Properties and Performance of Gas-to-Liquids Fischer-Tropsch Diesel Fuels

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History of F-T Diesel Fuel

- Fischer-Tropsch process developed in 1920's
- Produced when conventional fuels were unavailable
  - Germany during WWII
  - South Africa during apartheid era
- Worldwide production of FT products was >3 billion annual gallons in 2002, from coal and gas
- Mainly in South Africa and Malaysia
- Many FT projects at various stages worldwide

F-T Production (simplistic) - First Step

- Carbonaceous feedstock
  - Natural gas, coal, biomass
  - Not produced from petroleum
- Syngas formation
  - Mixture of CO and H_2
    - Autothermal reforming
    - Steam reforming
    - Partial oxidation
  - Syngas formation is ~70% of total cost of fuel production

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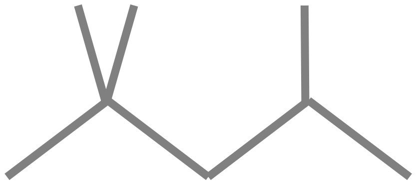
F-T Production (simplistic)- Second Step

F-T catalysis

- High temperature processes
  - 300-350^{o}C
  - Iron catalysts
  - Typically, lower MW branched hydrocarbons



- Low temperature processes
  - 200-240^{o}C
  - Iron or cobalt catalysts
  - Typically, higher MW straight chain hydrocarbons

F-T Production (simplistic) - Final Step

Post-processing

- In LT processes, heavy waxes are mildly cracked to produce diesel fuel
- HT hydrocarbons can be oligomerized to form diesel fuels

Example Fuel Properties

Typical fuel properties from recent literature review *(SAE 2003-01-0763)*

Comparison to No. 2 Diesel

Property	Method	Typical No. 2	Low T F-T	High T F-T (PetroSA COD)
HHV, MJ/kg	D240	43-48	45-48	45-48
Density, 15°C	D4052	0.8464	0.7695-0.7905	0.8007-0.8042
Distillation, °C	D86			
IBP		174	159-210	230
50%		253	244-300	254
90%		312	327-334	323
FBP		344	338-358	361
Cetane number	D613	44.9	>74	~50
Sulfur, ppm	D5453	300	<1	<1
Total Aromatics	D5186	~30	0.1-2	~10
Hydrogen, wt%	D5291	13-13.5	~15	~14.4

←Similar energy content but lower density (lower btu/gal)

←Higher Cetane Number

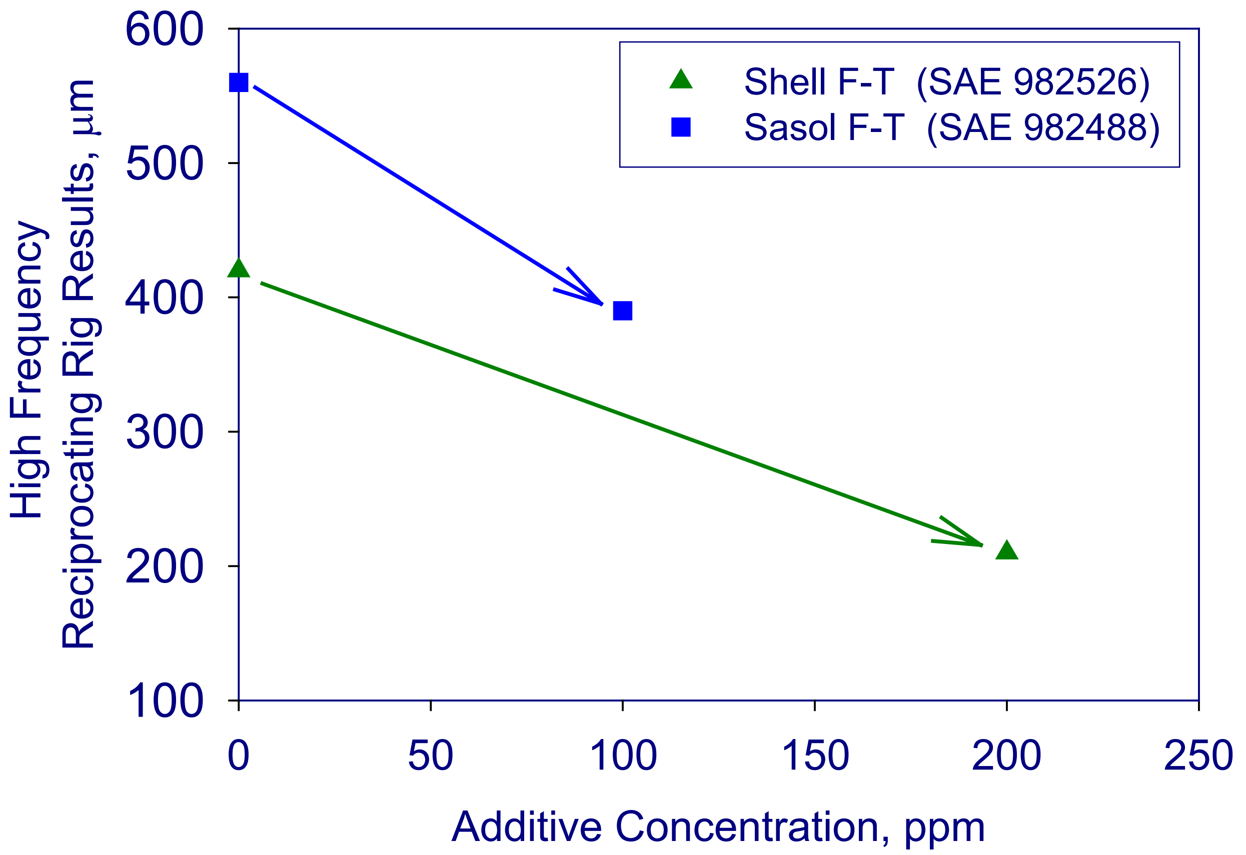
←Ultra-low sulfur

←Near zero or low aromatic

←High hydrogen content

Lubricity

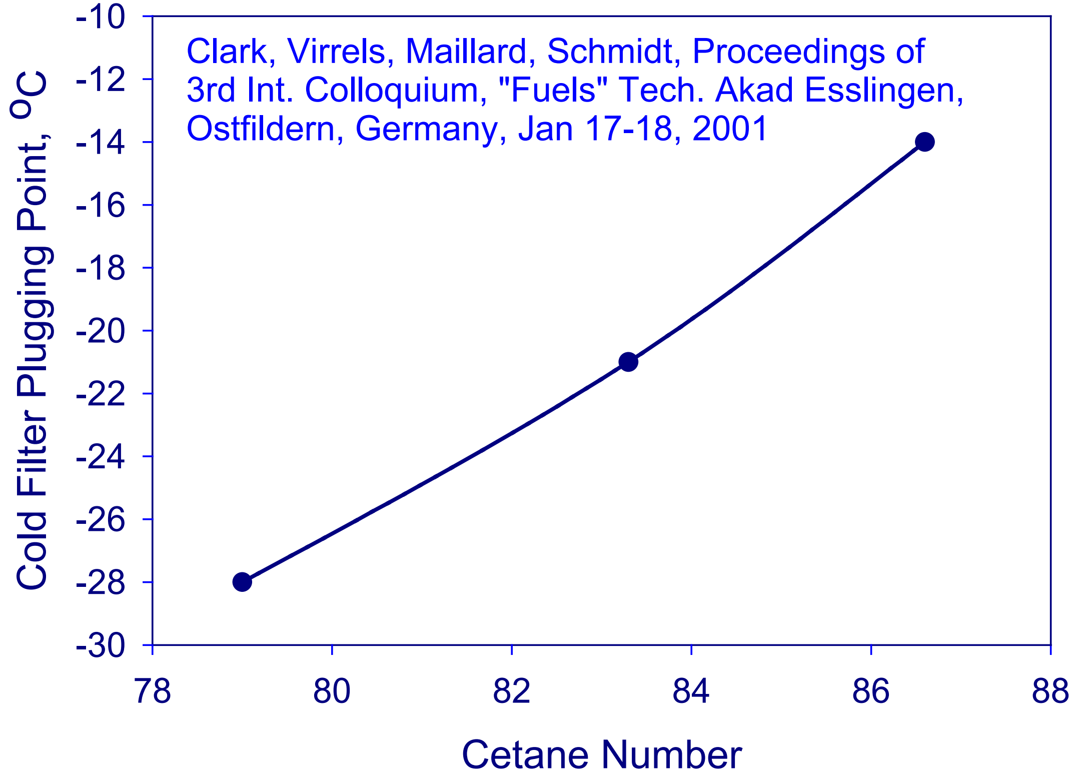
Zero or low aromatic fuels typically have marginal lubricity, but good response to additives



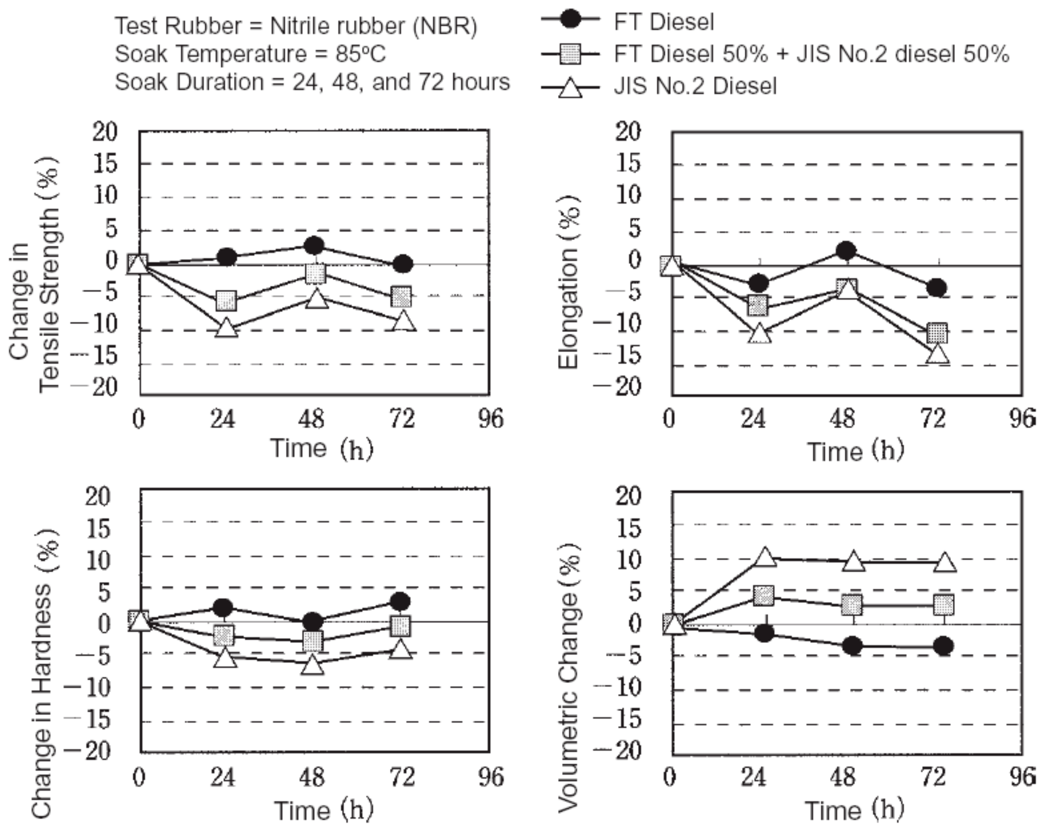
Cold Flow-CN Trade-off for F-T

Highly n-paraffinic F-T diesels have poor cold flow properties (but high CN)

- Unresponsive to cold flow additives in neat form
- Can be addressed through modification of processing conditions



Elastomer Compatibility



- Tensile strength, hardness, and elongation are retained after exposure to FT diesel
- Elastomer swelling is lower for nitrile rubber
  - May reduce sealing effectiveness
  - Low swelling caused by low aromatic content
- Swell of fluorocarbon materials is less significant

Tsukasaki, Y., Toyota Motor Corporation, *"Technical Trend of GTL Fuels for Automobile,"* JSAE Journal, Vol. 55, No. 5, Pages 67 ~ 72, May 2001.

Other Performance Issues

Biodegradability:

-limited experimental data suggests higher rates of biodegradation for FT fuels relative to conventional

Stability:

-highly paraffinic FT-fuels are susceptible to oxidative degradation and antioxidant additives are required

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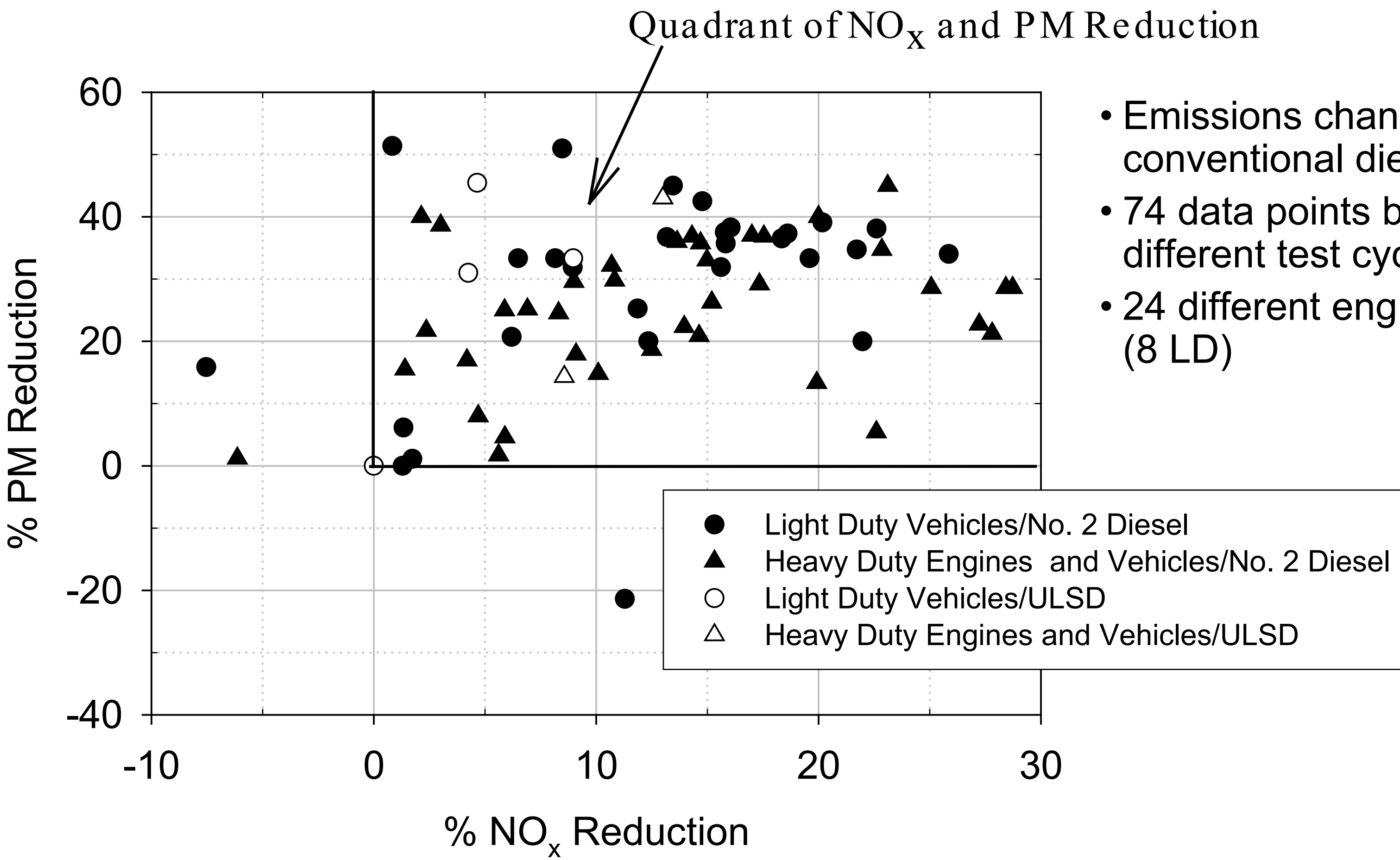
FT NO_x and PM Summary-HD/LD

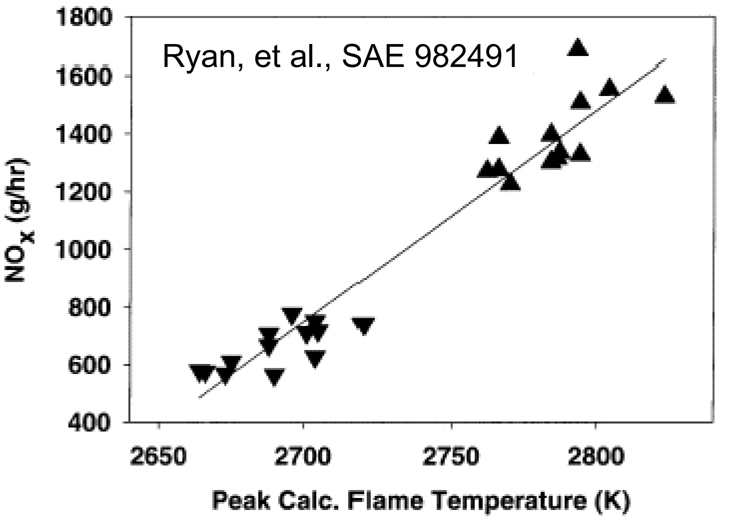


- Emissions changes relative to conventional diesel and ULSD
- 74 data points based on several different test cycles
- 24 different engines and vehicles (8 LD)

Source: *SAE 2003-01-0763*

Cause of Emissions Effects

- Reducing aromatic content is consistently associated with emissions reductions
    - In both old and new engines
    - Likely this is related to reduction in adiabatic flame temperature which is higher for aromatics
    - Reduced PM emissions may be related to lower polyaromatic content (PM precursor)



- *Emissions reductions observed for FT-diesel may be most reliably correlated with the low aromatic content, or alternatively the high hydrogen content*
- *In older engines the high CN may also be important*

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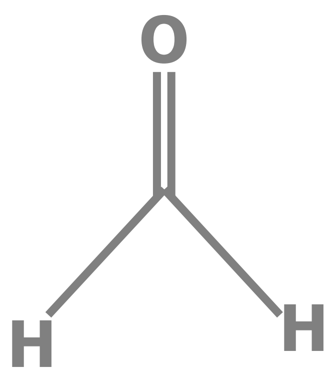
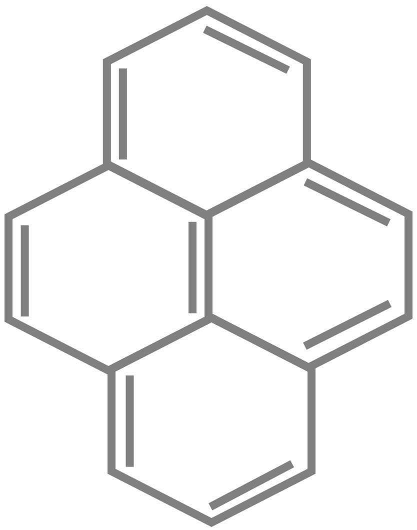
Toxic Emissions Testing

- Limited testing to date
  - Both LD and HD
- *Trend shows reduced emissions of selected toxic compounds from F-T diesel fuel compared to conventional diesel fuel*





Toxic Emission Results

Compound	Highest →	→		Lowest
Benzene	CARB	No. 2	ALS	**F-T**
Formaldehyde	No. 2	ALS	CARB	**F-T**
Naphthalene	No. 2	CARB	**F-T**	ALS
Fluorene	No. 2	CARB	**F-T**	ALS
Pyrene	No. 2	ALS	CARB	**F-T**
Chrysene	No. 2	CARB	ALS	**F-T**
Benzo(a)pyrene	ALS	CARB	No. 2	**F-T**

DB OM611 Light-duty diesel engine

Source: *SAE 2001-01-3628*

Summary

- Most FT fuels share common set of properties: near zero sulfur content, high cetane number, low aromatic content, high H/C ratio
- Positive performance attributes include:
    - Not made from peteroleum
    - Reductions in NOx and PM observed in a variety of LD and HD engines/vehicles
    - Very limited data indicate significant reduction in toxic emissions
    - Limited data suggest high rates of biodegradation
- Possibly negative performance attributes include:
    - FT fuels have poor lubricity but respond well to lubricity additives
    - Poor cold flow properties, but can be addressed through modified process conditions
    - Reduced elastomer swell can be expected for nitrile elastomers
    - Susceptible to oxidation
- Perhaps most useful as a high quality blending component?