



# Aerospace Combustion

## Lecture 2:

## Aerospace Propellants



## Content

- Requirements and Specifications for Propellants
  - Jet Fuels
    - Volatility, Fluidity, Stability, Lubricity,
    - Flammability , Emissions
  - Rocket Propellants
    - Performance
    - Storage
    - Ignition
- Specifications
  - Jet Fuels (properties)
  - Rocket Propellants
- Thermodynamic Specifics of Operating Conditions
  - Critical conditions
- Bio Fuels (Surrogates)

## Jet Fuels

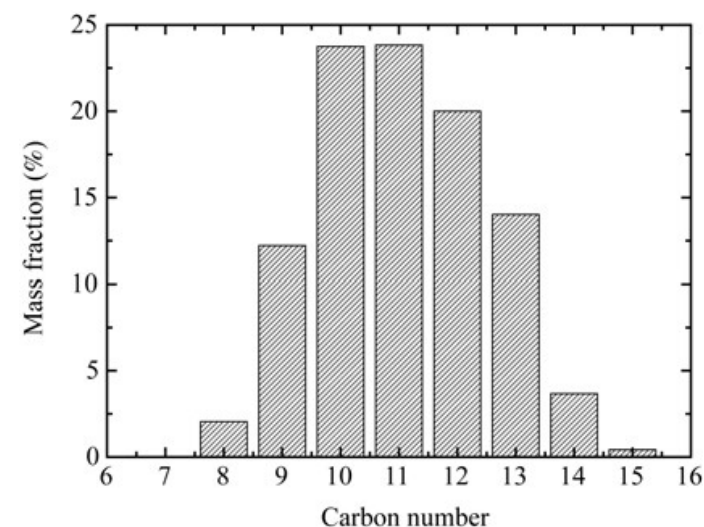
### Major Specification Items are:

- Flash Point and Auto-ignition Temperature
- Freezing Point and Pour Point
- Adiabatic Burn Temperature
- Density
- Specific Energy

- JET A-1 /(JET A): Standardized propellant widely used in civil aircraft
- JP-8: Similar to JET-A1 but with corrosion-prohibiting and anti-icing additives
- JP-5: high flash point kerosene primarily used on air-craft carriers

Name	Specification	Description	Flash point, C	Freeze point, C
Jet A-1	ASTM D1655, UK DefStan 91-91	Standard commercial jet fuel	>38	<-47
Jet A	ASTM D1655	U.S domestic jet fuel	>38	<-40
JP-8	MIL-DTL-83133	U.S. military jet fuel (Jet A-1 + 3 additives)	>38	<-47
JP-5	MIL-DTL-5624	U.S. Navy high flash jet fuel	>60	<-46
TS-1	GOST 10227-86	Russian jet fuel	>28	<-50*

\* Russian test method for “chilling point”



## Requirements for Jet Fuels

### Fuel Stability:

- Jet fuels are transported and stored for quite a long time until they are consumed and therefore have additives to prevent
  - corrosion of materials used in tank, supply lines, valves, seals, etc..
  - aging and particulate deposition in lines, filters, etc..
  - oxidation in the tanks since these are open to atmosphere
- Some engines use fuel as coolant
  - fuels have to be thermally stable to prevent coking

### Lubricity:

- quite often fuel is used as lubricant and should thus have sufficient lubricity and therefore fuels with higher viscosity are favored
- however the distillation curve requirement sets a limit there



Filter clogging due to bacteria and particulate deposition

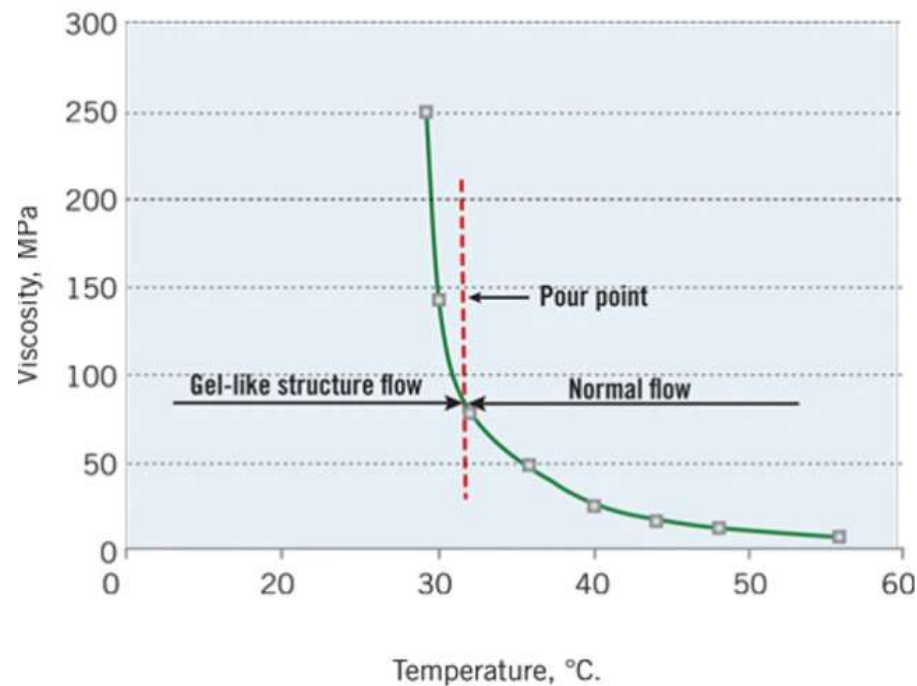
## Requirements for Jet Fuels

### Fluidity:

- Jet fuels have to function in summer and in winter and thus viscosity, freezing point and pour point are used to characterize the fluidity of a fuel

<b>Flash Point</b> (Temperature at which liquid form ignitable mixture with air)	38°C (100.4°F)
<b>Auto-ignition</b> (Temperature at which substance ignites without external aid)	210°C (410°F)
<b>Freezing Point</b>	-47°C (-52.6°F)
<b>Density at 15°C</b>	.8075kg/L
<b>Energy Density</b>	43.15MJ/kg

JET A-1 Data



## Requirements for Jet Fuels

### Volatility

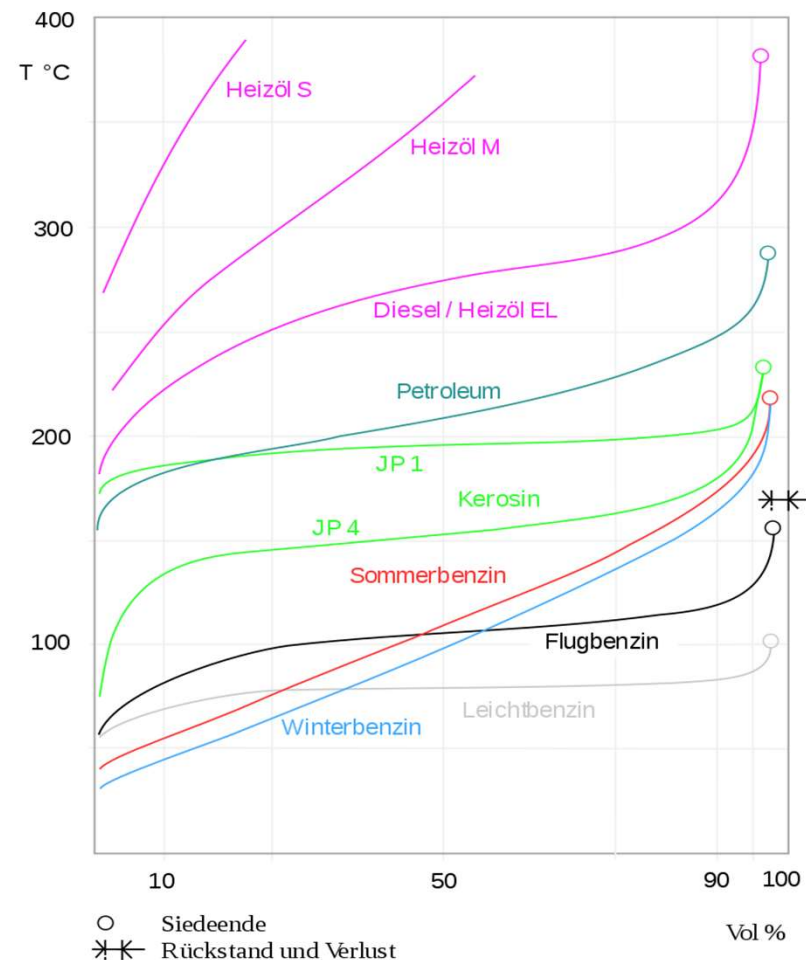
- Fuels have to vaporize before they burn therefore they have specific requirements for
  - vapor pressure, volatility
  - distillation curve
- However, too high volatility may cause losses or vapor lock
- Wide-cut jet fuels (blend of kerosene and gasoline with broader vaporization curve) are better suited for cold conditions than classical kerosene-type jet fuel

Fuel	Flash point	Autoignition temperature	Freezing point
Ethanol (70%)	16.6°C	363°C	
Petrol (Gasoline)	-43°C	246°C	
Diesel	> 62°C	210°C	
Jet fuel	> 38°C	210°C	
Jet A	> 38°C	210°C	< -40 °C
Jet A-1	> 38°C	210 °C	< -47 °C
JP5	> 60°C		< -46°C
JP7	> 60°C		
Jet B	-18°C		
Kerosene	> 38°C – 72°C	220°C	
Biodiesel	> 130 °C		

*Some fuel examples*

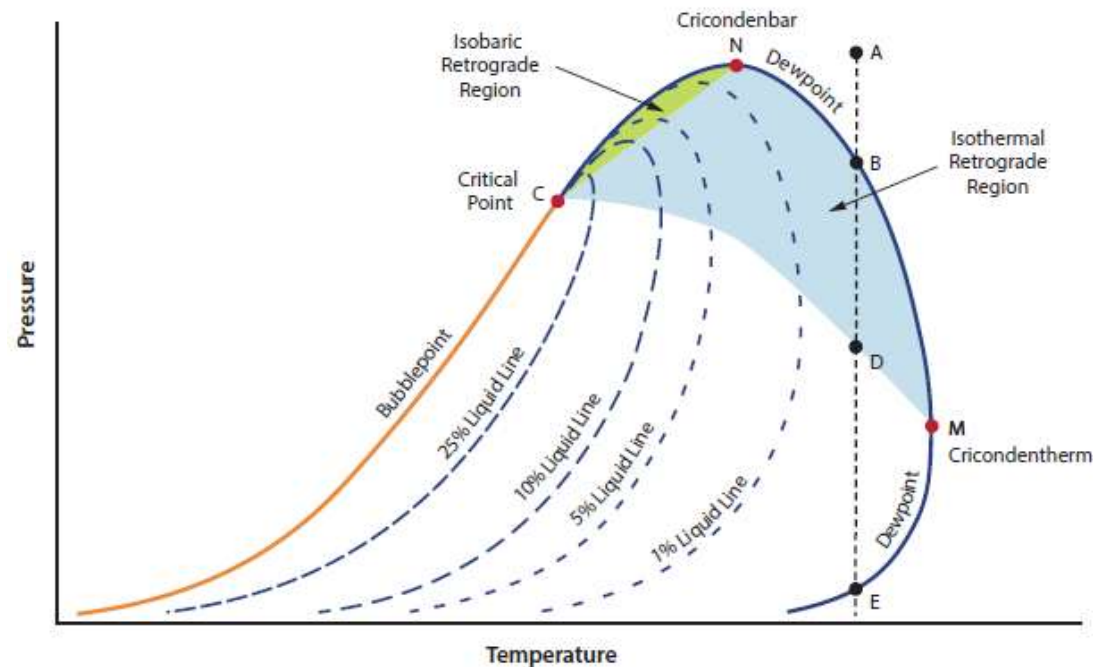
## Boiling Curve of Different Fuels

- Hydrocarbon mixtures may have a strange phase diagram due to their different phase change conditions
- Consequences for propellant classification as to flash point, dew point, pour points
- Impact on droplet vaporization and mixing



## Hydrocarbon Mixtures

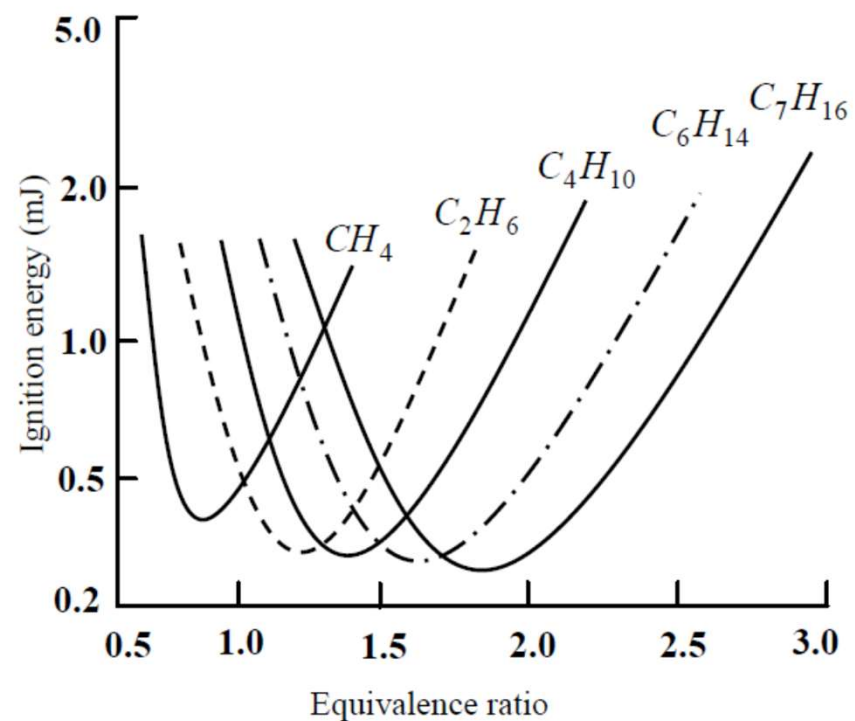
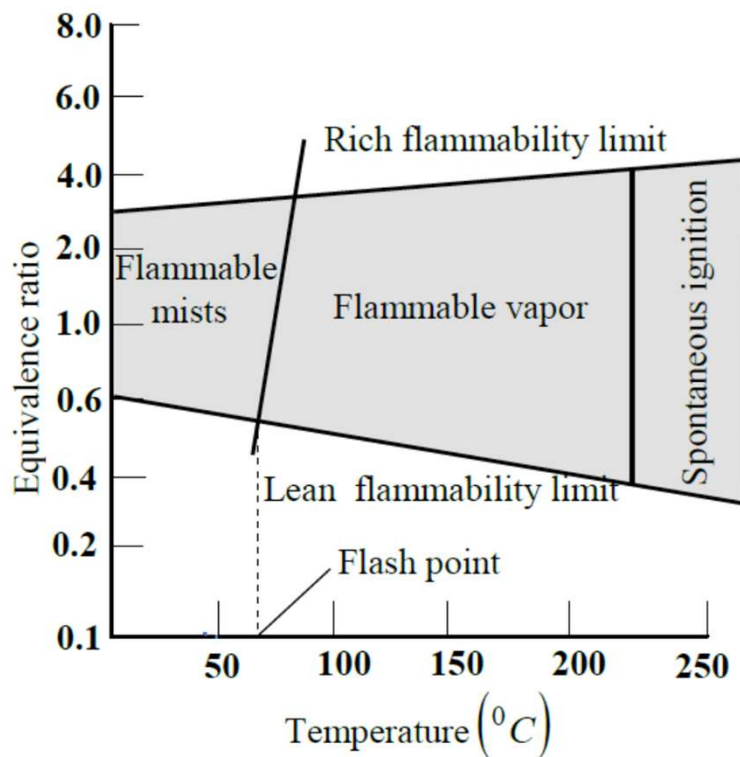
- Isothermal retrograde region (blue) where liquid condenses when pressure decreases (path from A to B to D. Condensation begins at point B and the maximum liquid occurs at point D well below the pressure that liquids first start to form.
- Isobaric retrograde region (green) where liquid vaporizes as temperature decreases. If we come into the phase envelope from the other side, the amount of liquid increases as we increase temperature.
- In facilities operations, the understanding of where the process is on a phase diagram can often help the engineer and operator to avoid extremely embarrassing design and operating mistakes.



- Criconbar: maximum pressure at which liquid and vapour may coexist (point N)
- Cricontherm: maximum temperature at which vapor and liquid may coexist (point M)

## Requirements for Jet Fuels

### Flammability



## Requirements for Jet Fuels

### Emissions

Typical emission per operation hour

~ 850 to air



~ 2.7 to  
kerosene



~ 723 to air



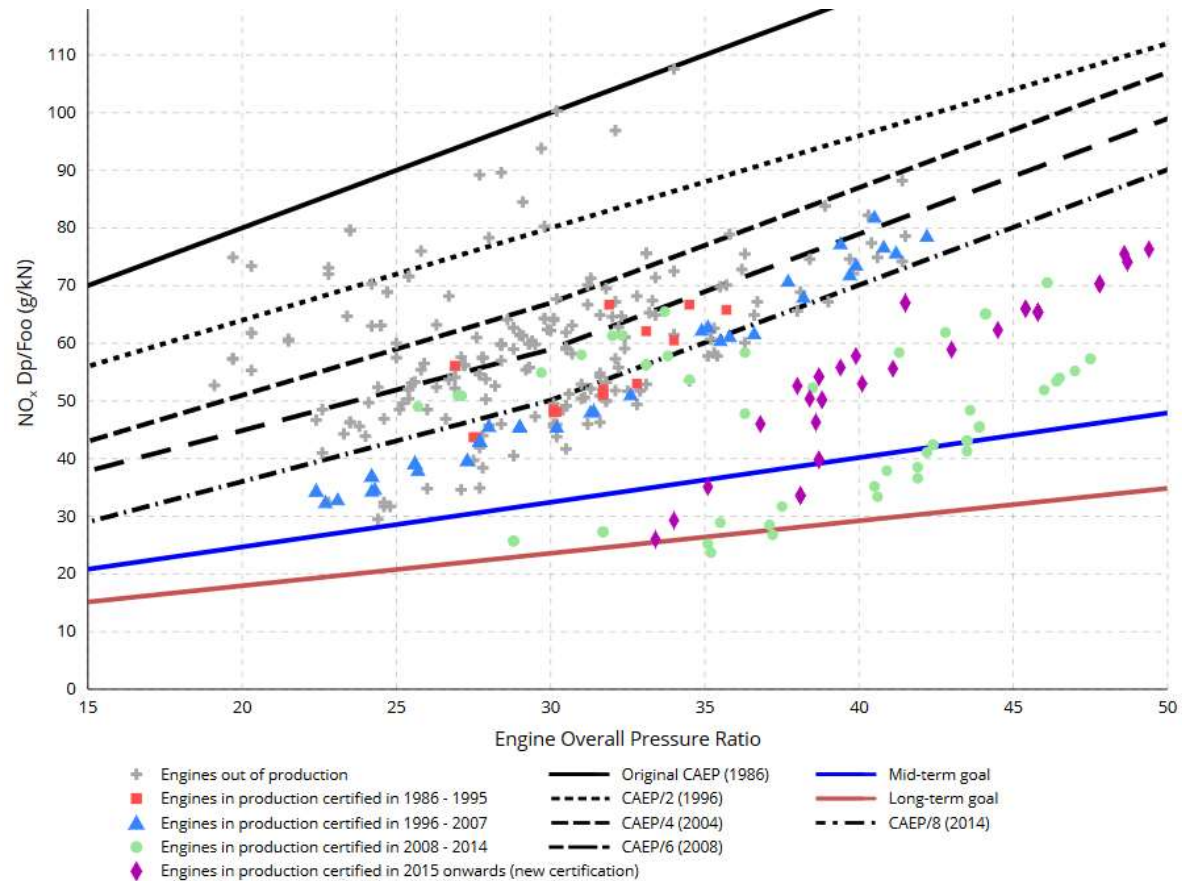
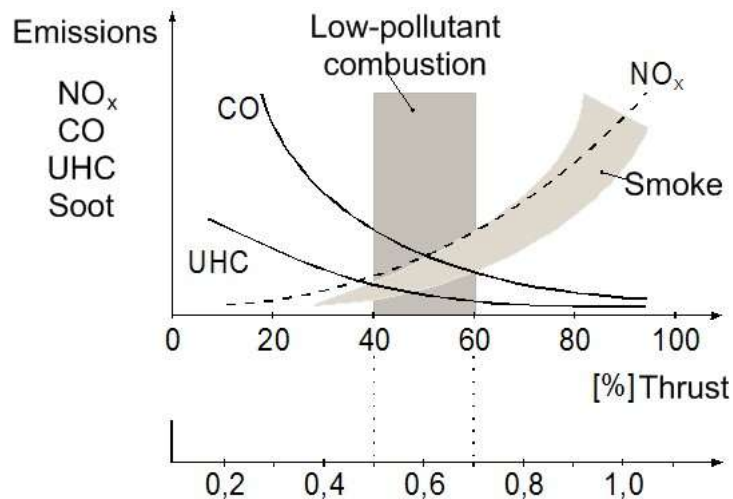
~ 130 to hot gases



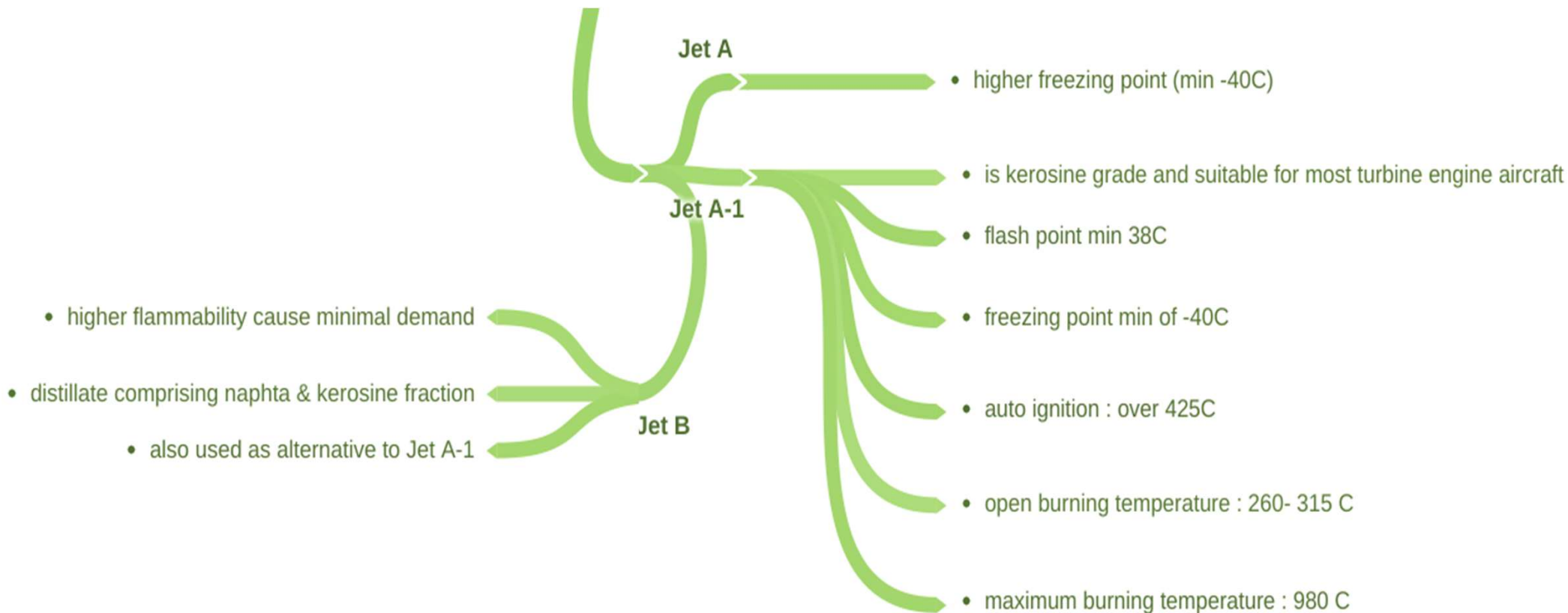
- 8.8 to CO<sub>2</sub>
- 3.3 to H<sub>2</sub>O
- 30 kg NO<sub>x</sub>
- 2.0 kg SO<sub>2</sub>
- 0.4 kg HC
- 0.1 kg PM + soot

## Requirements for Jet Fuels

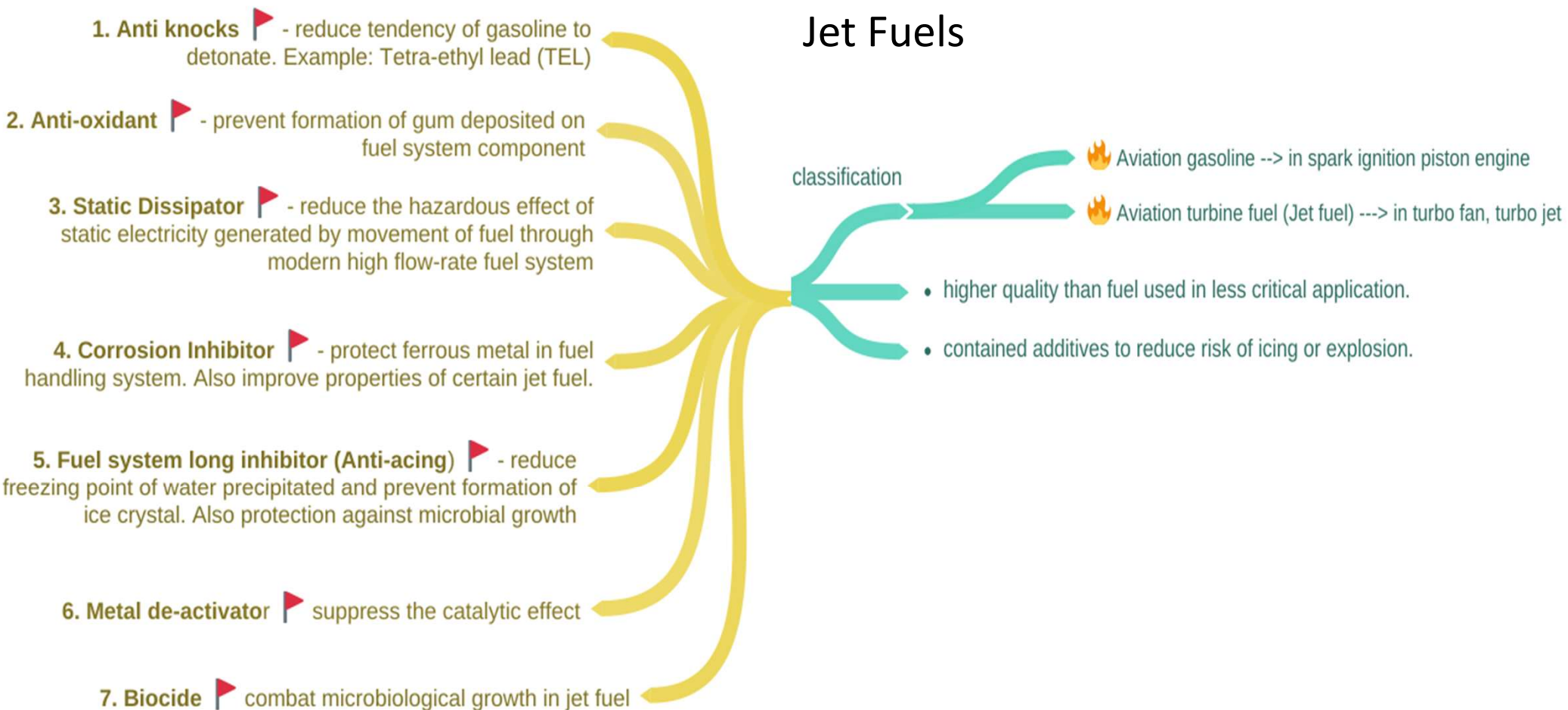
### Emissions



## Jet Fuels



## Jet Fuels





# Propellants



## Certification Sheets of JET A-1

(1/2)

PROPERTY	UNITS	LIMIT	METHOD
Visual Appearance		Clear, bright and visually free from solid matter and undissolved water at ambient, fuel temperature	
Saybolt Colour		Report	ASTM D6045
Particulate, at point of manufacture	mg/L	1.0 Max.	ASTM D5452
Particulate, at point of manufacture, cumulative channel particle counts	ISO Code		
≥ 4 μm (c)		Report	IP 564
≥ 6 μm (c)		Report	IP 564
≥ 14 μm (c)		Report	IP 564
≥ 21 μm (c)		Report	IP 564
≥ 25 μm (c)		Report	IP 564
≥ 30 μm (c)		Report	IP 564
Total Acidity	mg KOH/g	0.015 Max	ASTM D3242
Aromatics	% v/v	26.5 Max	ASTM D6379
Total Sulfur	% m/m	0.30 Max	ASTM D5453

Specific Energy	MJ/kg	42.80 Min	ASTM D3338
Copper Strip	Class	Max 1	ASTM D130
Thermal Stability, JFTOT			
Test Temperature	°C	260 Min	ASTM D3241
Tube Rating Visual		Less than 3. No Peacock (P) or Abnormal (A)	
PROPERTY	UNITS	LIMIT	METHOD
Pressure Differential	mm Hg	25 Max	ASTM D3241
Existent Gum	mg/100 ml	7 Max	IP 540
MSEP With SDA	Rating	Min 70	ASTM D3948
Electrical Conductivity	pS/m	Min 50 Max 600	ASTM D2624
Wear Scar Diameter	mm	0.85 Max	ASTM D 5001
Antioxidant, RDE/A/609	mg / l	17 - 24	Calc
Static Dissipator Additive Stadis 450, RDE/A/621	mg / l	Max 3.0	Calc



## Certification Sheets of JET A-1

(2/2)

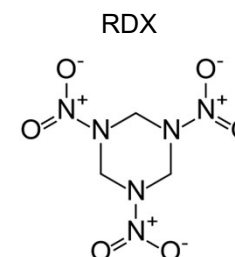
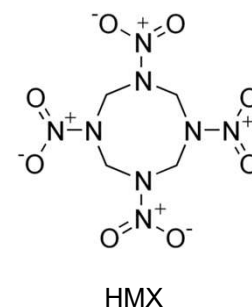
- Although the fuel seems to be standardized its composition may still vary to a certain extent.
- There could be a couple of hundred different species depending on the field the crude oil came from.

Sulfur, Mercaptan	% m/m	0.0030 Max	ASTM D3227
Non Hydroprocessed Components	% v/v	Report	
Mildly Hydroprocessed Components	% v/v	Report	
<b>PROPERTY</b>	<b>UNITS</b>	<b>LIMIT</b>	<b>METHOD</b>
Severely Hydroprocessed Components	% v/v	Report	
Synthetic Components	% v/v	Report	
<b>DISTILLATION:</b>			
Initial Boiling Point	°C	Report	ASTM D 86
10% Recovery	°C	205.0 Max	
50% Recovery	°C	Report	
90% Recovery	°C	Report	
End Point	°C	300.0 Max	
Residue	% v/v	1.5 Max	
Loss	% v/v	1.5 Max	
Flash Point	°C	38.0 Min	IP 170
Density @ 15 °C	kg/m <sup>3</sup>	775.0 to 840.0	ASTM D4052
Freezing Point	°C	-47.0 Max	ASTM D7153
Viscosity at minus 20 °C	mm <sup>2</sup> /s	8.000 Max	ASTM D445
Smoke Point	mm	25.0 Min	ASTM D1322

## Solid Propellant Rocket Engines

### Oxidizers

- |                                       |  |
|---------------------------------------|--|
| • Ammonium Perchlorate                | $\text{NH}_4\text{ClO}_4$ (AP)                   |
| • Nitronium Perchlorate               | $\text{NO}_2\text{ClO}_4$ (NP)                   |
| • Cyclo-trimethylene-trinitramine     | $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ (RDX) |
| • Cyclo-tetramethylene-tetranitramine | $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$ (HMX) |



### Fuels

- Aluminum
- Magnesium
- Boron

### Binders

- Hydroxyl-terminated Polybutadiene (HTPB)
- Polybutadiene acrylic acid acrylonitrile prep-polymer (PBAN)

### Typical AP-based Propellant:

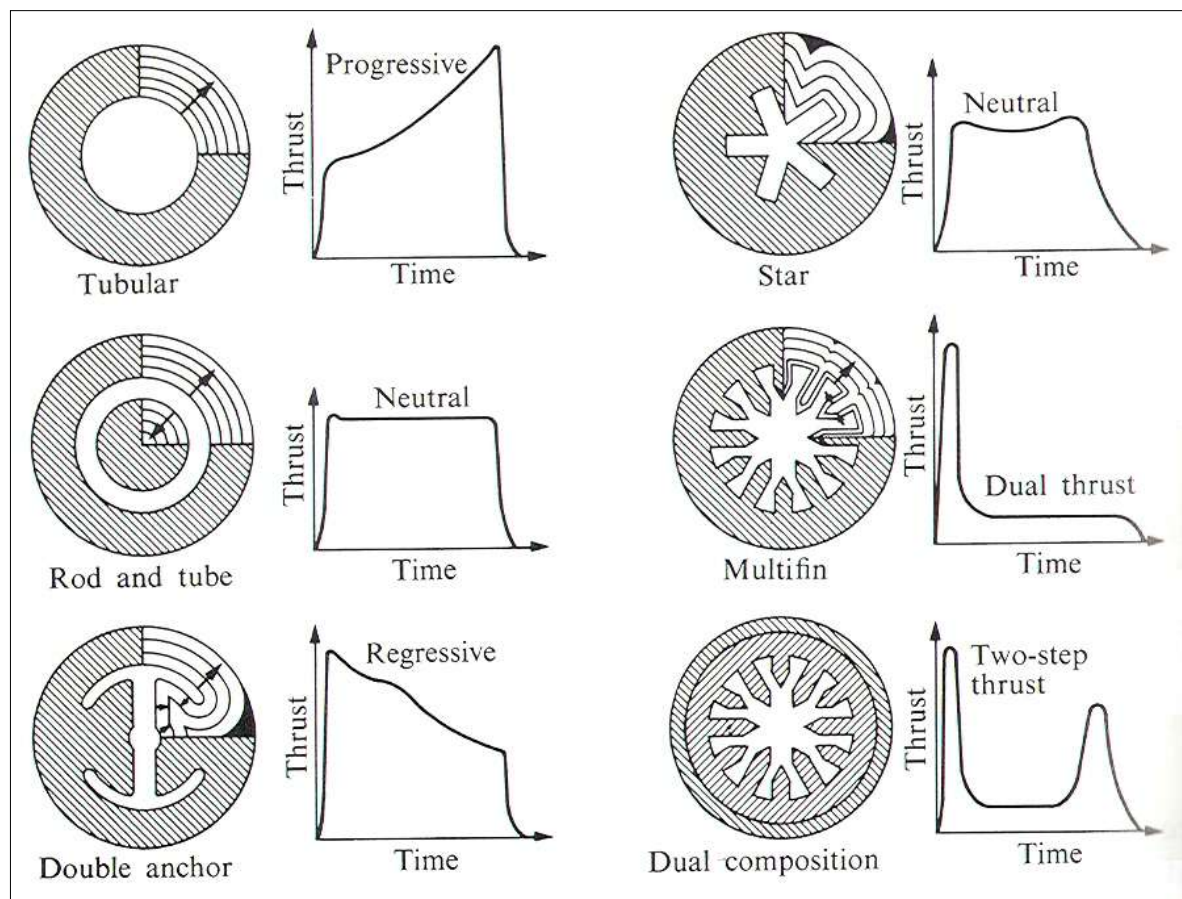
- 18 % Aluminum
- 69% AP
- 10% Binder
- 2 % Isodecyl Pelargonate (Plasticizer)
- 0.5 % Iron oxide (Burn Rate Catalyst)
- 0.2 % Aziridine (Bonding Agent)
- .....



## Solid Rocket Propellants / Additional Ingredients Issues

- Processing
  - Ingredient, density, reactivity, particle size/packing fraction, solids, loading effects
  - Mix procedure, mix temperature(s), order and number of addition, blade rpm, blade times, vacuum mixing, hold/purge times
  - End-of-mix viscosity, pot life, rheological behavior, castability
  - Cast technique, cure temperature, pressure and time, cure kinetics
- Aging behavior
  - Oxidative cross-linking (hardening), hydrolytic (typically softening), decomposition, reaction with contaminants
  - Effects of temperature, humidity, vacuum, atmosphere
  - Plasticizer migration, oxidizer dissolution, or recrystallization, stabilizer depletion
  - Effect on performance, ignition, mechanical, bond-line, ballistic, and hazard properties

# Propellant Grain



Possible configurations of programmed thrust control during the propulsive mission.

# Solid Rocket Motors

## Avio Production Facility at Collefero



Pictures:  
Avio



Mandrel for Ariane 5  
1. segment

- 1. Segment Ariane 5 ~ 25 t
  - Zefiro 23 ~ 23 t
  - Zefiro 9 ~ 9 t

Ariane 5, 1. segment





# Solid Propellants

## Composite Propellants / Binder System Ingredients

- Bonding agent
  - Promotes adhesion between binder and solid particles, generally required with HTPB propellants
  - Tepanol
- Plasticizer
  - Increases propellant strain
  - Inert plasticizers
  - Energetic plasticizers to tailor energy/hazard sensitivity
- Stabilizers
  - Anti-oxidants, thermal stabilizers, free radical scavengers, metal sequestering agents, et..
- Processing aids
  - Cure retarder (pyrocatechol, iso-cyanate blockers)
  - Lecithin, silicon oil (chains of  $-\text{Si-O-Si-O}-$  with methyl or phenyl groups attached)



## Composite Propellants / Additional Ingredients Issues

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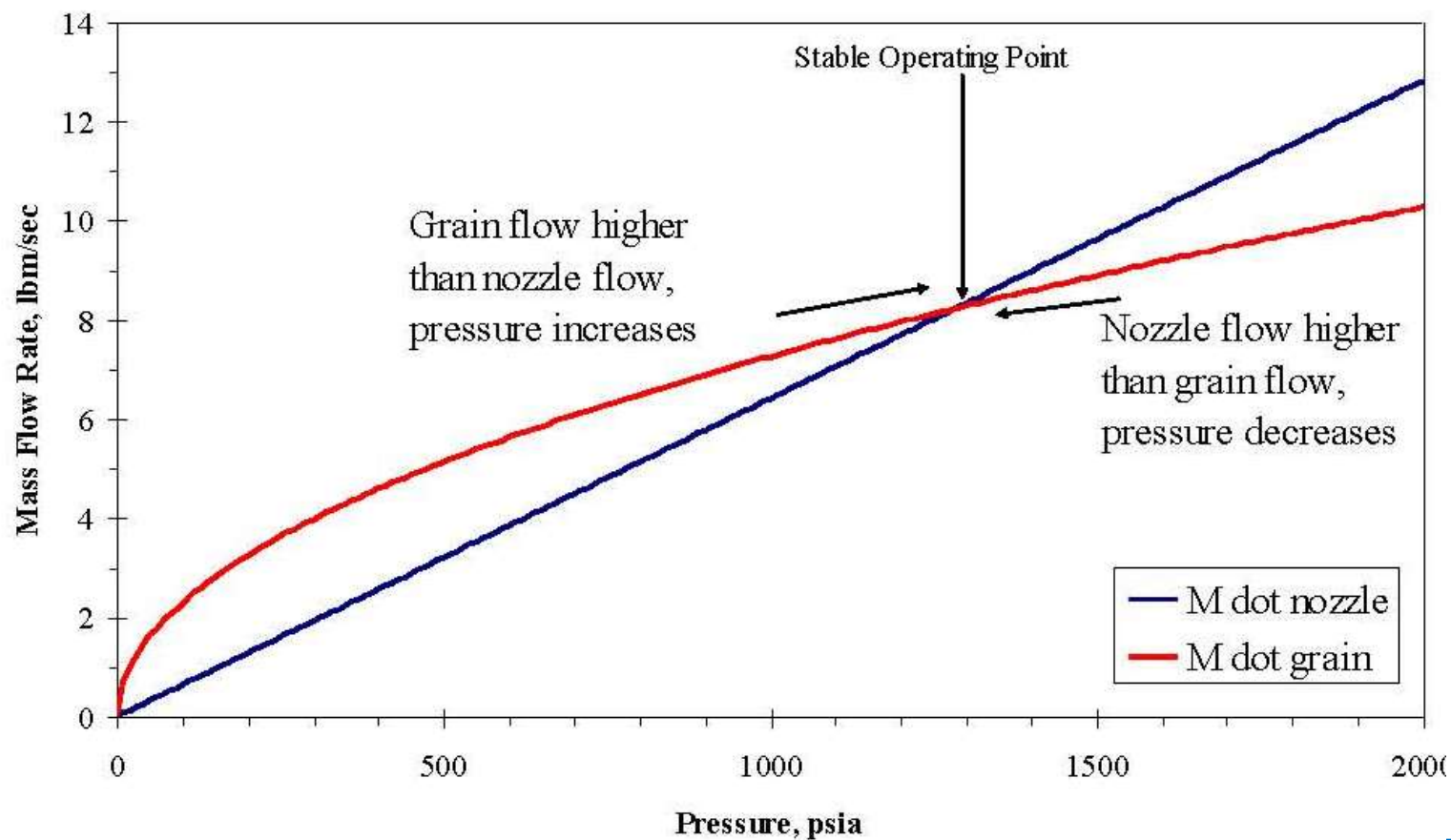
## Burning Rate $r_b$

For simple motors, burning rate can be modeled as  $R_b = a \cdot P_c^n$

- Mix to mix and lot to lot variations must be tracked for some programs while others may not be sensitive to wide variations in burning rate
- Contaminants, particle shape variation, and particle size distribution variation can all contribute to an out of spec burning rate
- Mixer size changes can result in burning rate changes due to shearing properties at different scales and speeds
- Different burning rate measurement devices have different scale factors to full scale motors
- A consistent and adequately accurate burning rate measurement program should be devised for each program

# Solid Propellants

SRM Mass Flow Rates - Stable Operation -  $n < 1$



Aerospace Combustion

Prof. Dr.-Ing. O. J. Haidn, Dr. – Ing Daniel Martínez Sanchis, Dr. – Ing Andrej Sternin

## Rough Igniter Sizing Methods

### Heat Flux Method

- Physics based model
- Requires extensive propellant and thermal data to do accurately
- Simplified form shown below
  - ignition delay is given, solve eqn. 1 for required heat flux
  - Eqn 2 is used to determine required igniter mass flow rate

$$t_i = \left( \frac{T_c \sqrt{\pi \rho c_p \lambda}}{2 \dot{q}} \right)^2 \quad (1)$$

$$\dot{q} = 0.0296 Q_{ign} \left( \frac{144 \dot{m}_i}{A_p} \right)^{0.8} \quad (2)$$

$t_i$  : ignition delay

$T_c$  :  $T_{\text{autoignition}} - T_{\text{ambient}}$

$\rho$  : propellant density

$c_p$  : specific heat at constant pressure

$\lambda$  : coefficient of thermal conductivity

$q$  : heat flux required for ignition

$Q_{ign}$  : available energy of igniter charge

$A_p$  : port area

$\dot{m}_i$  : mass flow rate required for ignition

# Solid Rocket Motors

## Igniter Design Procedure

### Critical Pressure Method (Von Elbe Equation)

- At low pressures, propellant ignition energy requirements are driven by the current chamber pressure
- Typical propellants have critical pressures of 50 – 200 psia
- The igniter should pressurize the chamber to the critical pressure for several milliseconds to ensure the propellant will ignite
- Von Elbe (ARC, 1963, Ref. 3) developed following equation

$$p^* = \left[ C_1 \frac{2\lambda n}{c\rho b} \right]^{\frac{1}{1+n}}; \quad C_1 = 12 \frac{A_s}{V} \rho RT; \quad b = \frac{r}{p^n}$$

$\lambda$ : propellant heat conductivity, Btu/hr-ft-°R

$n$ : propellant exponent

$c$ : propellant specific heat of solid, Btu / lbm-°R

$\rho$ : propellant density, lbm/in<sup>3</sup>

$A_s$ : surface area exposed to ignitor products

$V$ : Motor Free Volume, in<sup>3</sup>

$R$  = Propellant gas constant, ft-lbf/lbm-°R

$T$  = Propellant flame temperature, °R

$r$  = propellant burning rate

$p$  = chamber pressure



## Igniter Design Procedure

### Critical Pressure Method (Von Elbe Equation)

Determine mass required for successful ignition

- Scale from prior experience, or
- Use methods described earlier, or
- Estimate mass flow rate (Pyrogen Grain) and ensure this mass flow is present for sufficient time (several milliseconds).

$$\dot{m} = \left( \frac{g_c}{C^*} \right) A_t P^*$$

$g$  : gravitational constant, 32.2 lbf-ft/lbf-s<sup>2</sup>

$C^*$  : Characteristic velocity, ft/s

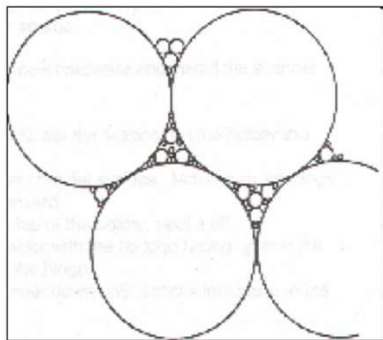
$A^t$  : Motor throat area, in<sup>2</sup>

$P^*$  : Critical pressure, psia

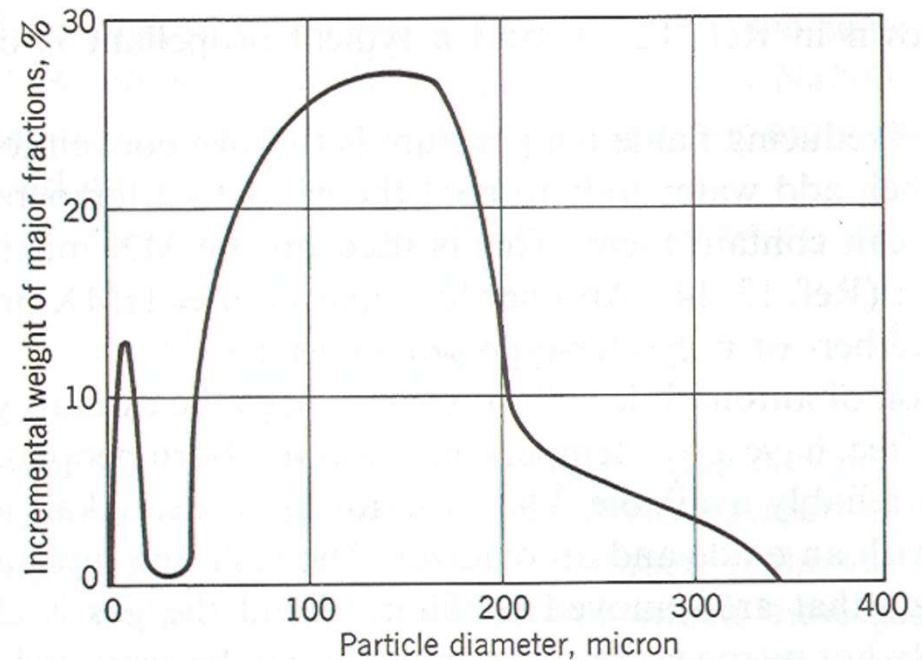
## Solid Rocket Propellants / Additional Issues

A large effort went into investigation of nano-Al. However, Al particles develop almost immediately a layer of Al<sub>2</sub>O<sub>3</sub> with a thickness of ~ 5 nm. Unfortunately, Al<sub>2</sub>O<sub>3</sub> has a higher melting point than Al and thus this oxide layer prohibits fast combustion. Additionally, the oxide layer reduces the mass fraction of Al in the motor.

→ Favorable Aluminum particle diameters should be in the 20 – 100 μm range.



For AP however, a bi-model size distribution is essential for agglomeration



Favorable bi-model AP particle size distribution: wide-cut at the larger diameter, narrow cut around 10 μm



## Liquid Rocket Propellants

### Fuels

- Hydrogen
- Methane
- Kerosene (RP-1)
- Hydrazine
- Mon-methyl Hydrazine
- Unsymmetrical Di-methyl Hydrazine

### Oxidizers

- Oxygen
- Nitrogen-tetroxide (NTO)
- Nitrous Oxide

\*Hydrazine and its derivatives, although highly toxic and carcinogenic are still in use and will be for quite a while since they react hypergolic with nitrogen-tetroxide which makes them favorable for long-time in-space applications (satellites).



## Classification of propellants for rocket engine application

- Way of ignition
  - hypergolic (auto-ignition, no external energy input)
  - catalytic (external energy transfer)
  - thermal, electric (external energy transfer)
- Storability
  - earth storable (stabil between  $-30 - + 70^{\circ}\text{C}$ )
  - space storable (liquid in orbit,  $-160 - - 140^{\circ}\text{C}$ )
  - cryogenic (liquified gases,  $< -170^{\circ}\text{C}$ )
- Energy content level ( $p_c/p_e = 68$ )
  - $I_{sp} < 280 \text{ s}$  low energy level propellant combination
  - $280 \text{ s} < I_{sp} < 330 \text{ s}$  mean energy level propellant combination
  - $I_{sp} > 330 \text{ s}$  high energy level propellant combination



## Requirements for liquid propellants

- High energy content (heat release, high combustion temperature, low molecular weight of products)
- High propellant density and low vapor pressure (tank size and wall thickness)
- Good ignition characteristics (low ignition delay) and stable combustion
- Low viscosity (small pressure loss in cooling channels)
- Optimum combination of heat capacity and thermal conductivity for effective cooling performance
- No thermal induced cracking tendency (propellant/material compatibility)
- Known and sufficient lubrication capability
- Low toxicity of propellant, its vapor and reaction products
- Easily available at low cost



## Rocket Propellants

All cryogenic propellants ( $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{O}_2$ ) are provided as liquids and thus are already in a very clean state.

Nevertheless, the quality specification for  $\text{H}_2$  and  $\text{O}_2$  is 3.0 which means 99.9%.

Methane isn't flown yet and in its liquid state it is around 99.5% as well.

Be careful since all impurities will change the thermodynamic properties of the mixture which may have severe consequences for cooling capabilities or atomization and vaporization etc.

### NASA specification for MMH

Properties	Limits	Test Paragraph
MMH (% by wt)	98.3	4.3.2
Water (% by wt)	1.5 max	4.3.2
Non-volatile residue (mg/l)	10 max	4.3.3
Particulate (mg/l)	10 max	4.3.4



## Rocket Propellants

### Excerpt of NASA specification to perform the testing of MMH

4.3.2 MMH assay and water. The propellant and water content of the sample shall be determined by one of the Gas Chromatographic (GC) methods described in Appendix A. In case of a dispute, the packed column method (A.2.1) shall be the referee.

4.3.3 Non-volatile residue (NVR). The NVR of the propellant shall be determined in duplicate by either of the methods described in Appendix B. In case of a dispute, the dropwise method (B.2.1) shall be the referee.

4.3.4 Particulate. The propellant sample shall be tested gravimetrically for contamination in accordance with ASTM D2276, with the following exceptions:

- a. Mix the sample thoroughly by shaking the sample container. Immediately pour 500 mL of the sample into a clean 500 mL graduated cylinder. Use this 500 mL of propellant for the particulate analysis.
- b. Use a Mitex disc PTFE hydrophobic, 10  $\mu\text{m}$ , 0.47 millimeters (mm), white filter or equivalent instead of that specified in ASTM D2276.
- c. Set the oven temperature to 70°C (158°F).
- d. Filtered American Chemical Society (ACS) grade isopropyl alcohol shall be used for rinsing the sample bottle and filter holder instead of petroleum ether specified in ASTM D2276.

## NASA specification for RP -1

RP-1 (Rocket Propellant 1) has been developed to fulfil the needs for the Apollo program

- No sulfur content to avoid cracking and polymerization
- alkenes and aromatics at very low levels to minimize polymerization and as a result RP-1 is less toxic than various jet fuels
- Minimize n-alkanes and maximize highly branched and cyclic molecules (ladderanes were favored) to increase resistance to thermal breakdown
- remaining hydrocarbons are at or near  $C_{12}$  mass. Because of the lack of light hydrocarbons, RP-1 has a high flash point and is thus less of a fire hazard than some jet fuels

Peak	Retention time, min	Profile	Corr. coef.	Conf.	Name	CAS Reg. No.	RMM	%
1	4.480	S	50	M	2,2-dimethylbutane	000075-83-2	86.11	2.375
2	4.619	A	64	H	3-methyldecane	013151-34-3	156.19	3.985
3	5.117	A	43	M	3-ethyl-4,4-dimethyl-2-pentene	053907-59-8	126.14	2.726
4	5.486	A	47	M	2,9-dimethyldecane	001002-17-1	170.2	6.280
5	5.808	S	94	H	2-methyl-cis-decalin	1000152-47-3	152.16	3.970
6	6.008	A	98	H	decahydro-2-methyl naphthalene	002958-76-1	152.16	2.574
7	6.307	S	50	M	cis-syn-1-methyl-decalin	1000158-89-1	152.16	4.652
8a <sup>†</sup>	6.468	S	46	M	1-hexyl-3-methylcyclopentane	061142-68-5	168.19	5.099
	6.537	A						
	6.653	S	43	M	cyclo dodecane	000294-62-2	168.19	
9	7.443	S	43	M	1-dodecene	000112-41-4	168.19	5.995
10	7.789	S	78	H	2-methylundecane	007045-71-8	170.2	3.124
11	7.996	S	59	M	3-methylundecane	001002-43-3	170.2	2.839
12	8.150	A	56	M	2,2-dimethyldecadi-3,5-ene	055638-50-1	166.17	2.735
13	8.464	S	NA	M	methylcyclo-dodecane	NA	182.22	3.580
14	9.194	S	90	H	dodecane	000112-40-3	170.20	5.327
15	9.746	S	50	M	2,7,10-trimethyl-dodecane	074645-98-0	212.25	3.765

## NASA specification for RP -1

Identification of Species of 2% or higher  
 (which represent 59% of the fuel)



RP -1 fuel

† The peak consists of two  
 coeluting solutes

Peak	Retention time, min	Profile	Corr. coef.	Conf.	Name	CAS Reg. No.	RMM	%
1	4.480	S	50	M	2,2-dimethylbutane	000075-83-2	86.11	2.375
2	4.619	A	64	H	3-methyldecane	013151-34-3	156.19	3.985
3	5.117	A	43	M	3-ethyl-4,4-dimethyl-2-pentene	053907-59-8	126.14	2.726
4	5.486	A	47	M	2,9-dimethyldecane	001002-17-1	170.2	6.280
5	5.808	S	94	H	2-methyl-cis-decalin	1000152-47-3	152.16	3.970
6	6.008	A	98	H	decahydro-2-methyl naphthalene	002958-76-1	152.16	2.574
7	6.307	S	50	M	cis-syn-1-methyl-decalin	1000158-89-1	152.16	4.652
8a <sup>†</sup>	6.468	S	46	M	1-hexyl-3-methylcyclopentane	061142-68-5	168.19	5.099
	6.537	A						
	6.653	S	43	M	cyclo dodecane	000294-62-2	168.19	
9	7.443	S	43	M	1-dodecene	000112-41-4	168.19	5.995
10	7.789	S	78	H	2-methylundecane	007045-71-8	170.2	3.124
11	7.996	S	59	M	3-methylundecane	001002-43-3	170.2	2.839
12	8.150	A	56	M	2,2-dimethyldecadi-3,5-ene	055638-50-1	166.17	2.735
13	8.464	S	NA	M	methylcyclo-dodecane	NA	182.22	3.580
14	9.194	S	90	H	dodecane	000112-40-3	170.20	5.327
15	9.746	S	50	M	2,7,10-trimethyl-dodecane	074645-98-0	212.25	3.765



# Propellants



NASA specification  
for RP -1

Identification of Species of 1% or  
higher (which represent 18.7 % of  
the fuel)

Light fraction of constituents of  
lightest components which  
represent 1.7 % of the fuel.

†signifies uncertainty in the  
location of the double bond  
or the methyl group

Peak	Retention time, min	Profile	Corr. coef.	Conf.	Name	CAS Reg. No.	RMM	%
laa	0.795	A	2	M	methane	107902-82-8	16.03	trace
la	1.924	A	50	H	nonane	000111-84-2	128.16	0.179
lb	2.615	A	90	H	1,3,5-trimethyl-cyclohexane	001795-26-2	126.14	0.654
1d	3.551	A	52	H	2-methyldecane	006975-98-0	156.19	0.817

Peak	Retention time, min	Profile	Corr. coef.	Conf.	Name	CAS Reg. No.	RMM	%
ha	21.776	S	30	M	5-methyl-2-undecene	056851-34-4	168.19	
hb	22.010	A	86	H	2,6,10-trimethyl-dodecene <sup>†</sup>	NA	210.25	
hc	22.433	A	59	U	3-methyl tridecane	006418-41-3	198.24	
			47		or tetradecane	000629-59-4	198.24	
hd	24.083	A	43	U	hexadecane,	000544-76-3	226.27	
			22		or 1-tetradecene	001120-36-1	196.22	

Peak	Retention time, min	Profile	Corr. coef.	Conf.	Name	CAS Reg. No.	RMM	%
a	3.144	A	50	M	2,7-di-methyl octane	001072-16-8	142.17	1.329
			38	M	or 2-methyl nonane	000871-83-0	142.17	
b	4.303	S	89	H	cyclodecene	003717-12-0	138.14	1.610
c	4.373	A	50	U	cis-deca-hydro naphthalene	108746-01-6	138.14	1.174
d	6.944	A	14	M	z-1,9-dodeca-diene	1000245-71-0	166.17	1.754
e	7.075	S	15	M	4-methyl-4-undecene	061142-40-3	168.19	1.663
f	9.846	S	20	M	x-tridecene <sup>†</sup>	NA	182.2	1.115
g	10.230	A	30	M	1-tridecene	111270-56-1	182.2	1.241
h	10.514	S	72	H	heptylcyclo-hexane	005617-41-4	168.19	1.429
i	10.698	S	43	M	x-tridecene	NA	182.2	1.305
j	11.359	A	45	M	x-tridecene	NA	182.2	1.977
k	11.881	S	58	M	2,10-di-methyl undecane	017301-27-8	184.22	1.507
l	12.349	A	NA	M	x-methyl tridecane	NA	197.2	1.494
m	12.787	S	94	H	2-methyl naphthalene	000091-57-6	142.08	1.249
aa	13.623	S	97	H	tridecane	000629-50-5	184.22	1.080

Heavy fraction of constituents of heaviest  
components. No mass % tabulated.

†location of double bond not clear



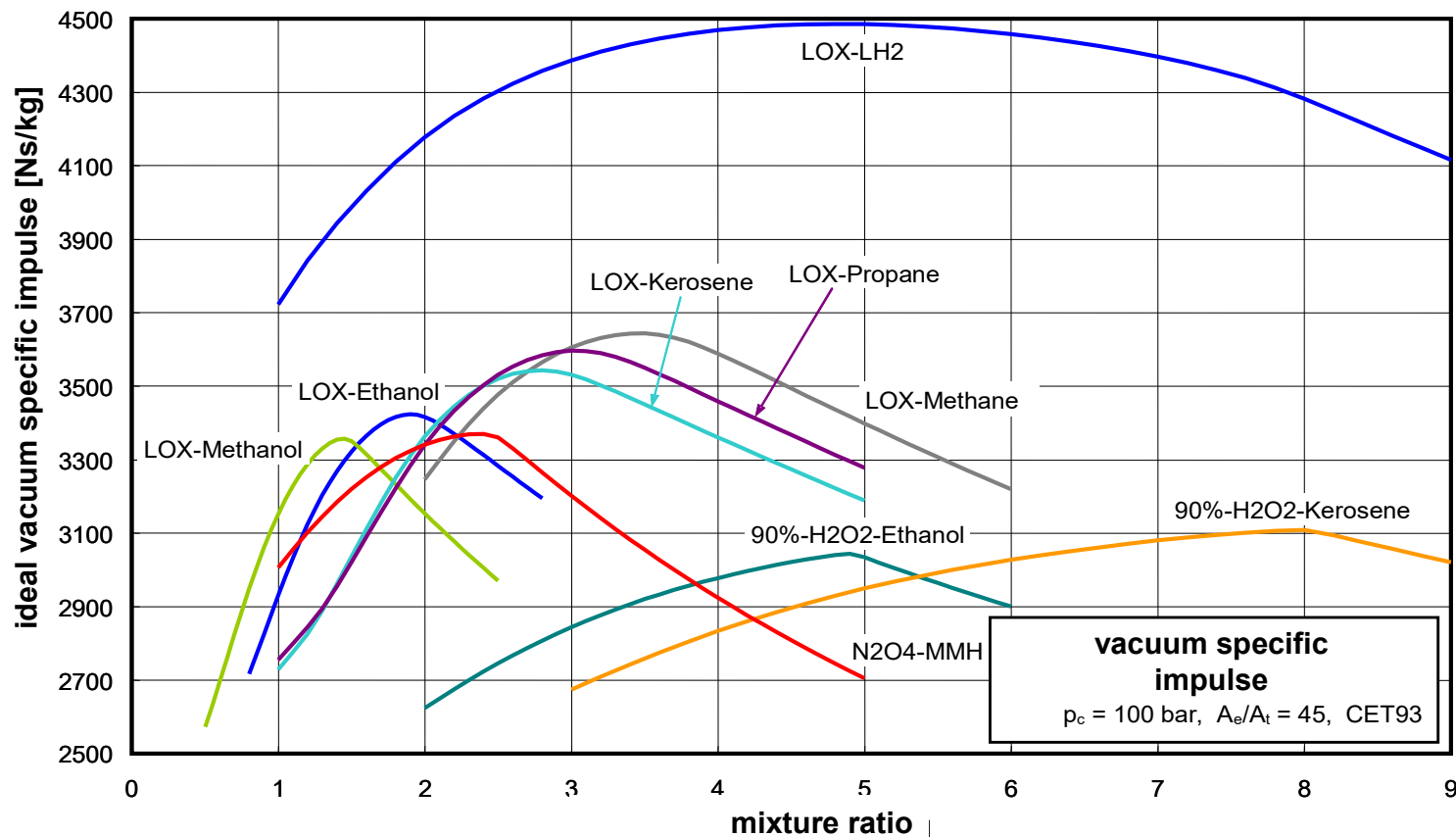
## NASA specification for a Surrogate RP -1

Fluid	CAS #	Formula	MW	Mole%
3-ethyl-4,4-dimethyl-2-pentene	53907-59-8	C <sub>9</sub> H <sub>18</sub>	126.24	9.98
Cyclodecene	3618-12-0	C <sub>10</sub> H <sub>18</sub>	138.25	2.11
2-methylnonane	871-83-0	C <sub>10</sub> H <sub>22</sub>	142.28	2.32
2-methylnaphthalene	91-57-6	C <sub>11</sub> H <sub>10</sub>	142.20	5.10
2-methyldecalin	2958-76-1	C <sub>11</sub> H <sub>20</sub>	152.28	22.35
3-methyldecane	13151-34-3	C <sub>11</sub> H <sub>24</sub>	156.31	10.84
1-dodecene	112-41-4	C <sub>12</sub> H <sub>24</sub>	168.32	2.64
Cyclododecane	294-62-2	C <sub>12</sub> H <sub>24</sub>	168.32	4.27
4-methyl-4-undecene	61142-40-3	C <sub>12</sub> H <sub>24</sub>	168.32	10.45
n-dodecane	112-40-3	C <sub>12</sub> H <sub>26</sub>	170.33	1.93
Heptylcyclohexane	5617-41-4	C <sub>13</sub> H <sub>26</sub>	182.35	14.22
1-tridecene	2437-56-1	C <sub>13</sub> H <sub>26</sub>	182.35	1.45
2,7,10-trimethyldodecane	74645-98-0	C <sub>15</sub> H <sub>32</sub>	212.41	10.38
n-hexadecane	544-76-3	C <sub>16</sub> H <sub>34</sub>	226.44	1.95

$\Sigma = 99.99 \%$

## Performance of Rocket Propellants

A key driver for the choice of propellant is their performance



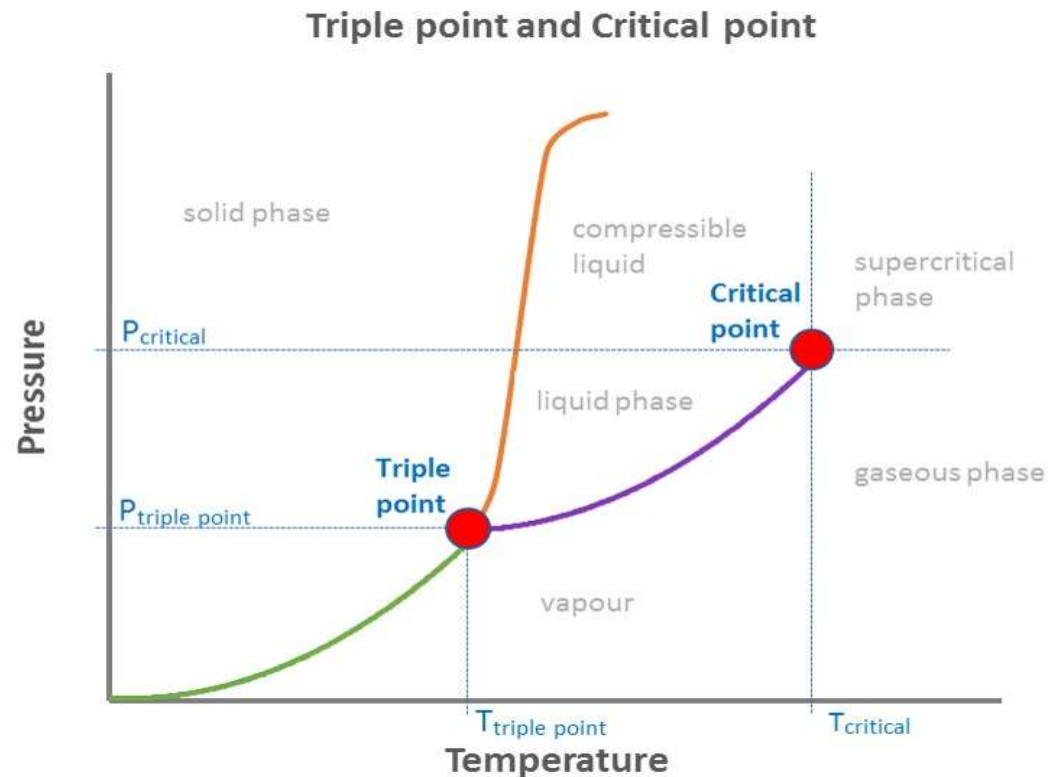


## Propellant / Engine Performance Data

Engine	Propellants	O/F	$p_c$ [bar]	Vac. thrust [kN]	$I_{sp}$ vac. [s]	Mass [kg]
Vulcain 2	LOX/LH <sub>2</sub>	6,1	115	1350	434	2100
SSME <sub>(Bl. 2)</sub>	LOX/LH <sub>2</sub>	6,0	206	2278	452	3526
RS68	LOX/LH <sub>2</sub>	6,0	96	3312	420	6800
VINCI	LOX/LH <sub>2</sub>	5,8	60	180	465	550
RL 10A	LOX/LH <sub>2</sub>	5,5	39	99	451	172
RD 170	LOX/Kerosene	2,63	245	8060	337	9750
RD 253	NTO/UDMH	1,90	147	1670	316	1280

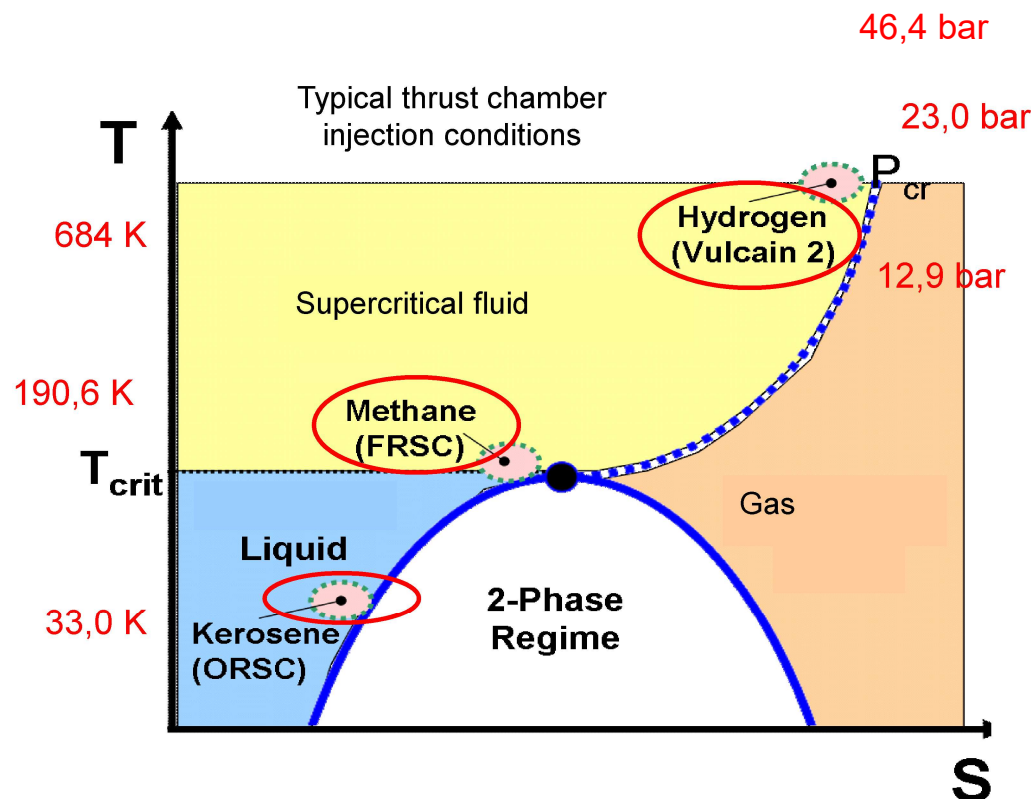
## Liquid Propellants – critical conditions

- Critical point at end of vapor pressure curve
- Densities of liquid and gaseous phase become identical
- Critical temperature indicates temperature below which a gas can be liquified
- Trans-critical state describes a fluid which is above its critical pressure but below its critical temperature
- Super-critical describes a state where both pressure and temperature are above their critical values



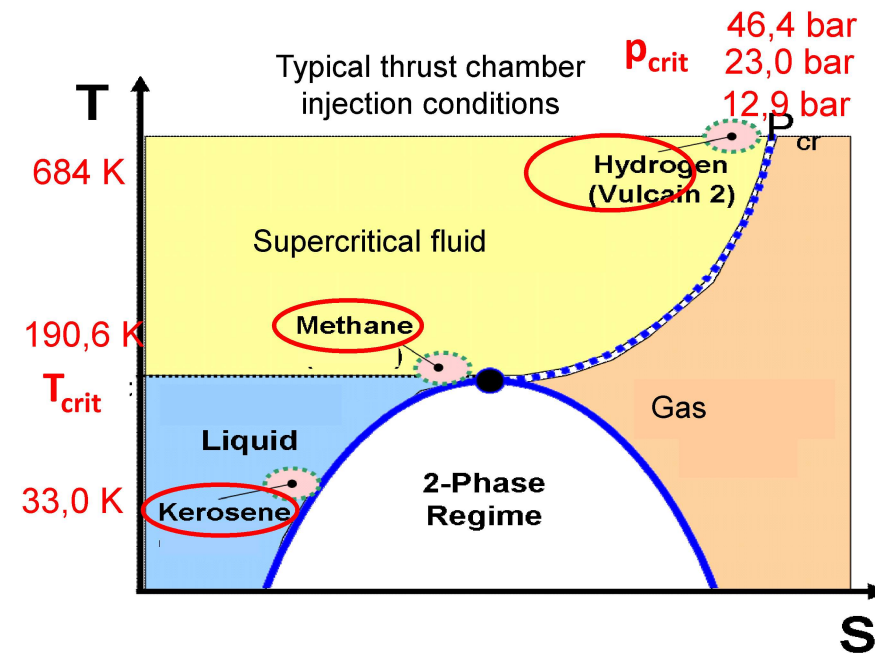
## Liquid Propellants – critical conditions

- At near-critical conditions the latent heat vanishes and almost all thermo-physical properties undergo significant changes
- For super-critical conditions surface tension has vanished (important for injector design)
- For regenerative cooling cycles critical conditions are essential for efficiency and performance
- Operation at super-critical pressures avoids phase change phenomena (competition between very efficient bubble boiling and the poor efficiency film boiling)



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- For super-critical conditions surface tension has vanished (important for injector design)
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- Operation at super-critical pressures avoids phase change phenomena (competition between very efficient bubble boiling and the poor efficiency film boiling)





## Liquid Propellants – critical conditions

D: 0.25 mm

Re: 3350 - 4090

$T_{LN2} = 87K$

$T_C = 292K$

$N_2$ :

$p_{cr} = 3.39 MPa$

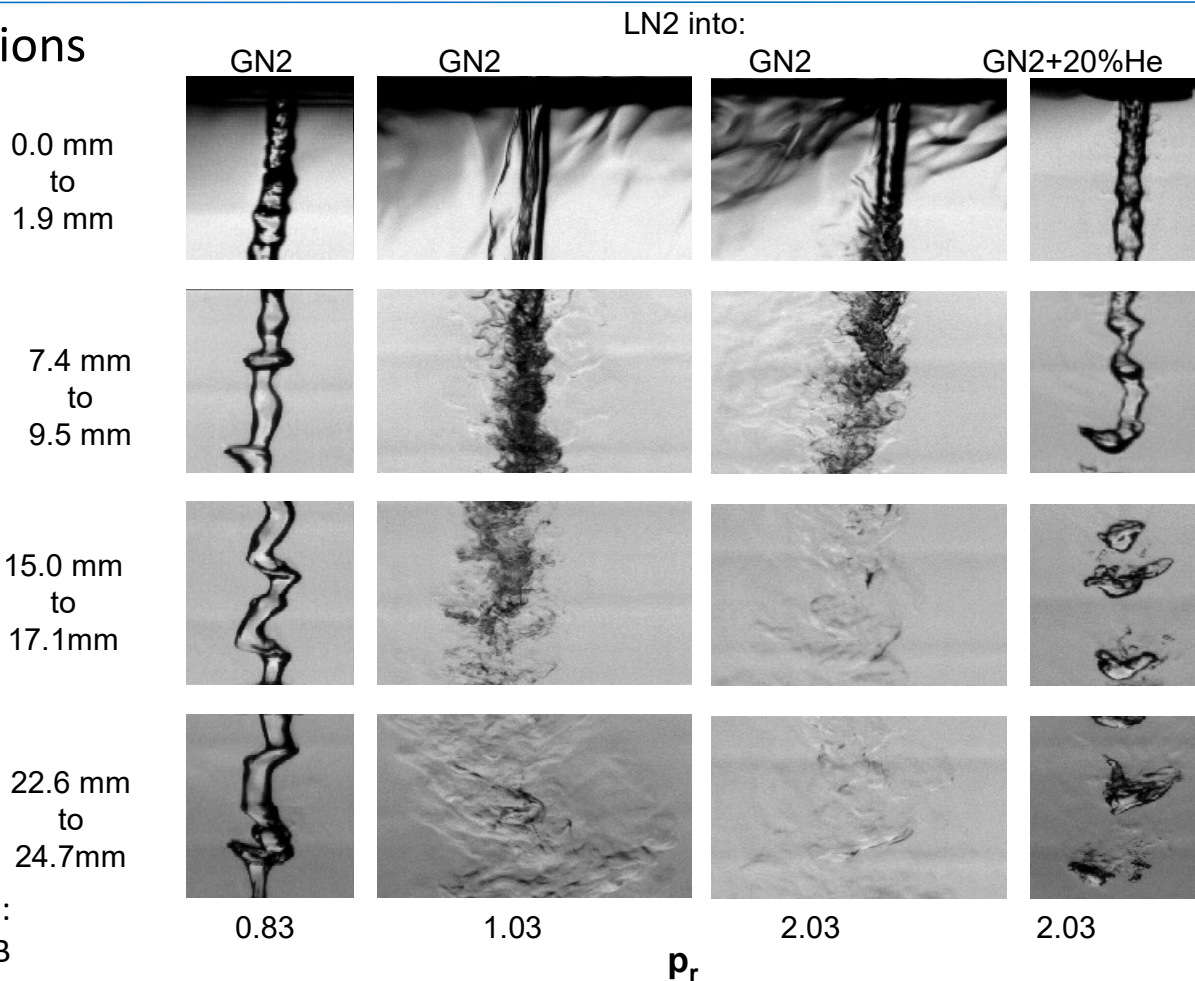
$T_{cr} = 126 K$

He:

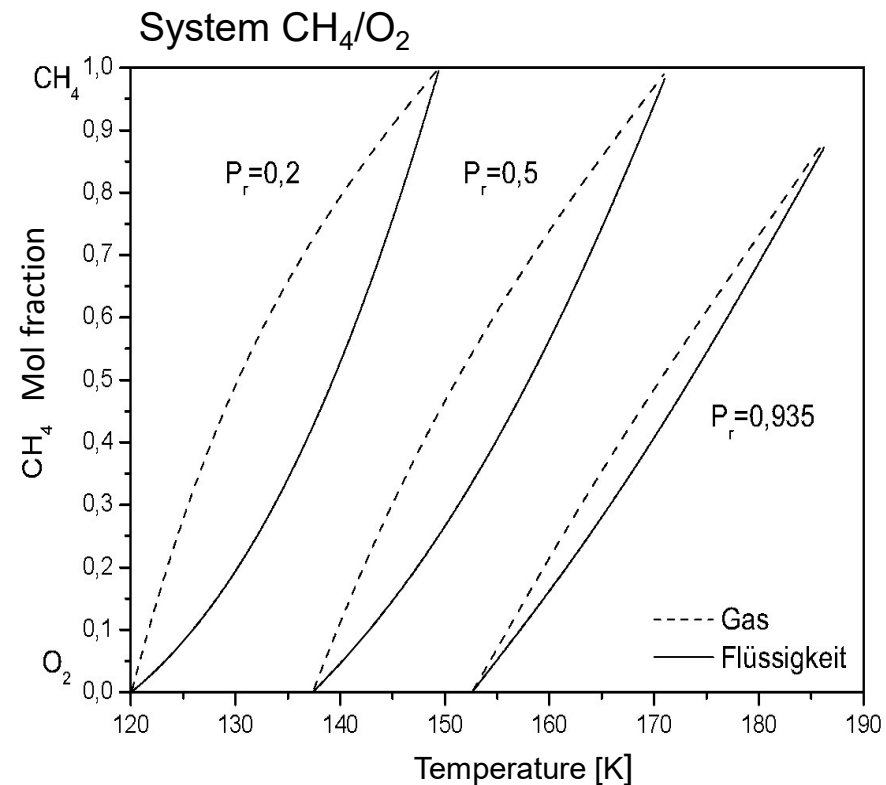
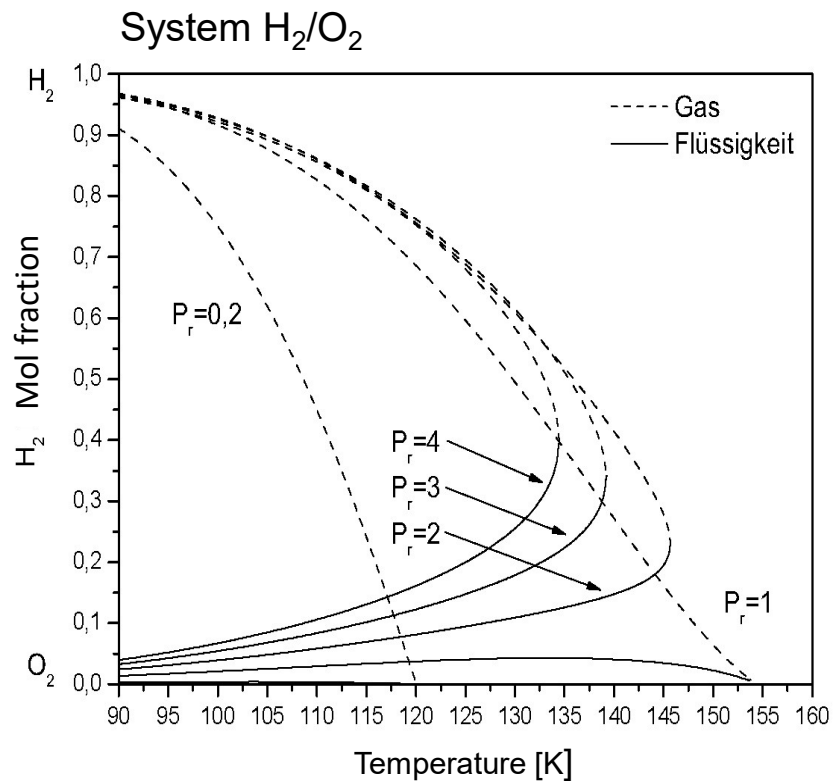
$p_{cr} = 0.23 MPa$

$T_{cr} = 9 K$

Flow Visualization:  
 Shadowgraphs Edwards AFB



## Liquid Propellants – critical conditions



Phase boundary for LOX/ $H_2$  even for  $p > p_{crit}$ , but not for LOX/ $CH_4$

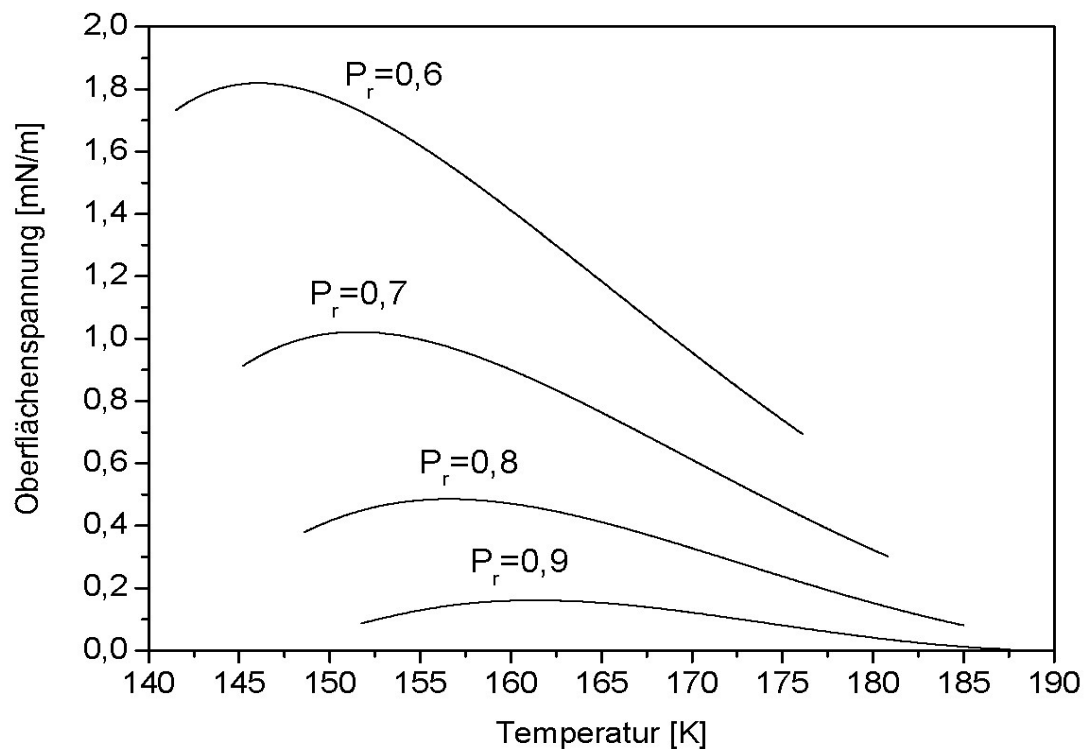
## Liquid Propellants – critical conditions

### Surface Tension

Macleod-Sudgen correlation for CH<sub>4</sub>/O<sub>2</sub> mixture

$$\sigma^{1/4} = \sum_{i=1}^N [P_i] \cdot (x_{i,f} \cdot \rho_{m,f} - x_{i,g} \cdot \rho_{m,g})$$

Surface tension vanishes near critical conditions





## Modeling Phase Equilibria

### Redlich-Kwong-Soave EOS

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)}$$

### Mixing Rules

$$a_{mix}^V = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij} \quad a_{mix}^L = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij}$$

$$b_{mix}^V = \sum_{i=1}^N y_i b_i \quad b_{mix}^L = \sum_{i=1}^N x_i b_i$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

Multicomponent mixture:  
to the phase equilibrium  
modeling

Pure Component  
Parameters

$$\alpha_i = \left[ 1 + \left( 1 - \kappa_i \sqrt{\frac{T}{T_{crit,i}}} \right) \right]^2$$

$$\kappa_i = 0.48508 + 1.5571 \omega_i - 0.15613 \omega_i^2$$

$$a_i = 0.42747 \alpha_i \frac{R^2 T_{crit,i}^2}{P_{crit,i}^2}$$

$$b_i = 0.08664 \frac{RT_{crit,i}}{P_{crit,i}}$$

Fugacity Coefficient for SRK EOS

$$\ln(\phi_i) = -\ln\left(z\left(1 - \frac{b_{mix}}{V}\right)\right) + \frac{b_i}{b_{mix}}(z-1) + \frac{a_{mix}}{b_{mix}RT} \left( \frac{b_i}{b_{mix}} - \frac{2 \sum_{j=1}^n \sqrt{a_i a_j} x_j}{a_{mix}} \right) \ln\left(1 + \frac{b_{mix}}{V}\right)$$

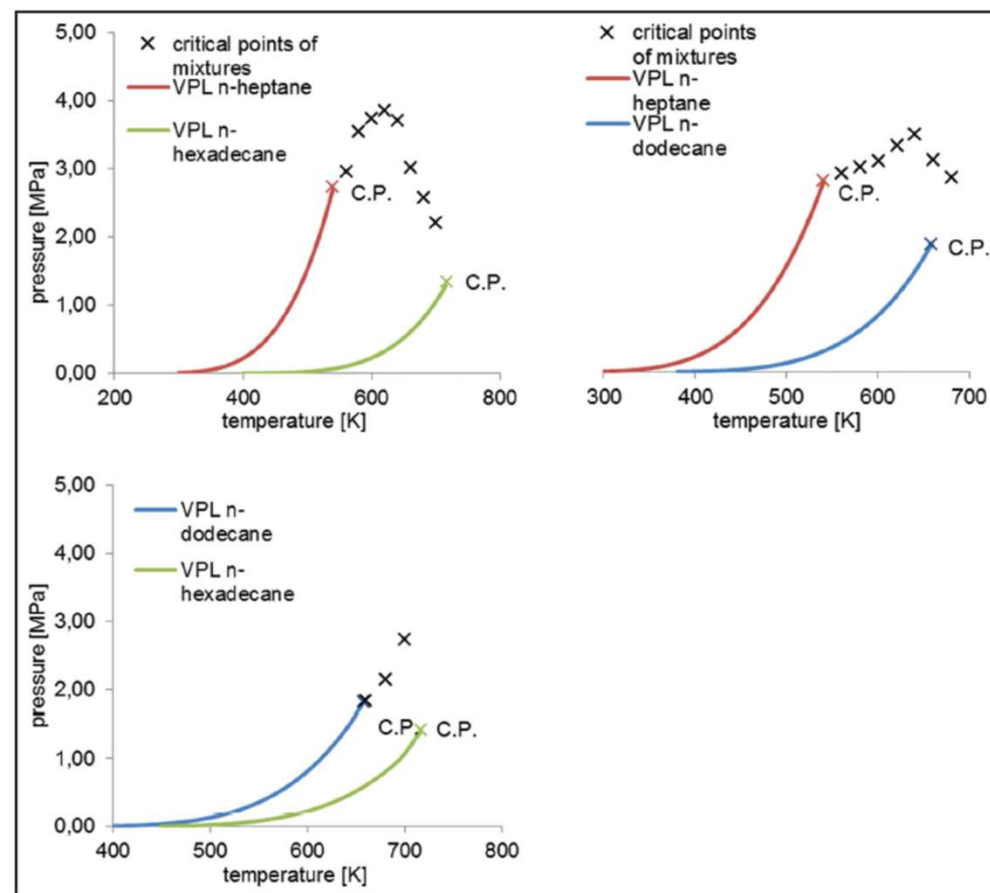
$$\left\{ \begin{array}{l} F(1) = P - \frac{RT}{v - b_{mix}^L} + \frac{a_{mix}^L}{v(v + b_{mix}^L)} \\ F(2) = P - \frac{RT}{v - b_{mix}^V} + \frac{a_{mix}^V}{v(v + b_{mix}^V)} \\ F(3) = \phi_1^L x_1 - \phi_1^V y_1 \\ \dots \\ F(n+1) = \phi_{n-1}^L x_{n-1} - \phi_{n-1}^V y_{n-1} \\ F(n+2) = \phi_n^L x_n - \phi_n^V \left(1 - \sum_{j=1}^{n-1} y_j\right) \end{array} \right.$$

## Liquid Propellants – critical conditions

It is important to know that going through critical conditions in a process yields substantial variations of thermo-physical fluid properties

Vapor-liquid equilibria of binary mixtures, critical points and vapor pressure lowering of mixtures

- n-heptane/n-dodecane,  $x_{n-C_7H_{16}}$ : 0.95-0.3
- n-heptane/n-hexadecane,  $x_{n-C_7H_{16}}$ : 0.9-0.1
- n-dodecane/n-hexadecane,  $x_{n-C_{12}H_{26}}$ : 0.99-0.9





## Critical Point Modeling

Redlich-Kwong-Soave EOS

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

Helmholtz energy

$$A - A_0 - \sum_i^N (\partial A / \partial n_i) \Delta n_i =$$

$$\frac{1}{2} \sum_j^N \sum_i^N \left( \frac{\partial^2 A}{\partial n_i \partial n_j} \right) \Delta n_i \Delta n_j + \frac{1}{6} \sum_k^N \sum_j^N \sum_i^N \left( \frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) \Delta n_i \Delta n_j \Delta n_k + O(\Delta n^4)$$

Condition of Stability limit

$$\det(Q) = 0$$

Multicomponent mixture:  
to the critical point calculation

$$Q_{ij} = \left. \frac{\partial^2 A}{\partial n_i \partial n_j} \right|_{T,v} = RT \left. \frac{\partial \ln f_i}{\partial n_j} \right|_{T,v}$$



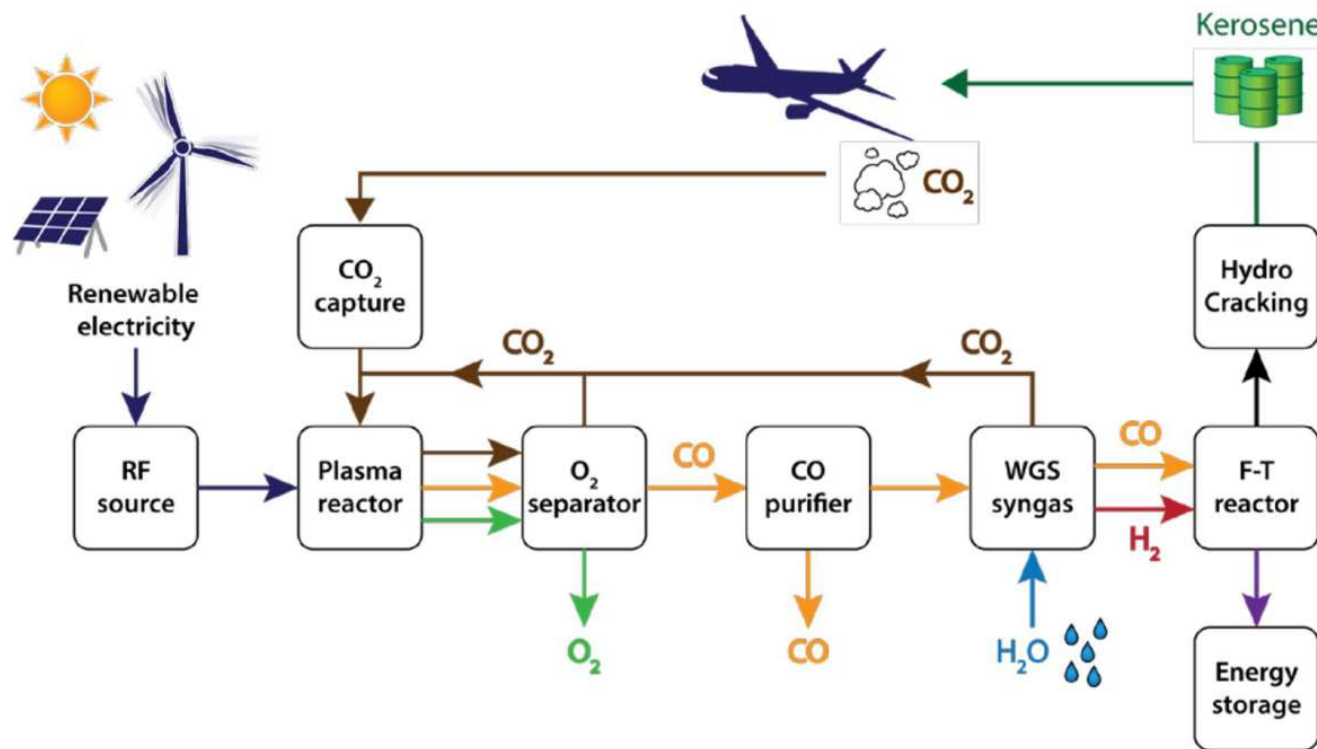
# Propellants

## Alternative Fuels for Aviation



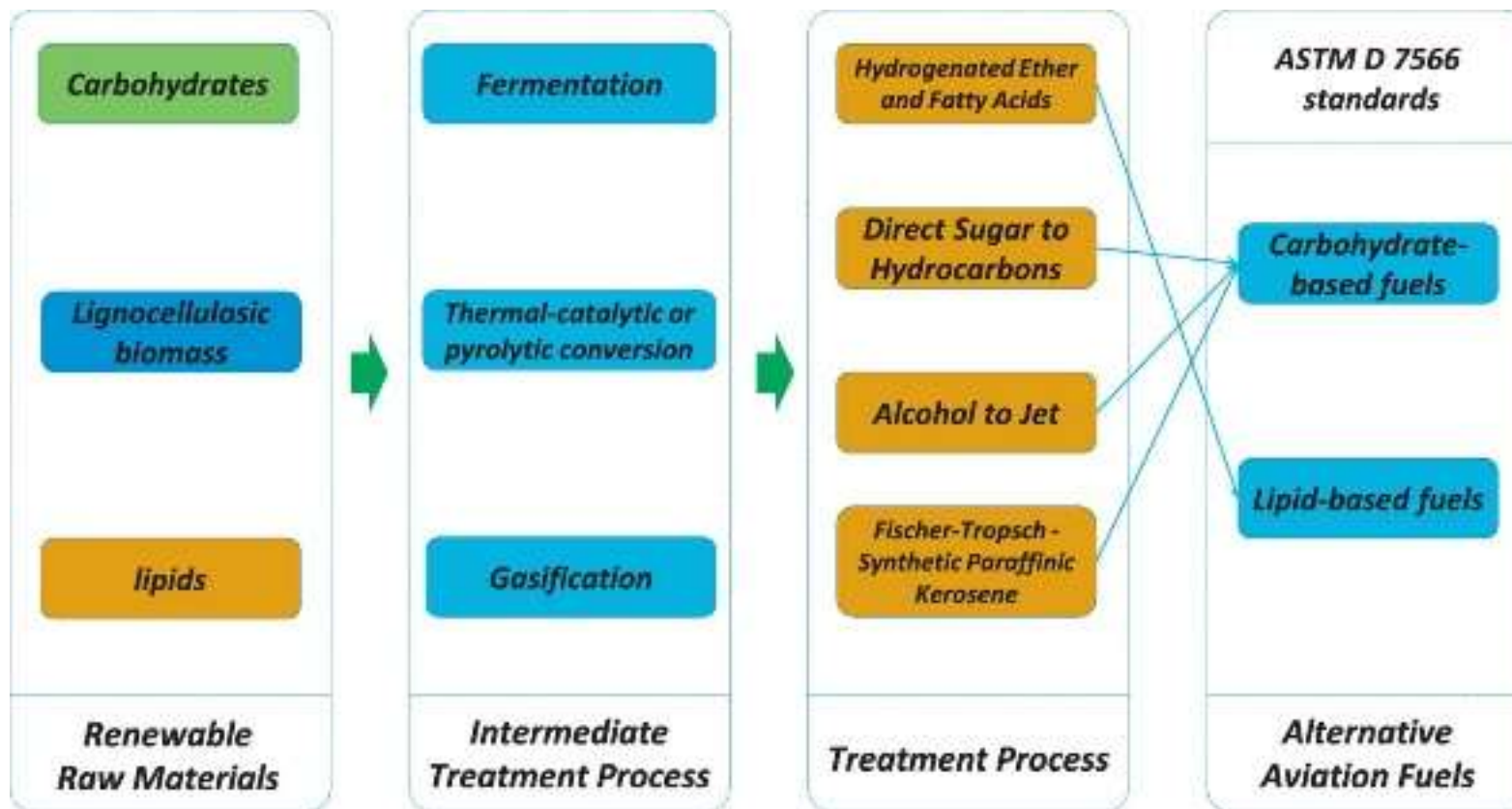
## Bio-Fuels (Surrogate Fuels)

- Phase 1 bio-fuels very similar to conventional fuels but have renewable sources. Hence, no changes in the processes and combustion devices are required.
- Since 2009 five fuels have been qualified and these are blended with conventional fuels.
- Phase 2 bio-fuels will be designed such that they meet future requirements for reduced emissions, and will most likely necessitate a re-design of combustion devices.



Process path of renewable fuels

## Production Routes of Biofuels





## Impact of Biofuels on Engine Operation

Safety  
 Flash Pt., Freezing Pt.  
 Microsep

Certification  
 All Characteristics

Cost of Ownership  
 ThermalStab.  
 Exist. Gum  
 Sulfur  
 Durability  
 As Above  
 Lubricity  
 Acidity  
 Performance  
 Heating Value  
 Density  
 Flash/Freezing Pts.  
 Maintenance  
 Same as Durability

System Design & Materials  
 All Characteristics

Future Technology  
 Specific Heat, Thermal Stab.  
 Aromatics, Sulfur/polar Materials

Legacy Hardware  
 Aromatics, lubricity

Fluid Performance  
 Prediction  
 Freezing Pt., viscosity  
 Distillation, Thermal stability

Physical Properties

Deposition (coking)  
 Thermal stability, Gum,  
 Distillation

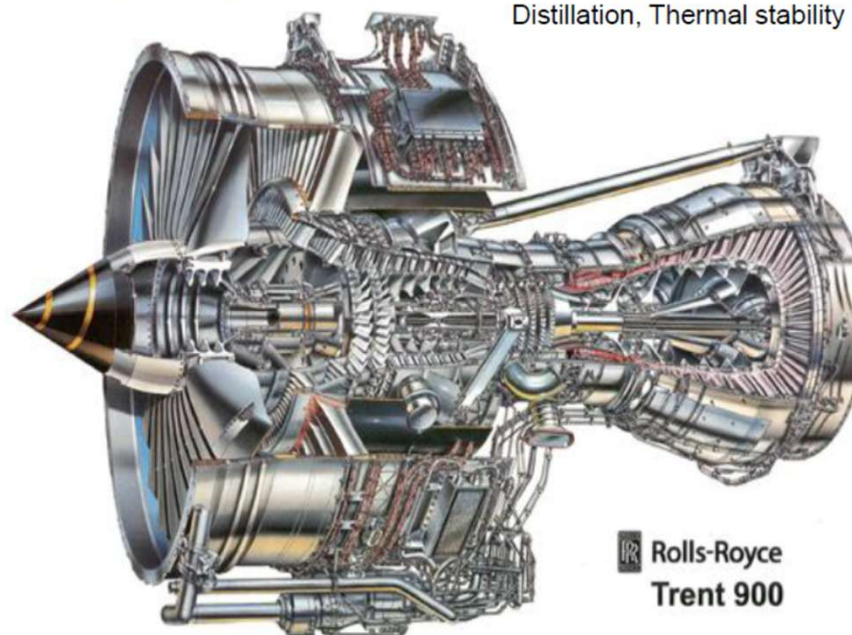
Hot-End Life  
 Thermal Stability, Acidity  
 Aromatics, Sulfur

Emissions  
 Aromatics, Sulfur  
 distillation

Cold Start & Alt re-light  
 Flash Pt., Heating Value  
 Distillation, viscosity

Material Compatibility  
 Aromatics, freezing pt.  
 Acidity, Copper Strip

Chemical Properties





## Cost of Biofuels

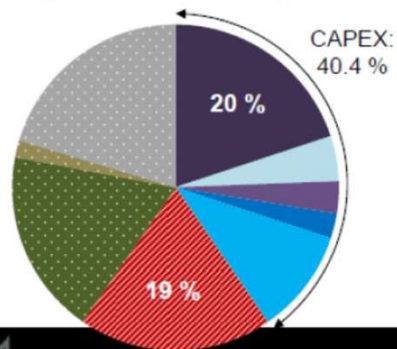
### Comparison of Costs BTL / PBTL / PTL

Plant size: 100 MW<sub>th</sub>

- Electrolyzer
- Fischer-Tropsch
- Power<sup>[3]</sup>
- Maintenance
- Entrained flow gasification
- Selexol
- Biomass<sup>[4]</sup>
- Labor costs
- Pyrolyse
- Remaining (CAPEX)
- Remaining (Utilities)
- Remaining (OPEX)

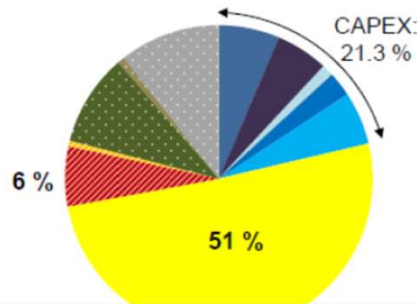
#### Biomass-to-Liquid (BTL)

Investment: ca. 395.2 mio. €  
 Fuel production: 24.17 Mt  
 Fuel costs: ca. 2.34 €/l



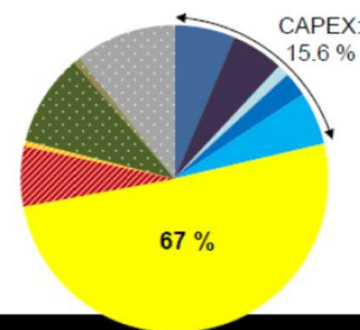
#### Power&Biomass-to-Liquid (PBTL)

Investment: ca. 751 mio. €  
 Fuel production: 91.27 Mt  
 Fuel costs : ca. 2.24 €/l



#### Power-to-Liquid (PTL)

Investment: ca. 672.5 mio. €  
 Fuel production: 91.27 Mt  
 Fuel costs : ca. 2.74 €/l

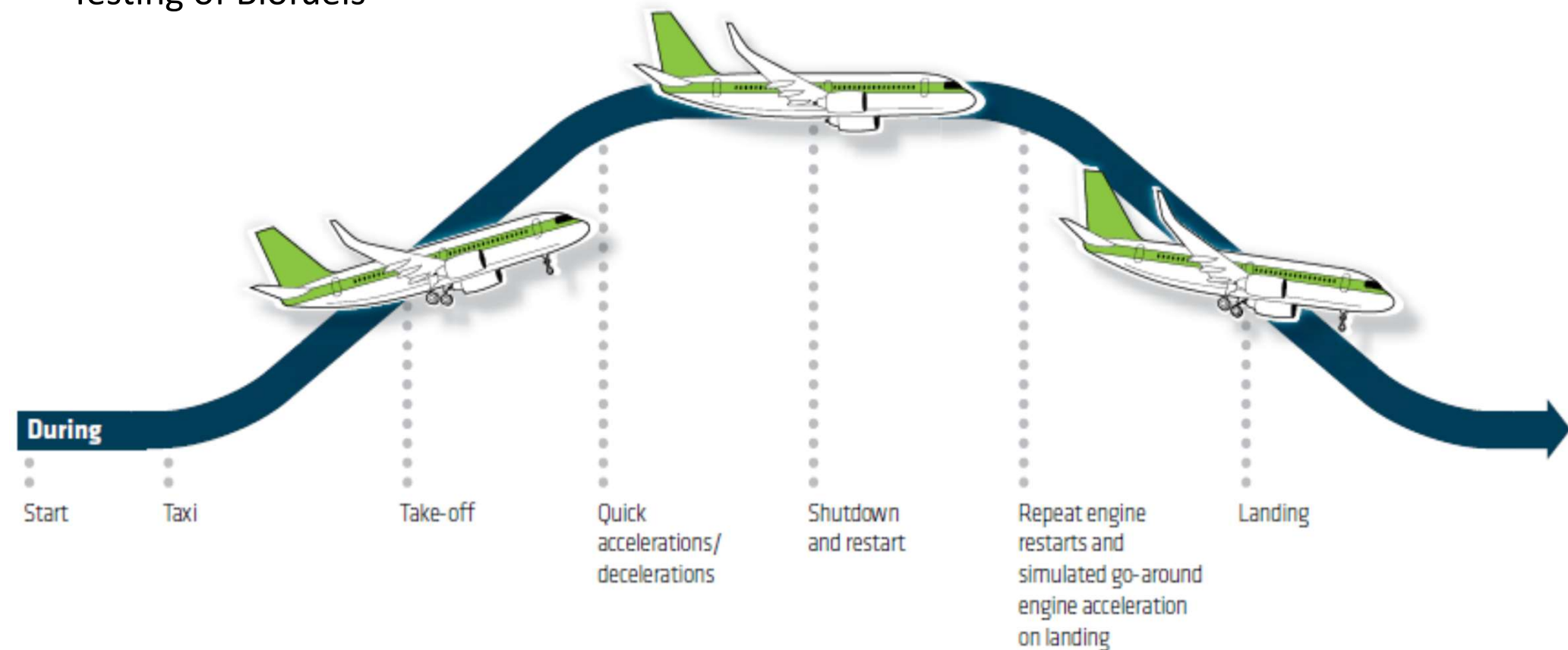


Rolls-Royce proprietary information - private

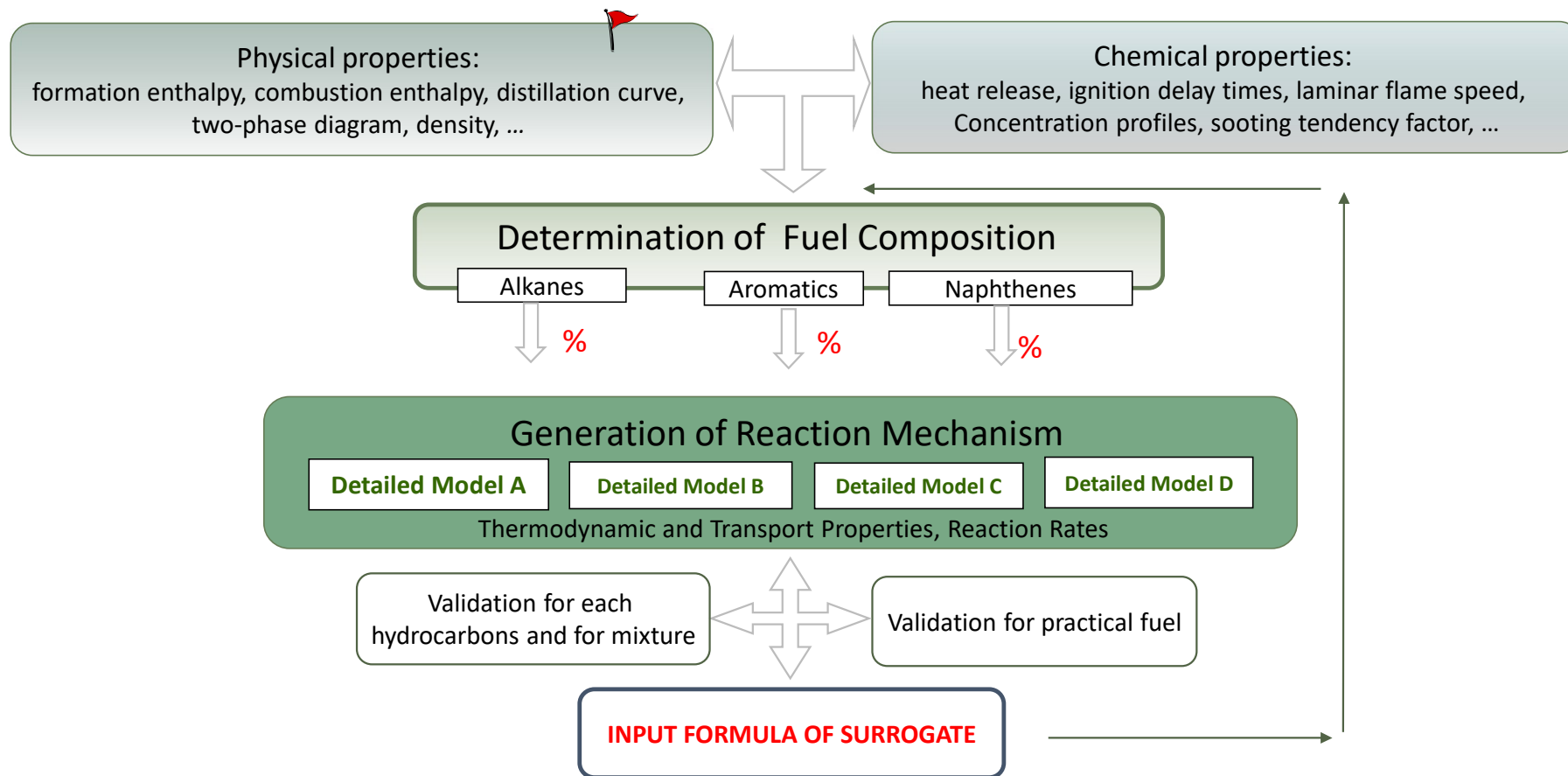


Rolls-Royce

## Operation Profile During Testing of Biofuels

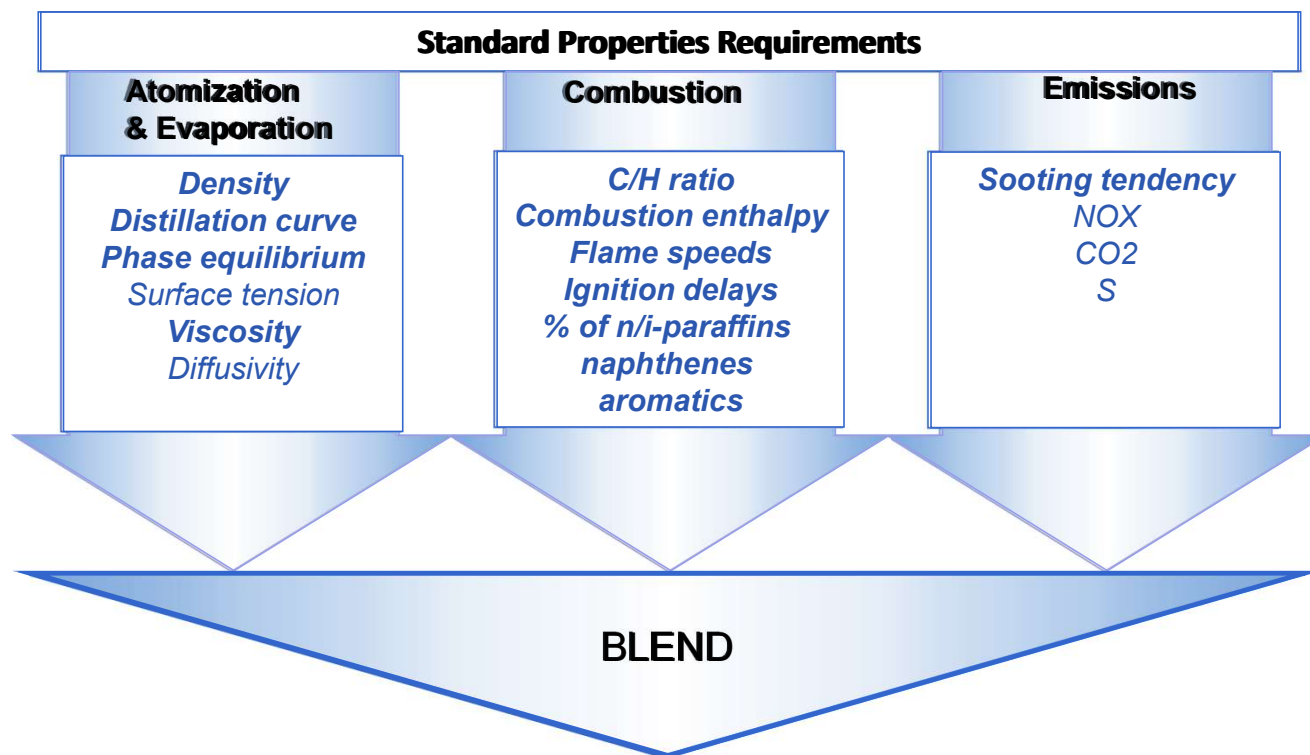


## Surrogate Fuel Design



## Surrogate Fuel Design

Universal fundamental values to characterize the blend





# ANNEX : JET A-1 Specification

Property	Limits	Test Method		Remarks
		IP	ASTM	
<b>APPEARANCE</b>				
Visual appearance	Clear, bright and visually free from solid matter and un-dissolved water at ambient fuel temperature			
Colour	Report		D 156 or D 6045	See Note 1
Particulate contamination mg/L Max	1.0	423	D 5452	See Note 2
Particulate, cumulative channel particle counts, ISO Code & Individual Channel Counts		564 or 565 or 577		See Note 3
≥ 4 µm(c)	Report			
≥ 6 µm(c)	Report			
≥ 14 µm(c)	Report			
≥ 21 µm(c)	Report			
≥ 25 µm(c)	Report			
≥ 30 µm(c)	Report			
<b>COMPOSITION</b>				
Total Acidity, mg KOH/g Max	0.015	354	D 3242	See Note 4
Aromatics, % v/v. Max	25.0	156	D 1319	
OR Total Aromatics, % v/v Max	26.5	436	D 6379	See Note 5
Sulphur, Total, % m/m Max	0.30	336	D 1266 or D 2622	or D 4294 or D 5453
Sulphur, Mercaptan, % m/m Max	0.0030	342	D 3227	
OR Doctor Test	Negative	30	D 4952	See Note 6
<b>Refinery Components at point of manufacture:</b>				
Non Hydroprocessed Components, %v/v	Report (Incl. 'nil' or '100%')			See Note 7
Mildly Hydroprocessed Components, % v/v	Report (Incl. 'nil' or '100%')			
Severely Hydroprocessed Components, % v/v	Report (Incl. 'nil' or '100%')			
Synthetic Components, %v/v	Report (Incl. 'nil' or '50%')			See Note 4 for limits for synthetic components



# ANNEX : JET A-1 Specification



Property	Limits	Test Method		Remarks
		IP	ASTM	
<b>INCIDENTAL MATERIALS</b>				
Fatty Acid Methyl Ester (FAME), mg/kg	Max	50	585 583 590 599	ASTM D7797 See Notes 8, 9 and 10
<b>VOLATILITY</b>				
Distillation			123	D86 or D7345., See Note 11
Initial Boiling Point, °C	Report			
Fuel Recovered				See Note 11
10% v/v at °C	max	205.0		Or IP 406 or D 2887, see Note 12
50% v/v at °C		Report		
90% v/v at °C		Report		
End Point, °C	max	300.0		
Residue, % v/v	max	1.5		
Loss, % v/v	max	1.5		
Flash Point, °C	min	38.0	170 or 523	D 56 or D 3828
Density at 15°C, kg/m³		775.0 min to 840.0 max	160 or 365	D 1298 or D 4052 See Note 13
<b>FLUIDITY</b>				
Freezing Point, °C	max	-47.0	16 or 435 or 528 or 529	D 2386 or D 5972 or D 7153 or D 7154
Viscosity at -20°C, mm²/s(cSt)	max	8.000	71	D 445 or D7042, See Note 15
<b>COMBUSTION</b>				
Specific Energy, net, MJ/kg	min	42.80	12 or 355	D 3338 or D 4809 See Note 16
Smoke Point, mm	mon	25.0	598	D 1322 See Note 17
<b>OR</b>				
Smoke Point, mm	min	18.0	598	D 1322 See Note 17
<b>AND</b> Naphthalenes, % vol.	max	3.00		D 1840



# ANNEX : JET A-1 Specification

Property	Limits	Test Method		Remarks
		IP	ASTM	
<b>CORROSION</b> Corrosion, Copper strip, classification (2 hours +/- 5 min. at 100 °C +/- 1°C)	max 1	154	D 130	
<b>STABILITY</b> Thermal Stability (JFTOT) Control temperature, °C Filter Pressure Differential, mm Hg One of the following requirements shall be met: (1) Annex B VTR  (2) Annex C ITR or Annex D ETR, average over area of 2.5mm <sup>2</sup>	min max  nm max 250 25 85	323	D 3241	See Note 16
<b>CONTAMINANTS</b> Existent Gum, mg/100ml  Microseparator (MSEP), rating Fuel with Static Dissipator Additive OR Fuel without Static Dissipator Additive	max  min min 7 70 85	540	D381 D 3948	See Note 19
<b>CONDUCTIVITY</b> Electrical Conductivity, pS/m	50 min to 600 max	274	D 2624	See Note 20



## What you should not forget

- What are typical requirements for jet fuels ?
- What is typical ratio of mass of air and mass of fuel going through the engine of a long-range aircraft ?
- Name one production route for a bio-fuel ?
- Name a typical oxidizer and a fuel for a solid rocket motor.
- Name a few manufacturing challenges of a solid fuel.
- Which are the most common propellants for liquid rocket engines ?
- Why is a standard JET-A1 kerosene not suited for rocket engine applications ?
- Can you draw a performance diagram of typical rocket engine propellants ?