Synthetic fuels for aviation

Current status and challenges in kinetic modeling

Based on Chi Zhang, Xin Hui, Yuzhen Lin, Chih-Jen Sung, "Recent development in studies of alternative jet fuel combustion: Progress, challenges, and opportunities", Renewable and Sustainable Energy Reviews 54, 2016, 120–138.

Need for alternative jet fuels

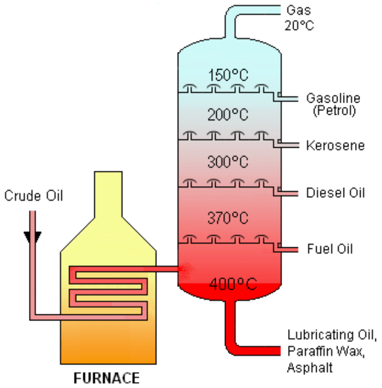

Figure: Fractional distillation process to obtain kerosene from crude oil

Need for alternative jet fuels

- Increasing energy demand for aviation
  $\Longrightarrow$ need for non-conventional alternative jet fuels
- Aviation emissions
  - Similar to ground transportation: CO, CO_2, H_2O, NOx, SOx, UHC, PM
  - 2–3% of total emissions, $<$ 3% NOx
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- Many alternative jet fuels choices:
  - Synthetic fuels, bio-fuels, alcohol fuels, liquid hydrogen, liquid methane, ...
- 'Drop-in' fuels – most feasible choice for alternative jet fuels
  - Substitute for conventional jet fuel
  - Completely interchangeable and compatible with conventional jet fuel
  - Does not require any modifications to the current aircraft engine or fuel distribution system
- Hydrocarbon-based 'drop in' fuels
  - Have similar energy content as the conventional jet fuels
  - Blended with or used as a total replacement of conventional jet fuels
  - Not considering liquid methane, hydrogen, oxygenated fuels

Hydrocarbon-based ‘drop in’ fuels

- Variety of sources: coal, oil shale, tar sand, plants, and animal fats
- Composition of fuel differ based on their feedstocks & production process.
- Two main types: Synthetic jet fuels & Bio-jet fuels
- Synthetic (FT) jet fuels: Synthetic processing
  - From natural gas or coal
  - Feedstock gasified to produce synthesis gas ($H_2 + CO$)
  - Fischer-Tropsch process to give liquid hydrocarbons
  - Coal-To-Liqid, Gas-To-Liquid
  - Non-synthetic (not from fossils): Biomass-To-Liquid, Coal-and-Biomass-to-Liquid
- Bio-jet fuels: Hydroprocessing (HRJ, HEFA)
  - From agricrops, trees, wood, fibre, plant oils (Jatropha, algae)
  - Remove chemically bound oxygen to get the desired fuel

Merits and de-merits of Fischer-Tropsch fuels

Merits:

- Contains hardly any aromatics – mainly made of normal- and iso-paraffins
- Burns cleaner than conventional fuels in aircraft engines
- 2–4% lesser CO_2, 50–90% less PM, 100% less S than conventional fuels
- Excellent low temperature properties
- Superior thermal stability
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De-merits:

- Life cycle analysis: total C emissions $\sim 2\times$conventional jet fuels
- CO_2 sequestration needed
- Potential failure of engine seals due to lack of aromatics
- Aromatics cause the engine seals to swell and prevent leakage
- Fully synthetic jet fuels must have minimum aromatics (8% by volume) to prevent seal failure
- Semi-synthetic jet fuels – no such requirement – used as a blend with conventional jet fuel (contains aromatics)

Merits and de-merits of bio-jet fuels

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- Renewable sources
- Carbon neutral (C emissions can be reabsorbed in plant growth)
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De-merits:

- Low energy density (Why?)
- Poor high temperature thermal stability
- Storage instability
- Technology development is needed
- Need balance between fuel and food uses

Status quo

Synthetic jet fuels	Biojet fuels
Uses coal and natural gas as feed-stock	Plant based feed stock – competes with farmland for food
Limited CO_2 reduction capacity	Carbon neutral

Synthetic jet fuels are more attractive than bio-jet fuels as drop-in replacements!

Properties on conventional vs FT fuels

Table 1
ASTM standard and properties of conventional and alternative jet fuels.

Property	ASTM standard	Jet A	JP-8	S-8
POSF number	–	4658	3773	4734
Composition				
n-Paraffins (wt%)	–	28	19	17.7
Iso-paraffins (wt%)	–	29	38.2	82
Cyclo-paraffins (wt%)	–	20	24.1	< 0.4
Aromatics (wt%)	Report	20	13.5	< 0.1
Total sulfur (wt%)	Max 0.3	–	0.0064	< 0.001
Distillation				
Initial boiling point (°C)	Report	158	152	182
10% recovered (°C)	Max 205	184	173	195
20% recovered (°C)	Report	192	179	–
50% recovered (°C)	Report	213	198	228
90% recovered (°C)	Report	248	239	–
Final boiling point (°C)	Max. 300	269	260	280
Flash point (°C)	Min. 38	47	48	49
Freezing point (°C)	Max. -47	-49	-49	-59
Density @ 15 °C (kg/m^3)	775–840	806	790	757
Viscosity @ -20 °C (cSt)	max 8.0	5.2	4.1	4.6
Neat heat of combustion (MJ/kg)	min 42.8	42.8	43	44.1
Smoke point (mm)	min 19.0	21	25	> 43
H/C molar ratio	–	1.957	1.937	2.152
Molecular weight (g/mol)	–	142	153	168

Ignition delays

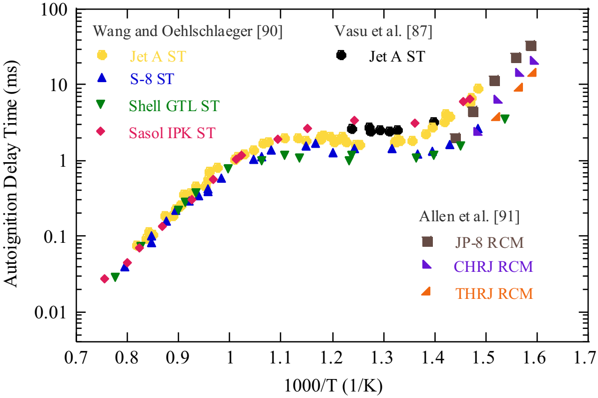


Fig. 6. Autoignition delay times of various stoichiometric jet fuel/air mixtures at a pressure of 20 atm measured in two shock tubes (STs) and a rapid compression machine (RCM). Data are taken from Refs. [87,90,91].

Speciation profiles

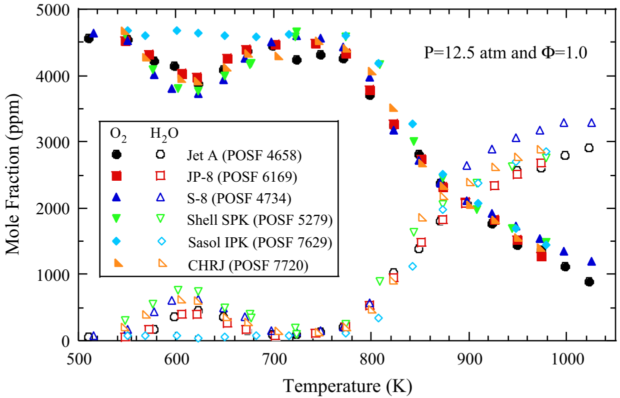
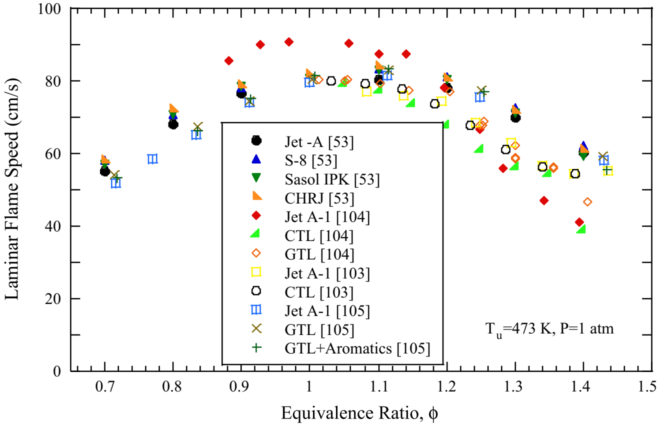


Fig. 11. Comparison of species data from flow reactor oxidation of conventional and alternative jet fuels [99].

- Above: Flow reactor speciation – Dooley (2012)
- Not shown: Jet-stirred reactor – Dagaut et al. (2010, 2014)

Premixed flames



ig. 8. Laminar flame speeds of various jet fuel/air mixtures at preheat tempera-
ure of about $T_u = 473$ K and pressure of $P = 1$ atm. Data are taken from Refs.
53,103–105].

Counterflow diffusion flames

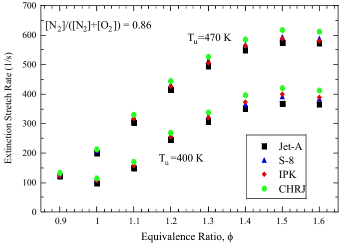


Fig. 9. Extinction strain rates of Jet A/oxidizer, S-8/oxidizer, IPK/oxidizer, and CHRJ/oxidizer at 400 K and 470 K preheat temperatures as a function of equivalence ratio [53].

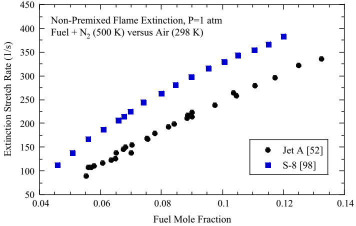


Fig. 10. Extinction strain rates of Jet A [52] and S-8 [98] in atmospheric non-premixed flames with fuel/N_2 temperature of 500 K and air temperature of 298 K.

Surrogate formulation and kinetic models

Table 5
Surrogates for various alternative jet fuels.*Sources*: Refs. [98,113–115,121–124].

Reference	Target real fuel	Surrogate fuel	Validation targets
Huber et al. [121]	S-8	n-Nonane/2,6-dimethyloctane/3-methyldecane/n-tridecane/n-tetra-decane/n-pentadecane/n-hexadecane 0.03/0.28/0.34/0.13/0.20/0.015/0.005 (by mole)	Density, thermal conductivity, sound speed, viscosity, distillation curve
Huber et al. [122]	Bio-SPK	4-Methyloctane/2,5-dimethylnonane/2,3,5-trimethyldecane/n-tridecane/n-pentadecane 0.105/0.281/0.164/0.227/0.223 (by mole)	Distillation curve
Mawid [123]	S-8	n-Decane/iso-octane 0.60/0.40 (by volume)	Autoignition delay time and species profile
Naik et al. [113]	S-8	Iso-octane/n-decane/n-dodecane 0.32/0.25/0.43 (by mole)	Laminar flame speed, extinction strain rate, NO_x
	Shell GTL®	Iso-octane/n-decane/n-dodecane 0.28/0.61/0.11 (by mole)	
Dooley et al. [98]	S-8	n-Dodecane/iso-octane 0.519/0.481 (by mole)	Species profile, autoignition delay time, extinction strain rate
Slavinskaya et al. [124]	GTL	Propyl-cyclohexane/2,7-dimethyloctane/2-methyldecane/n-decane 0.15/0.17/0.32/0.36 (by volume)	Physical properties
		Propyl-cyclohexane/n-decane/iso-octane 0.15/0.36/0.49 (by volume)	Autoignition delay time
		Propyl-cyclohexane/n-decane/2-methyldecane/iso-octane 0.15/0.36/0.32/0.17 (by volume)	
Mzé-Ahmed et al. [114]	CTL	n-Decane/iso-octane/n-propylcyclohexane/n-propylbenzene 0.395/0.130/0.373/0.102 (by mole)	Species profile, autoignition delay time, laminar flame speed
Dagaut et al. [115]	GTL	n-Decane/iso-octane/n-propylcyclohexane 0.577/0.332/0.091 (by mole)	Species profile, autoignition delay time, laminar flame speed
		n-Decane/iso-octane/n-propylcyclohexane 0.699/0.214/0.087 (by mole)	

Chronological order for kinetic models:
Mawid (2008); Naik (2010); Mze-Ahmed (2010); Dooley (2012);
Dagaut (2014, detailed mechanism $\sim$ 3000 species)

State of the art kinetic models

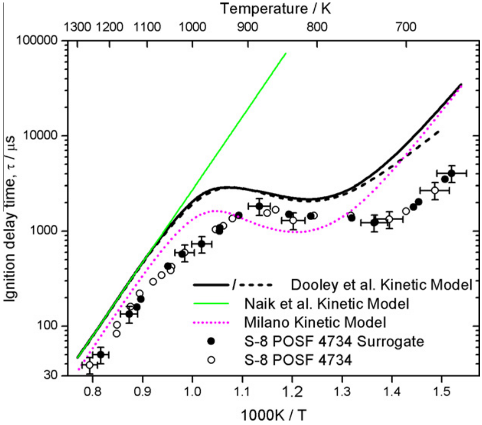


Fig. 3. Reflected shock ignition delay times, with representative uncertainty bars, see text, at conditions of ϕ = 1.0 in air at ~20 atm for S-8 POSF 4734 and S-8 POSF 4734 Surrogate (*n*-dodecane/*iso*-octane 51.9/48.1 mole %). Symbols are experiment and lines are kinetic model computations with the models of Dooley et al. [3], Ranzi et al. [21] and Naik et al. [12]. Dashed lines are computations imposing a pressure gradient of 2%/ms. All other computations are performed with assumptions of constant volume/constant internal energy.

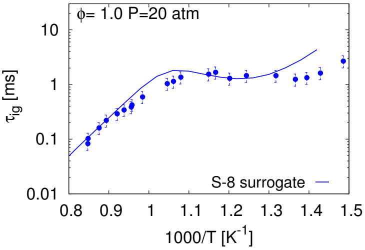
Concluding remarks

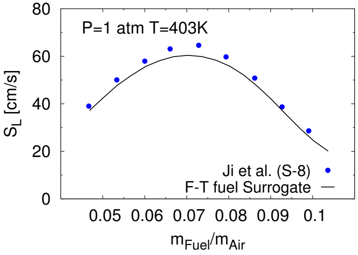
Kinetics of FT fuels

- Scope for a lot of improvement!
- Can we do better than the existing models?
- Win on accuracy as well as compactness?

Future (no, immediate!) directions

- Combination of *n*-dodecane, methylcyclohexane, and iso-octane (even without low T chemistry) is promising as a FT surrogate[1]!





- Integrate kinetics of iso-octane (valid at low–high T) into CLA
  - Put in just what is needed
- Formulate a surrogate for a FT fuel (say S-8)
- Assess the surrogate + kinetic mechanism

[1] K. Narayanaswamy, "Chemical kinetic modeling of jet fuel surrogates", PhD. thesis, 2014