SAND2019-9975C

Predicting physical properties of bio-renewable molecules in search for a drop-in Jet-A fuel

PRESENTED BY

Alexander Landera, Ray Bambha, Anthe George

8/28/2019

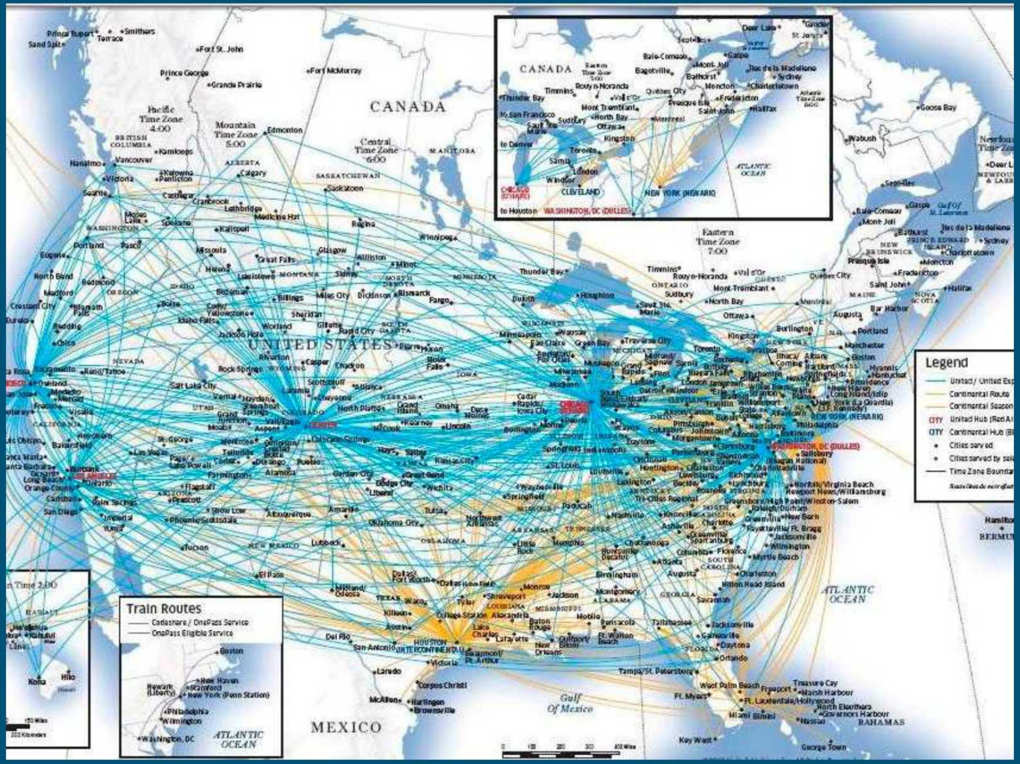
Background

- 44,000 flights either take off, or land in the U.S daily
- In 2017, 25,212,000 hours were logged by General Aviation aircraft
- In April of 2019, 650,732 miles were flown, in the U.S by commercial aircraft
- In the calendar year ending April 2019, commercial aircraft flew 18.17 million miles, in the U.S
- In 2016, airlines spent 135 billion dollars on fuel

These numbers represent…

- An opportunity to decrease emissions by creating more fuel efficient aviation fuels
- An opportunity to introduce better performing fuels (lower viscosity, better cold flow)
- An opportunity to decrease fuel costs

This can be accomplished by looking at a wide variety of fuel components, especially bio-renewable components, such as from the terpene family



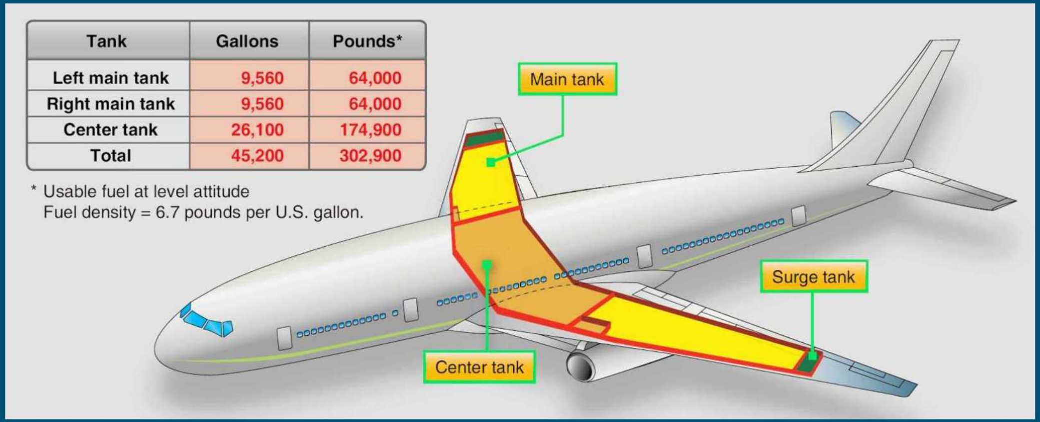
- faa.gov/air_traffic/by_the_numbers
- transtats.bts.gov/TRAFFIC/

Properties important to aviation fuel

Performance

- Specific energy is the amount of energy available per kg (>42.8)
- Energy density is the amount of energy available per liter

If Specific energy increases, fuel accounts for less weight, and more weight can be added (ie. more passengers, or luggage)
If Energy density increases, less volume of fuel is needed, and more volume opens up (ie. more passengers, or luggage)



Operability

- Freezing point (< -40 °C)
- Kinematic viscosity (-20°C <8 cSt; -40°C <12 cSt)

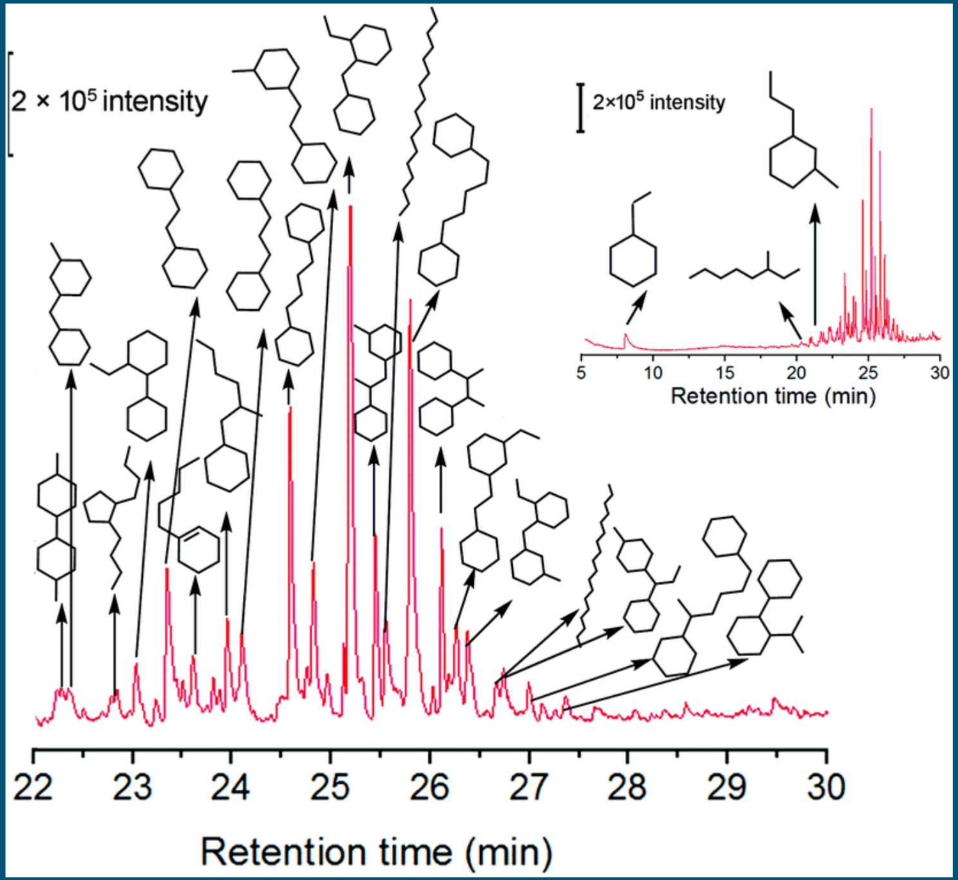
If freezing point is too high, fuel may freeze in flight
If viscosity is too high, fluidity becomes a problem

What type of molecules are in aviation fuel

Jet fuel can contain 1000s of molecules

- Avoid oxygenates
- Avoid unsaturated double bonds
- Limit aromatic content

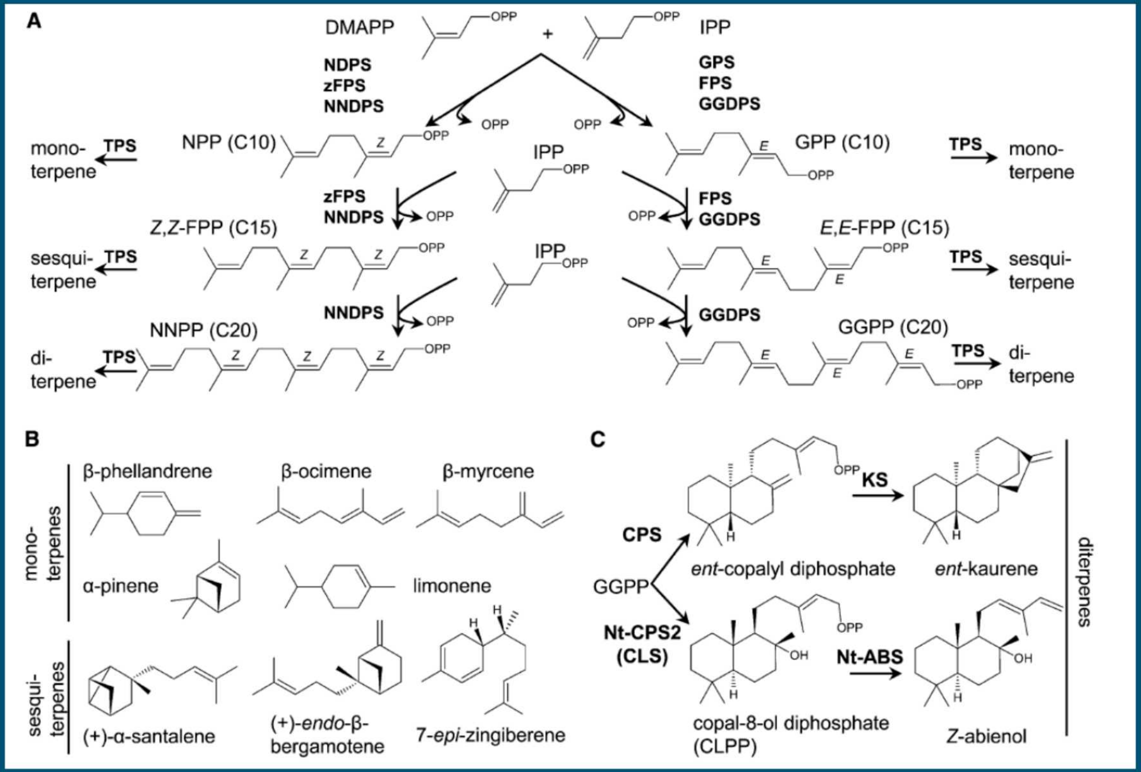
Property	n-Alkanes	iso-Alkanes (Weakly Branched)	Monocyclo-alkanes	Dicyclo-alkanes	Aromatics	HPF Molecules
Specific Energy	++	++	+	-	--	++
Energy Density	-	-	+	++	+	++
Thermal Stability	+	+	+	+		
Flash Point	-	-	+	+	+	--
Freeze Point	-	-	+	-	+	--
Viscosity	+	+	-	--	0	-
Boiling Point	+	++	0	-	-	0
Density	-	-	+	++	+	++
Sooting	++	++	+	+	--	
DCN	++	+			-	



Green Chem., 2015, 17, 5131-5135

High Performance Fuels (HPF)

- These are natural products, which have properties that are favorable for blending into aviation fuel
- These come from biomass (lignin), small organisms (e.coli), and other organisms
- While these molecules can still not be produced in significant quantities, genetic engineering, and other techniques are being used to speed up their production

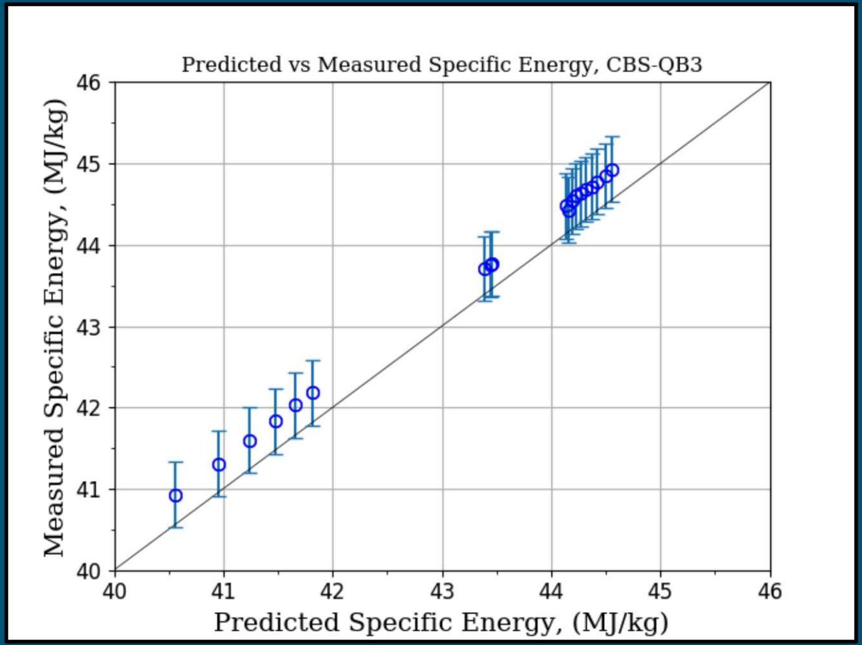


www.plantcell.org/cgi/doi/10.1105/tpc.113.111013

Methodology

ED and SE calculations

- Ab-initio calculations CBS-QB3
- Density and HOV is calculated
- using the SAFT-γ-mie EoS

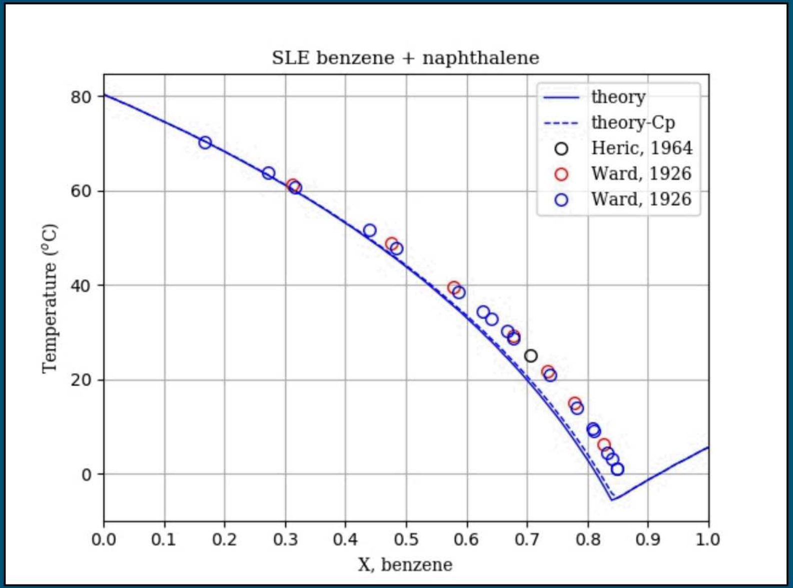


Solid-Liquid-Equilibrium (SLE) equation

$$x_k \gamma_k^l = exp\left\{\left(\frac{\Delta H_k^{sl}}{RT_{mk}}\right)\frac{T-T_{mk}}{T} + \frac{\Delta C_{pk}^{sl}}{R}\left[ln\left(\frac{T}{T_{mk}}\right) - \frac{T-T_{mk}}{T}\right] + I\right\}$$

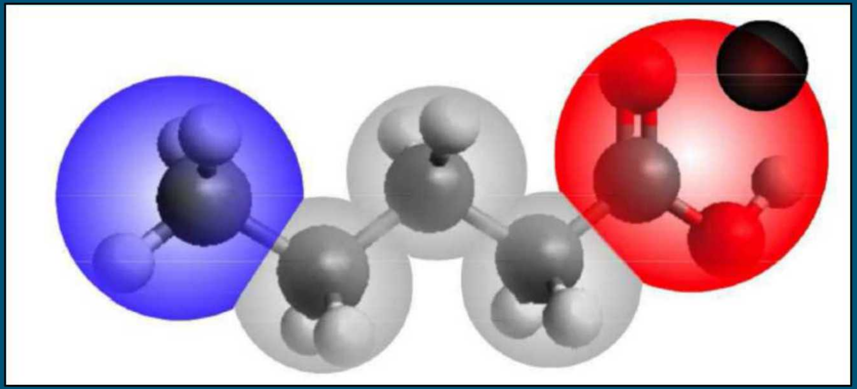
Parameters required

- ΔH_k^{sl} $(enthalpy\ of\ fusion)$
- $\Delta C_{pk}^{sl}$$(heat\ capacity\ term)$
- T_{mk} $(melting\ point)$
- γ_k^l (calculated through SAFT-γ-mie EoS



Methodology cont.

SAFT-γ-mie EoS



- Group contribution method
- Each group has unique ε, σ, λ^r
- Parameters between different groups are obtained through combining rules
- $A = a^{ideal} + a^{mono} + a^{chain} + a^{assoc}$

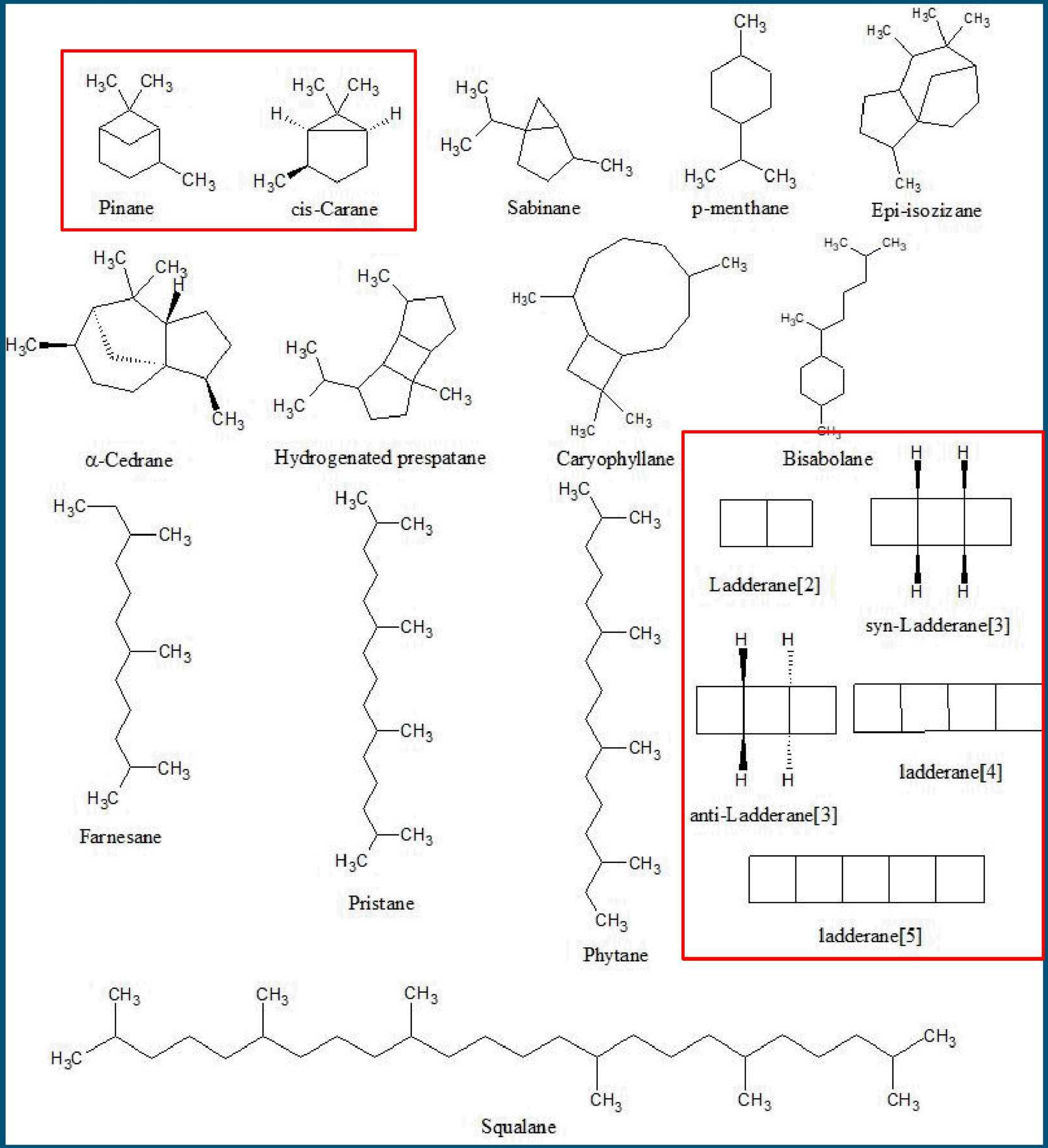
Viscosity: superTRAPP

$$\eta(T,\rho) = \eta_{ref}(\frac{T}{g}, \rho h)\left[\frac{M^{1/2}}{Mref^{1/2}}\right] g^{1/2} h^{-2/3} \chi_\eta$$

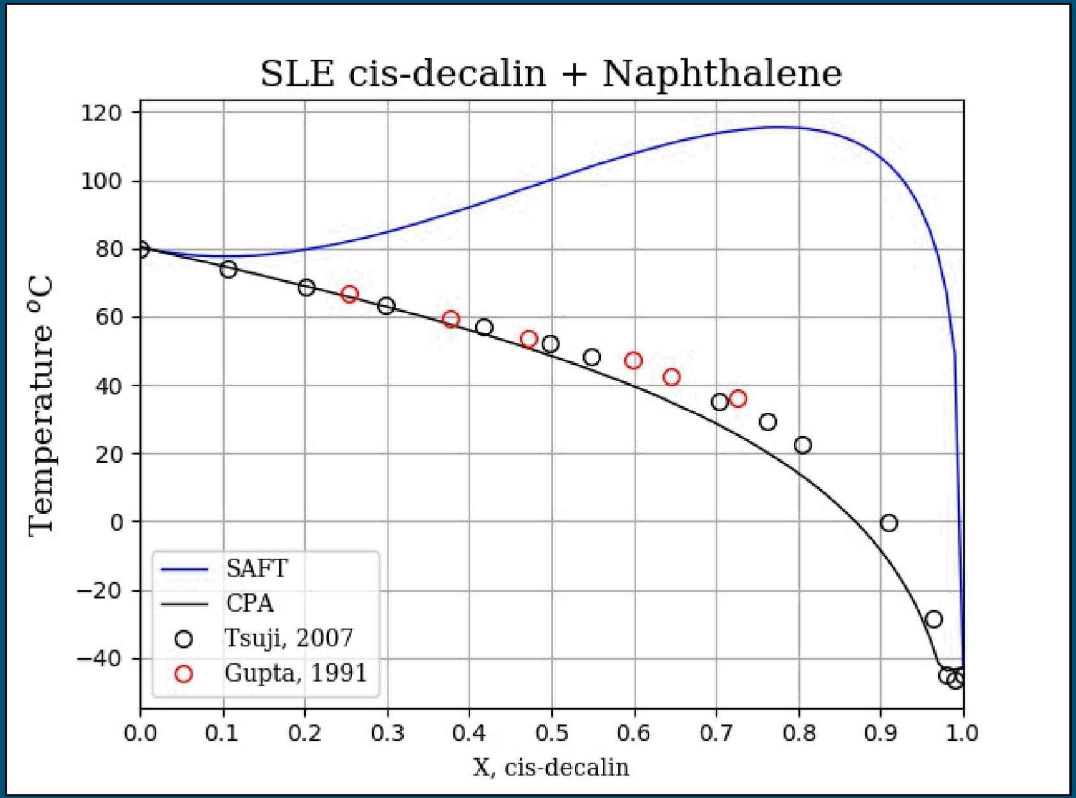
- g and h are obtained from empirical expressions
- M is the molecular weight of the fluid
- χ_η is a correction factor, which corrects for non-correspondence
- The reference fluid chosen is propane
- Typical errors for binary systems of ~ 5.0%

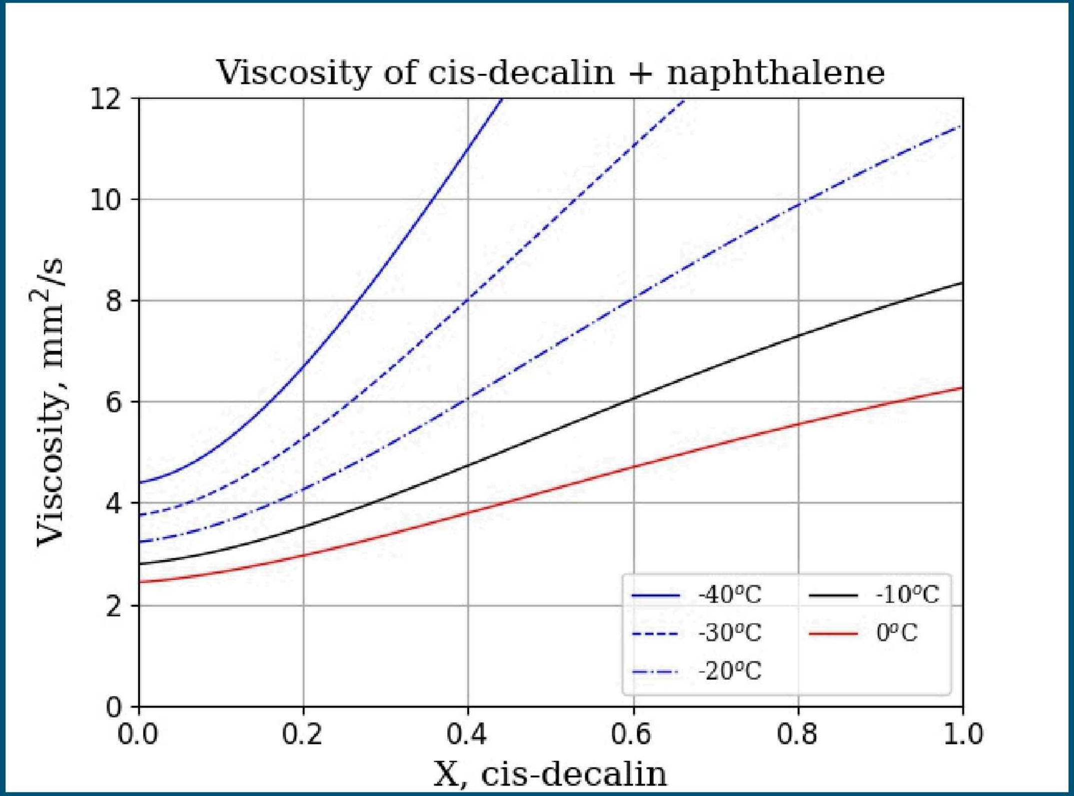
Energy density and specific energy of HPF molecules

Molecule	Formula	Mol. Weight g/mol	Specific Energy MJ/kg		Energy Density MJ/L	
			Calc.	Lit.[1]	Calc.	Lit.[1]
pinane	$C_{10}H_{18}$	138.25	43.66	42.94	37.18	36.56
cis-carane	$C_{10}H_{18}$	138.25	44.40	-	38.14	-
sabinane	$C_{10}H_{18}$	138.25	43.69	42.80[2]	35.44	34.71[2,3]
p-menthane	$C_{10}H_{20}$	140.26	43.71	43.33	35.14	34.58
epi-isozizane	$C_{15}H_{26}$	206.37	42.72	-	38.75	-
alpha-cedrane	$C_{15}H_{26}$	206.37	42.79	42.7[4]	39.62	39.41
prespatane (saturated)	$C_{15}H_{26}$	206.37	43.27	-	38.94	-
caryophyllane	$C_{15}H_{26}$	208.39	43.72	43.54	37.16	37.01
bisabolane	$C_{15}H_{30}$	210.40	43.76	43.36	35.99	35.64
farnesane	$C_{15}H_{32}$	212.42		43.95		33.89
pristane	$C_{19}H_{40}$	268.52		43.84		34.24
phytane	$C_{20}H_{42}$	282.56		43.84		34.53
squalane	$C_{30}H_{62}$	422.83		43.63		35.17
ladderane[2]	C_6H_{10}	82.14	44.98	44.60	42.37	42.3[8]
ladderane[3], syn-	C_8H_{12}	108.18	44.73	44.30	48.50	46.3[8]
ladderane[3], anti-	C_8H_{12}	108.18	44.47	44.07	48.22	46.3[8]
ladderane[4]	$C_{10}H_{14}$	134.21	44.12		52.30	49.2[8]
ladderane[5]	$C_{12}H_{16}$	160.25	43.90		55.60	51.4[8]
Jet-A				≥42.8		≥33.2[6]
HPF threshold				≥43.55		≥36.18

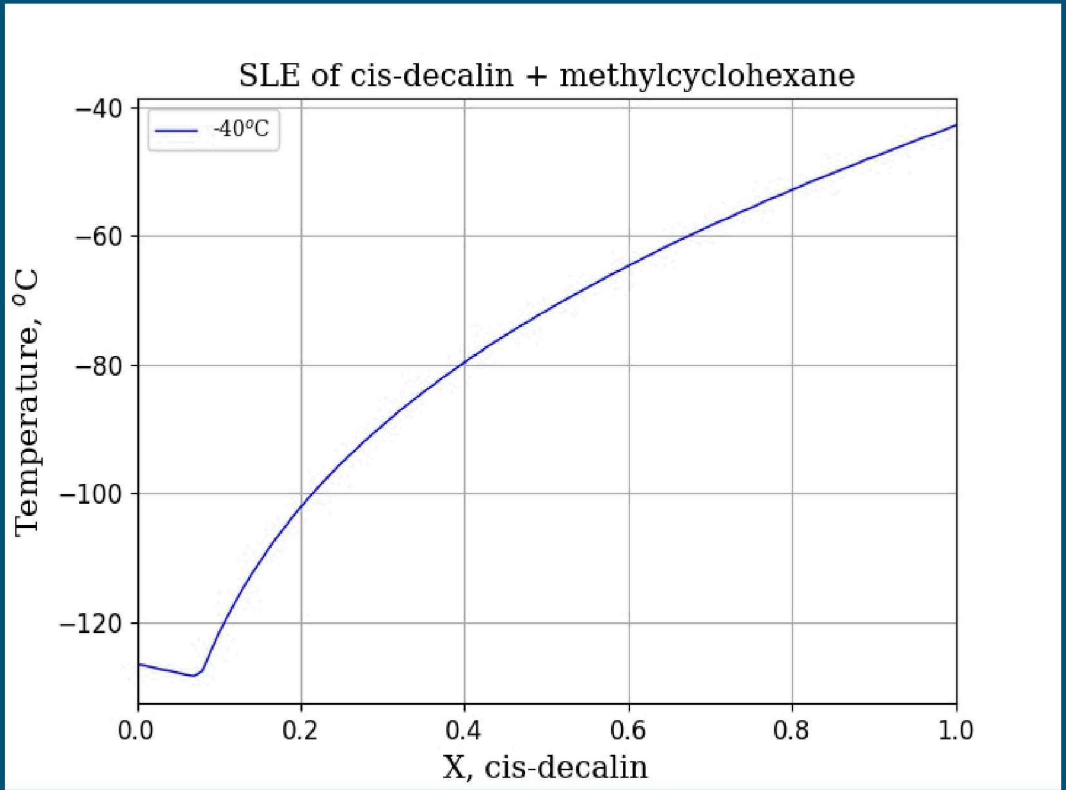


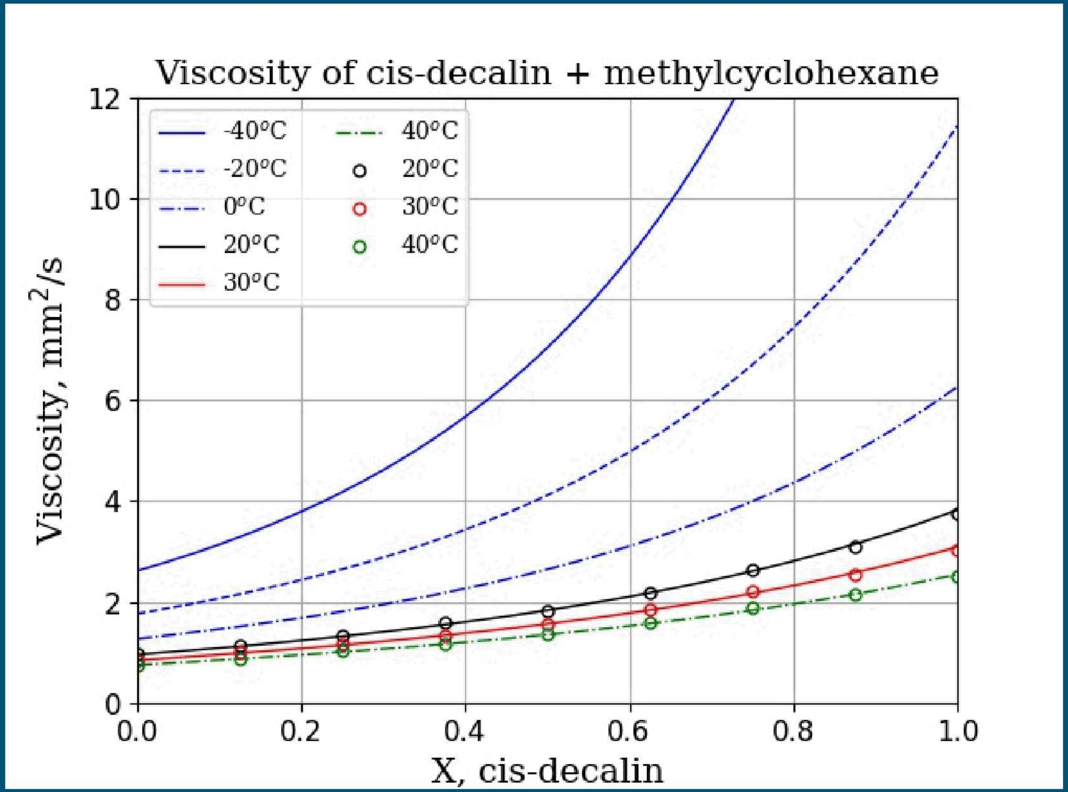
Cis-decalin + naphthalene





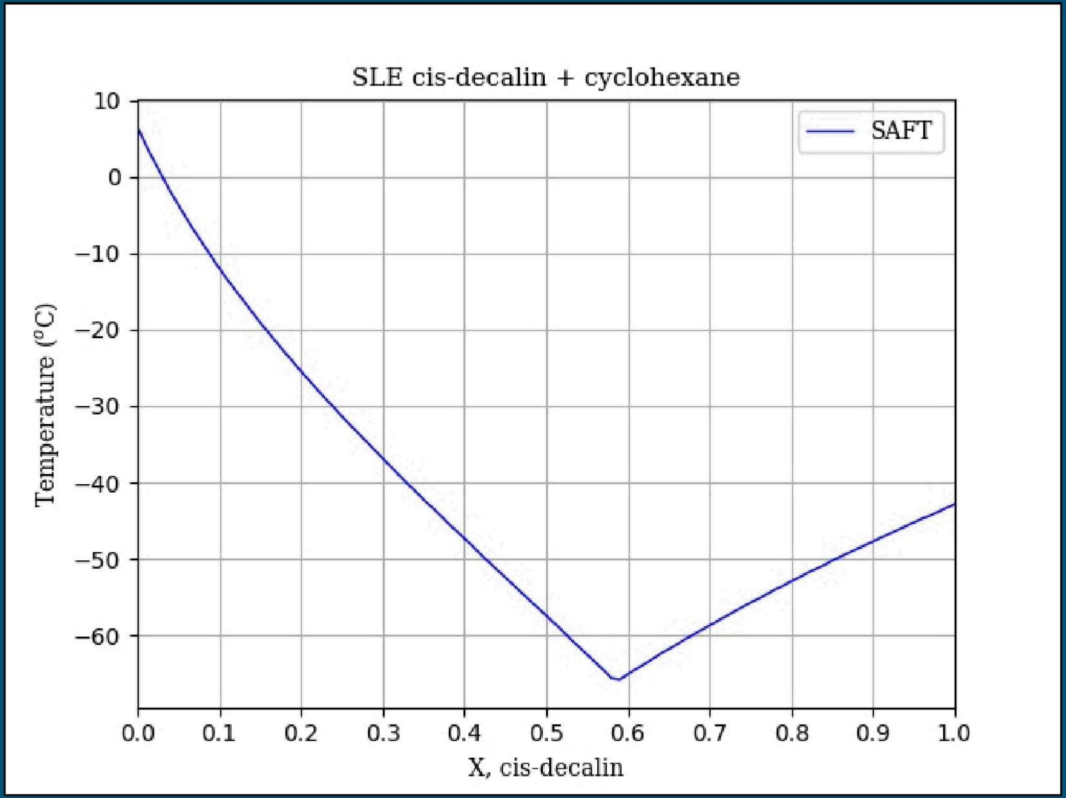
Cis-decalin + methylcyclohexane

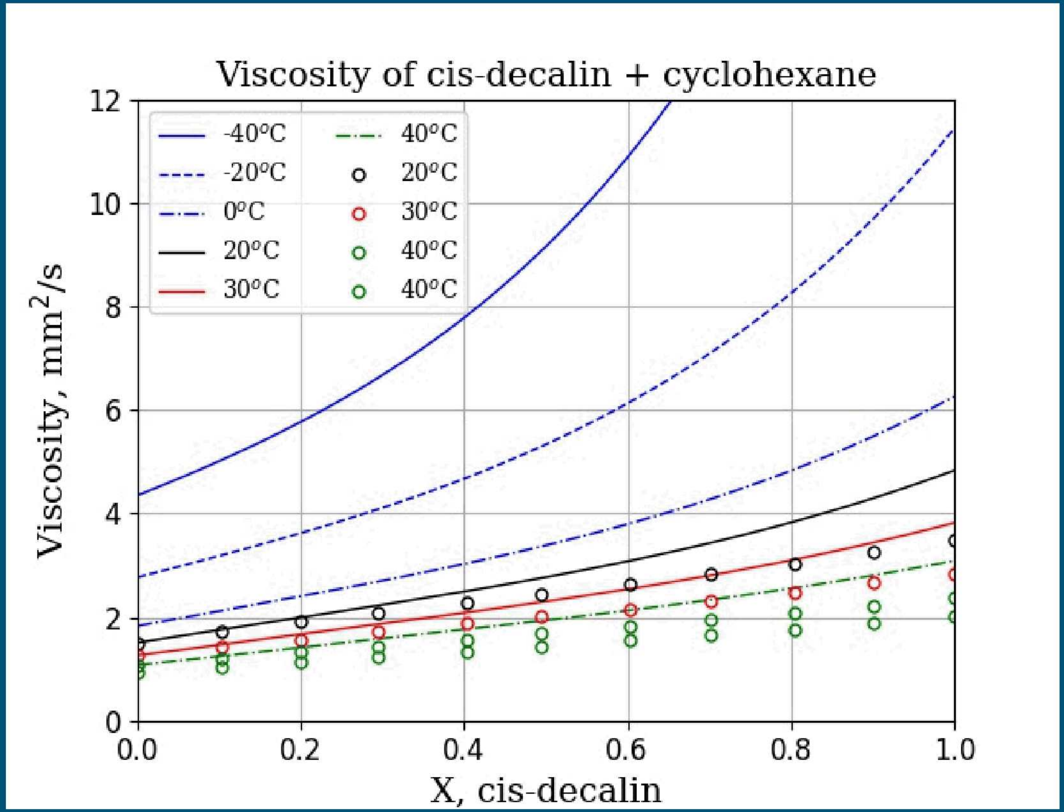




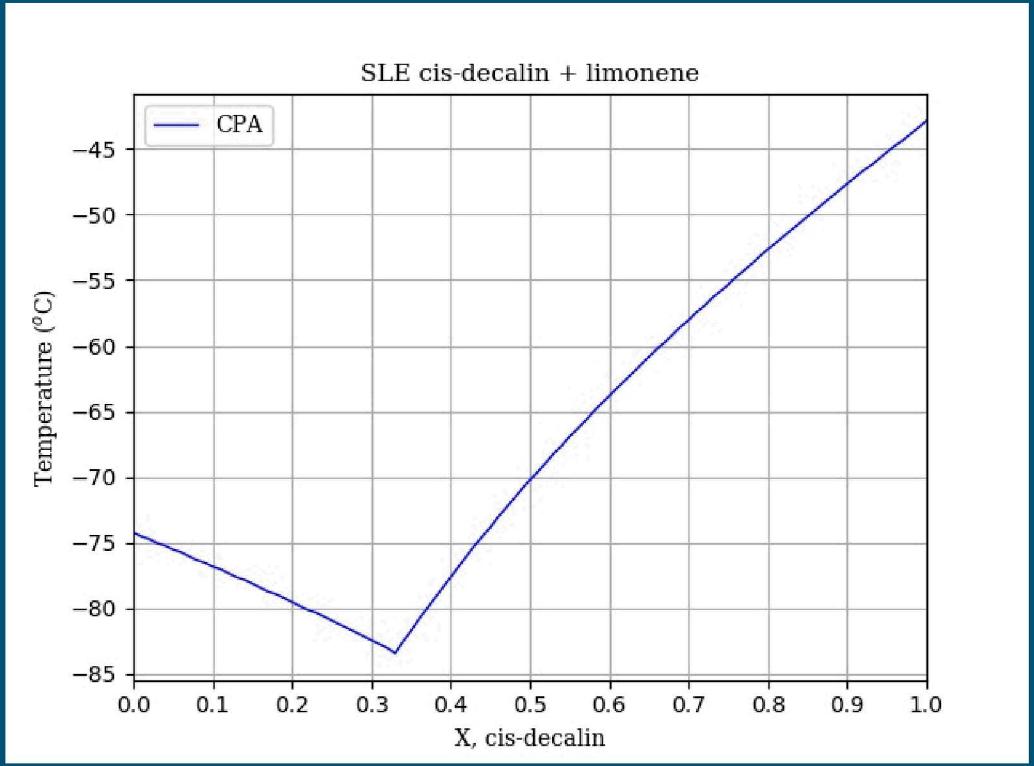
Viscosity is limiting, but no very much so

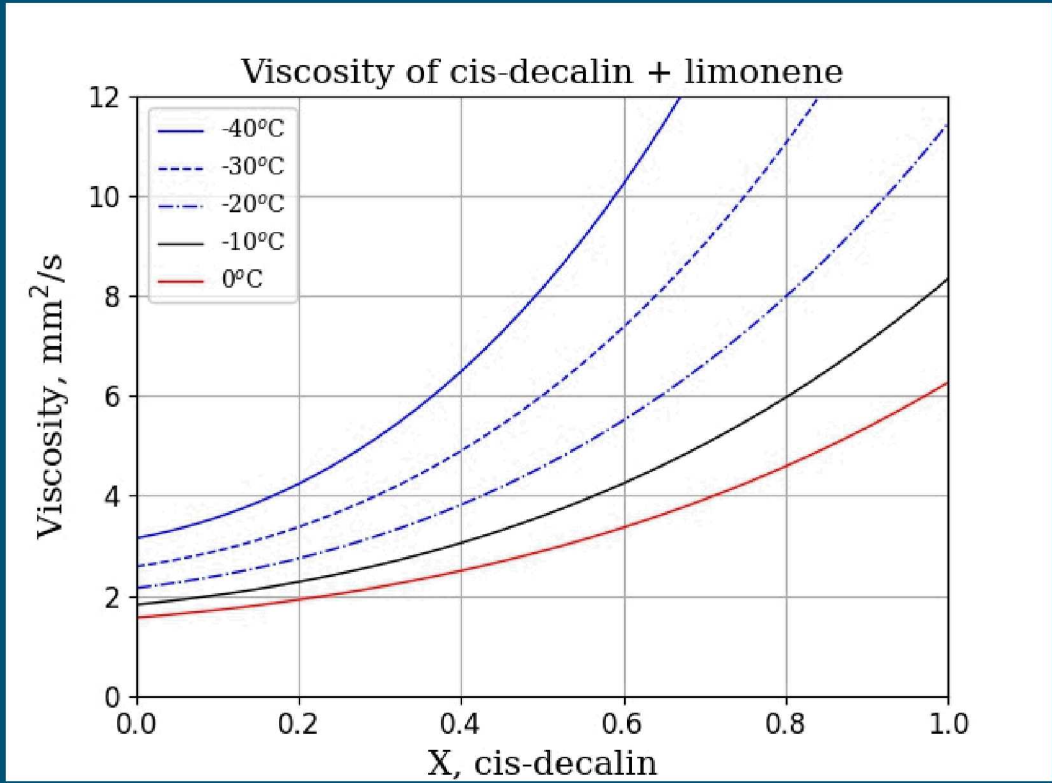
Cis-decalin + cyclohexane



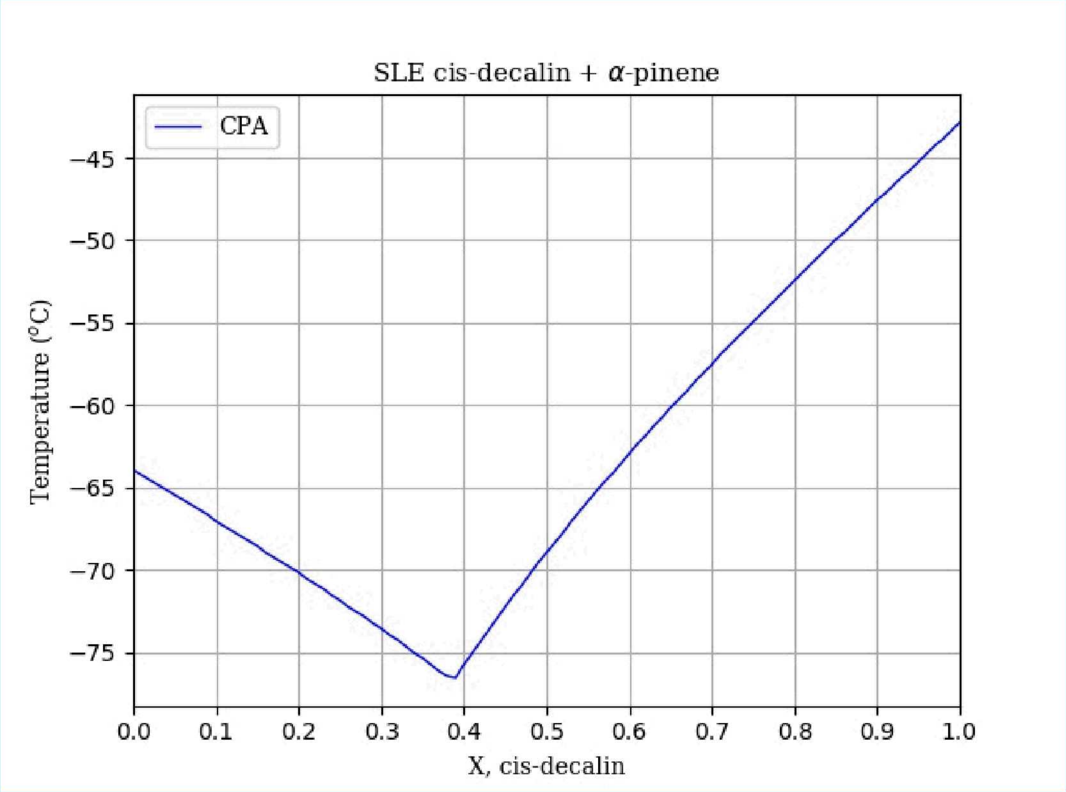


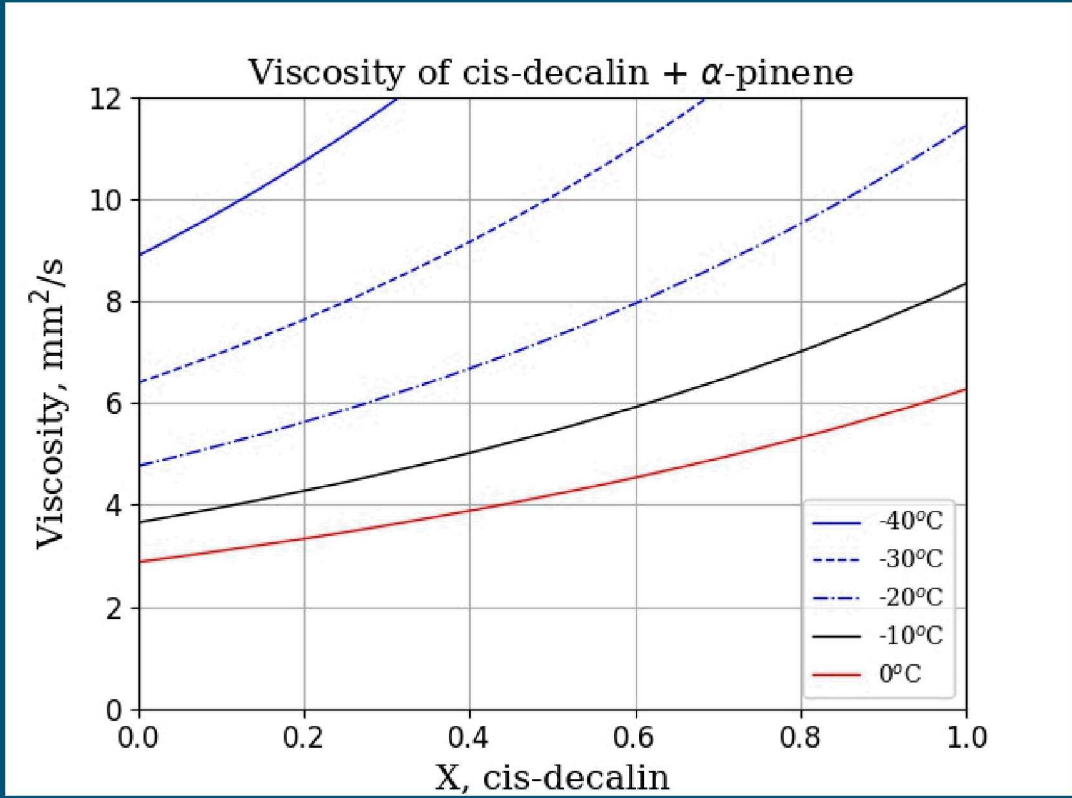
Cis-decalin + limonene





Cis-decalin + α-pinene





Conclusions

- Cyclic alkanes can complement and augment the physical properties of other jet fuel components, making them valuable jet fuel molecules
- Theoretical methods are available, which can accurately describe the physical properties of fuels over wide compositional ranges
- The addition of small amounts of decalin can lower the freezing point by interacting with cyclohexane
- Methylcyclohexane has a pure freezing point of -130 °C. Including it can potentially be beneficial to the overall freezing point of fuel.
- The viscosity of decalins limit their use in jet fuel
- Their energy content (SE, ED) are comparable to Jet-A