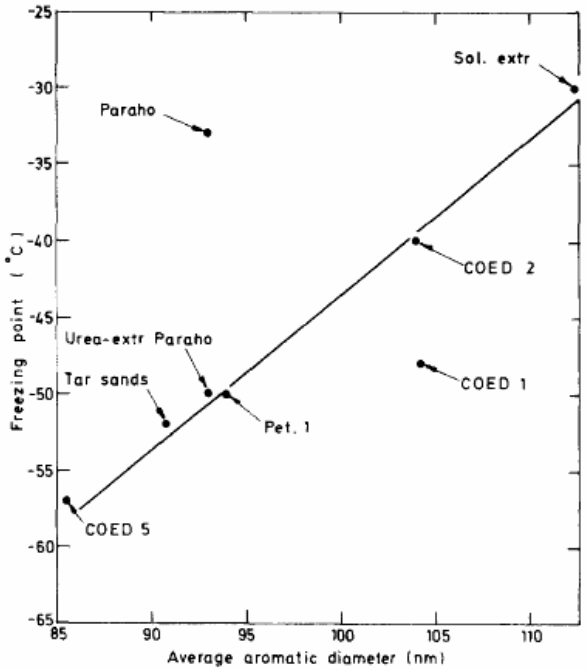

[8]

- Freezing point: linked to the heaviest n-paraffin and to the size of the aromatic compounds?

➡ Very few data available in the literature

➡ Importance of establishing models

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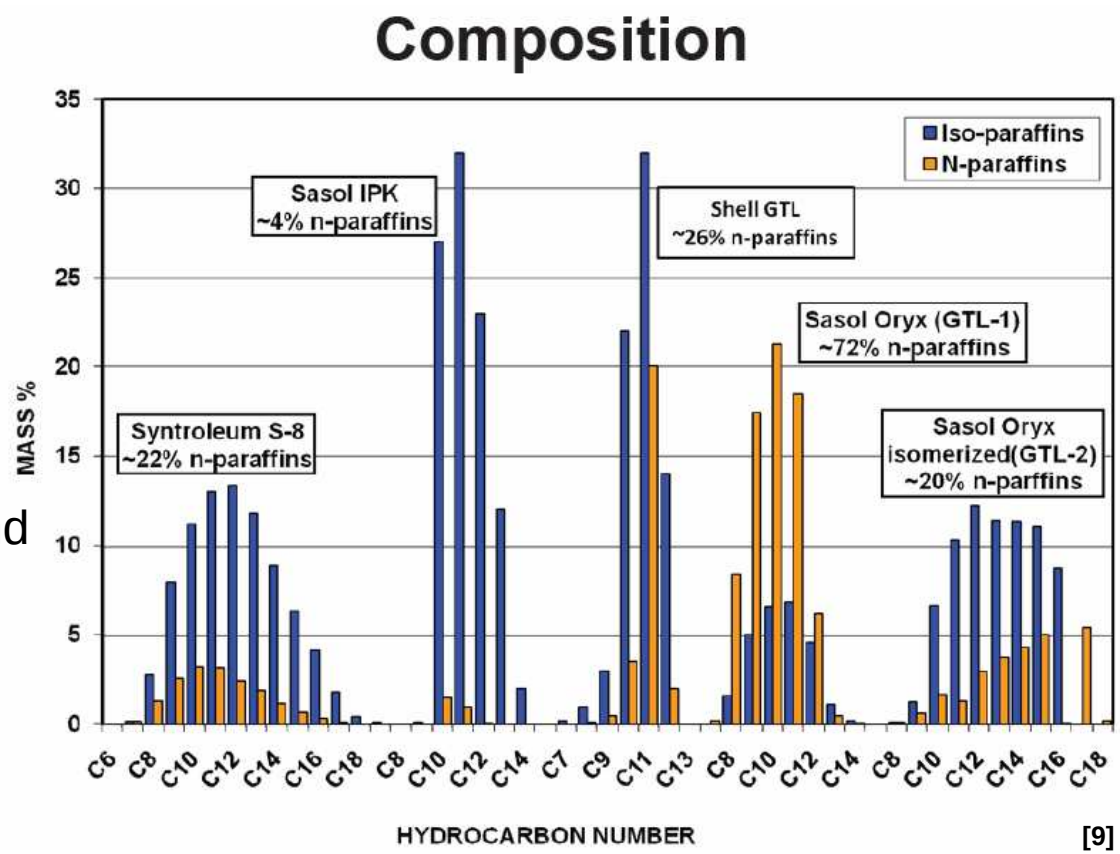
The challenge of alternative jet fuels

♦ XtL and HEFA

- Non crude oil origin
- Chemical composition significantly different
  - ⇒ no aromatic
  - ⇒ no sulphur compound
  - ⇒ mainly normal and iso paraffins



[9]

- By blending with conventional jet fuel ⇒ direct impact on the aromatic content

➡ Evolution of the fuel property values as a function of the blending rates?

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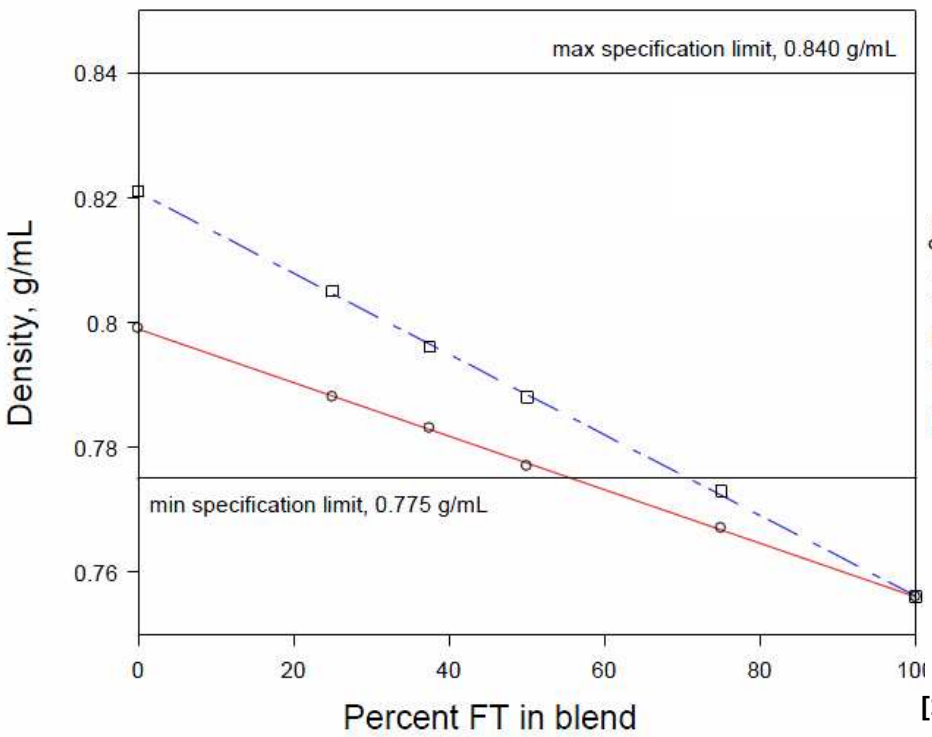
The challenge of alternative jet fuels

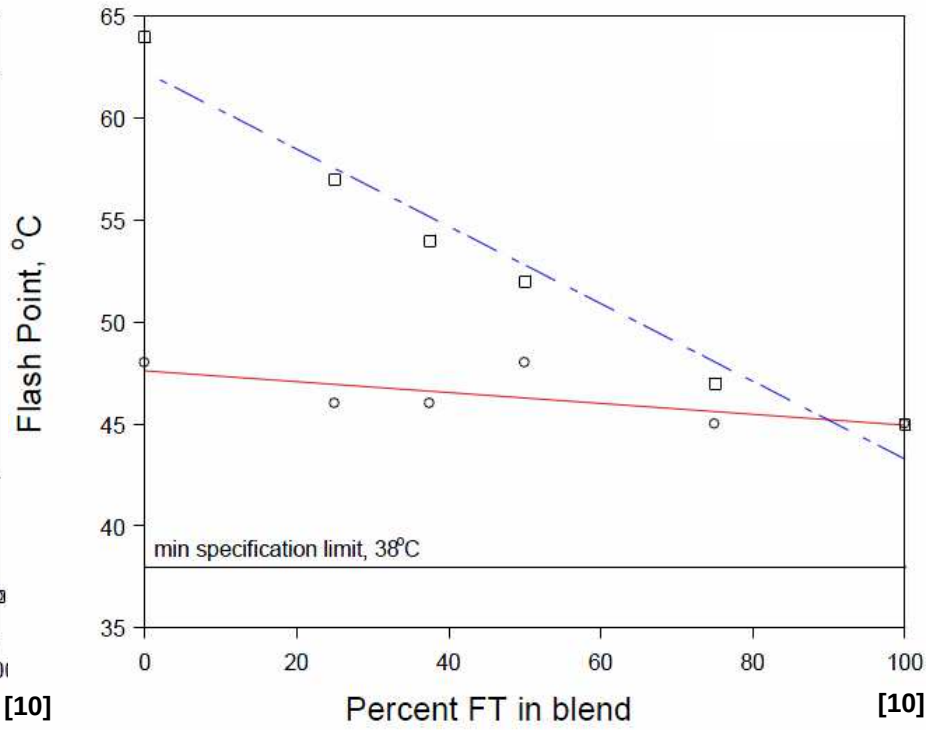
♦ Evolution of the fuel properties with the blending rate

Density



[10]

Flash point



[10]

➡ Density, flash point, distillation end point temperature, freezing point…

➡ **At first approximation, linear dependence observed with the blending rate**

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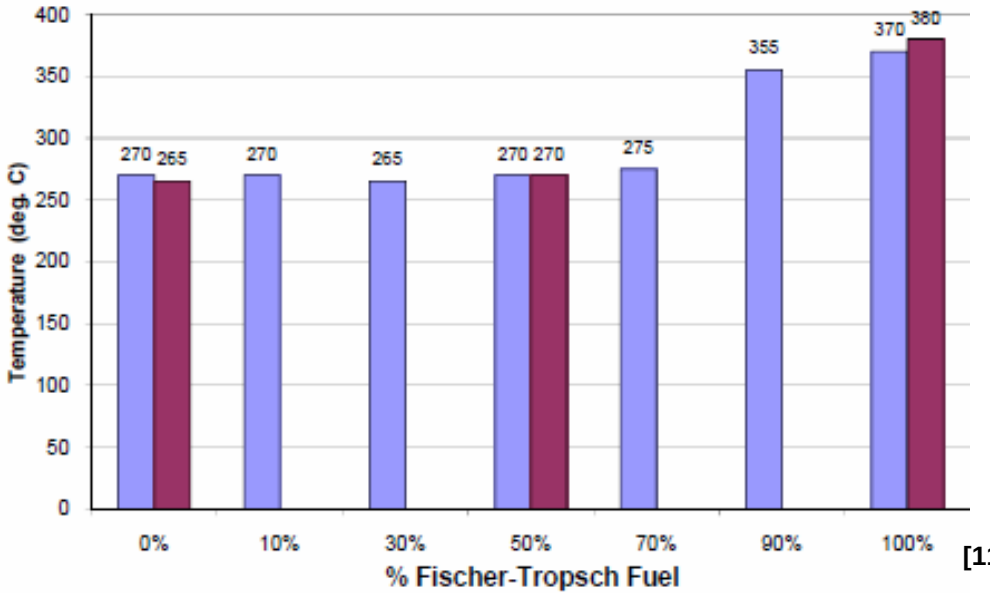
The challenge of alternative jet fuels

♦ Evolution of the fuel property values with the blending rate

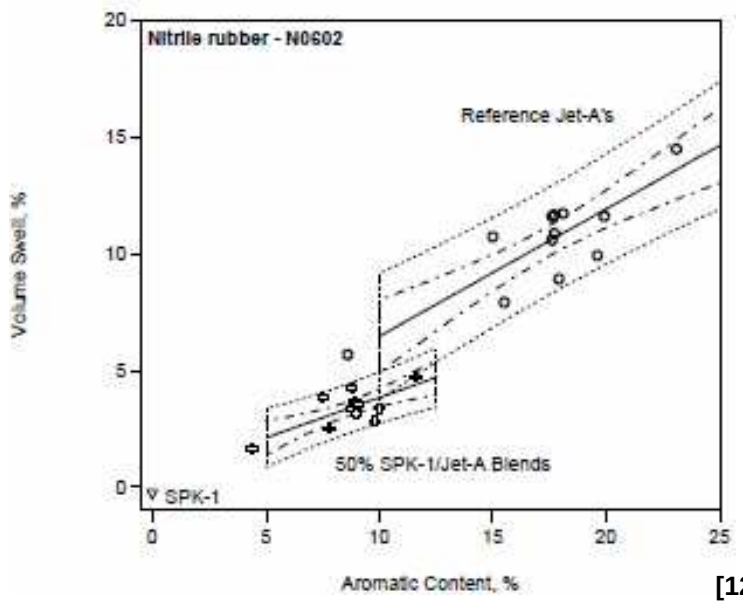
Thermal stability breakpoint



[11]

⇒ breakpoint dependent on minor fuel component degradation

Material compatibility



[12]

⇒ volume swell behaviour lower than the predicted range for Jet-A fuels

➡ **Non linear dependence with the blending rate**

➡ Importance of the identification of the key parameters

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Conclusions

- **Current situation**
  - Jet fuel developed as a whole, focusing on safety and performance within the entire flight envelope
    - Specifications based more on usage requirements than on the detailed chemistry of the fuels
    - Comprehensive knowledge not reached to determine how families of compounds or single species affect properties
- **Needs to better understand the chemical composition impact**
    - Identification of the key parameters
    - Development of accurate fuel properties models

➡ **Significant work !**

- **Work useful to:**
  - ⇒ Fuel producers → to assess alternative jet fuel potential (models to predict key intrinsic properties)
  - ⇒ OEMs → to improve simulation codes by proposing accurate fuel property models (simulate and predict key sub-processes)

➡ **MODE-AF** main objectives → FP7 program unfortunately non financed

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Future works

♦ EXPLIC : ONERA program

- Main objectives
  - ⇨ To better understand the consequences of the modification of the fuel composition on its properties
  - ⇨ To determine the acceptable blending limits of alternative jet fuels with “classic” jet fuels
- Focus
  - ⇨ To determine the minimal concentration of the aromatic compounds
  - ⇨ To better understand the role of the aromatics and the influence of the chemical composition on material compatibility, density, emissions…
  - ⇨ To study the impact of alternative fuel with a disrupted profile blended with “classic” jet fuels

♦ Others?

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