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TEXAS A&M UNIVERSITY at QATAR

Synthetic Fuel Formulation from Natural Gas via GTL:
A Synopsis and the Path Forward

Elfatih Elmalik[1,2], Iqbal Mujtaba[1], Nimir Elbashir[2]

[1] University of Bradford, UK

[2] Texas A&M University at Qatar

Water & Energy Workshop

Monday February 16th 2015

Hamad Bin Khalifa University, Doha, Qatar

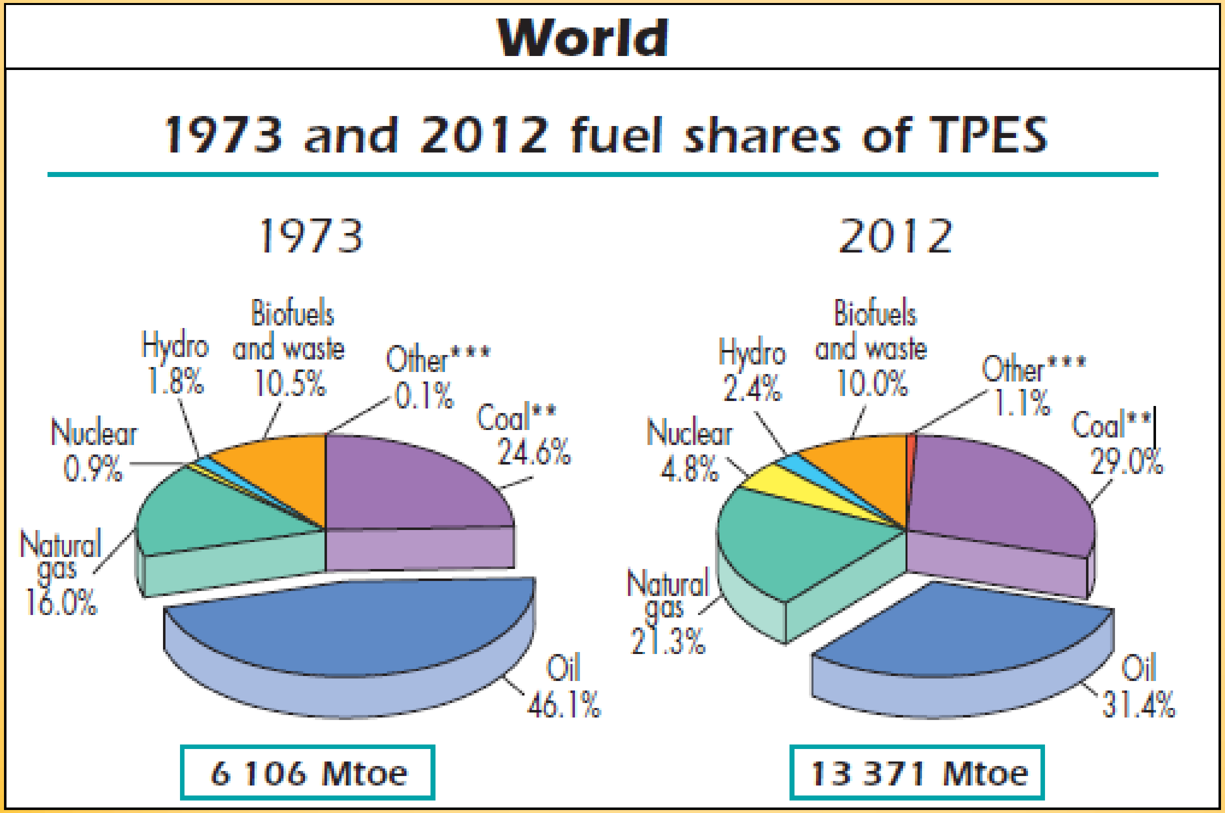
Outline

- **Introduction: World Energy**
- Local Efforts: “Qatar Consortium”
- Fuel Characterization Laboratory
- Synthetic Fuel Challenges
- Approach & Methodology
  - Experimental
  - Computational
- Summary & The Path Forward

World Energy: Production

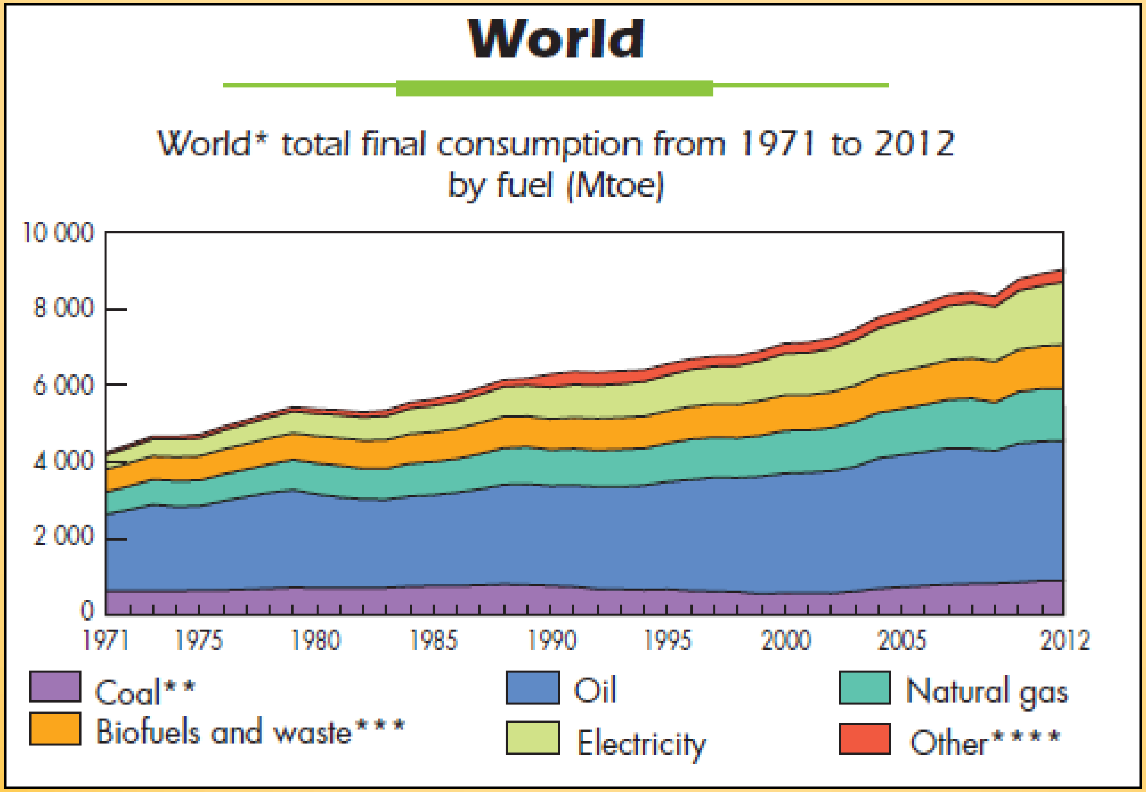
Total Primary Energy Supply*: 13,371 Mtoe

Source: International Energy Agency, Key World Energy Statistics 2014



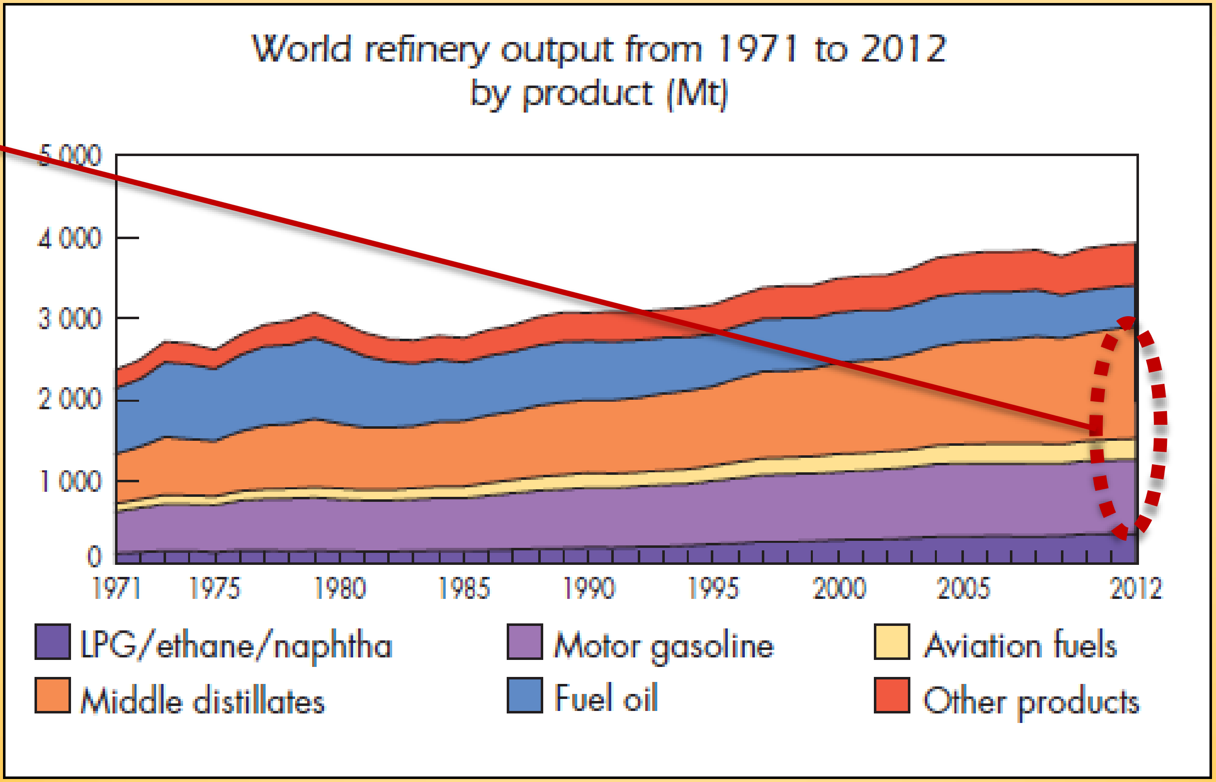
World Energy: Consumption

Total Energy Consumption:
8,979 Mtoe



World Energy: Refinery Products

Total Refinery Production:
3,905 Mt

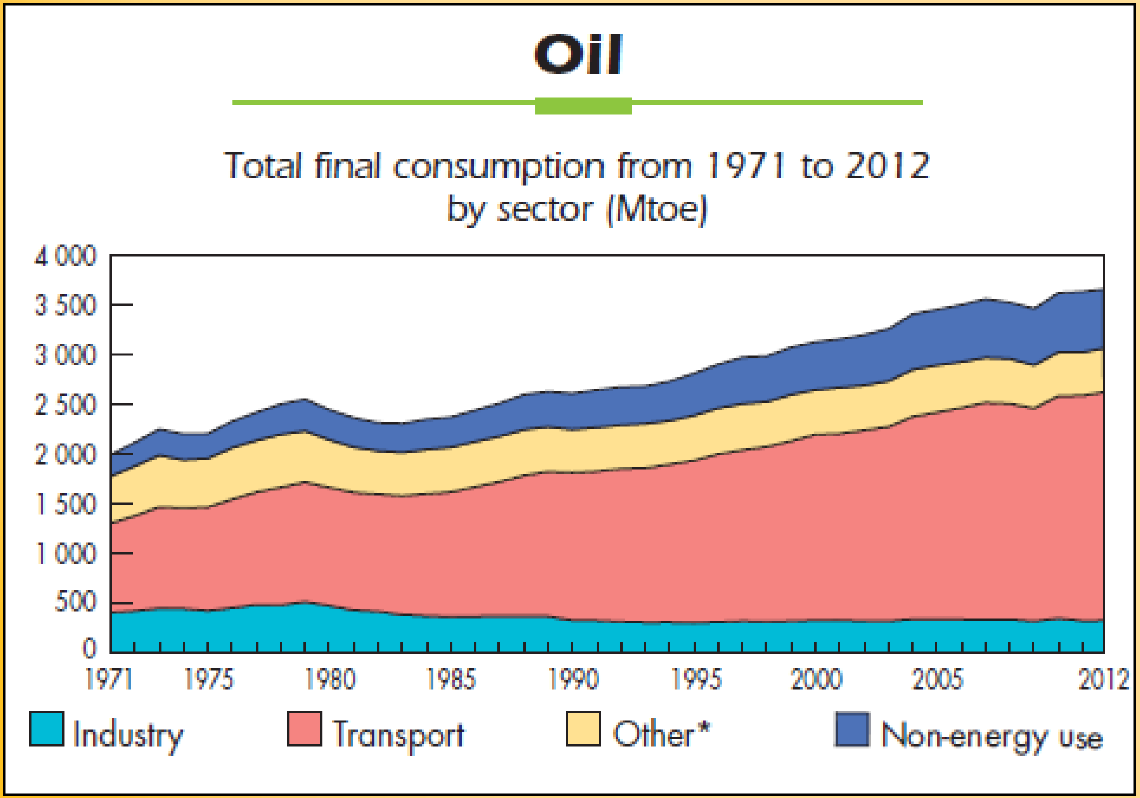


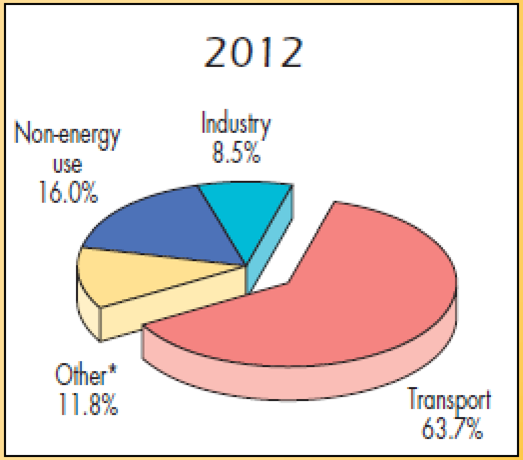
World Energy: Difficulties

- Global energy consumption is only 66% of the TPES.
- Transportation fuels account for more than 70% of refinery output worldwide.
- Gas-to-Liquids (GTL) products are currently grouped together with coal liquefaction plants, diminishing their true impact.

World Energy: Oil Consumption

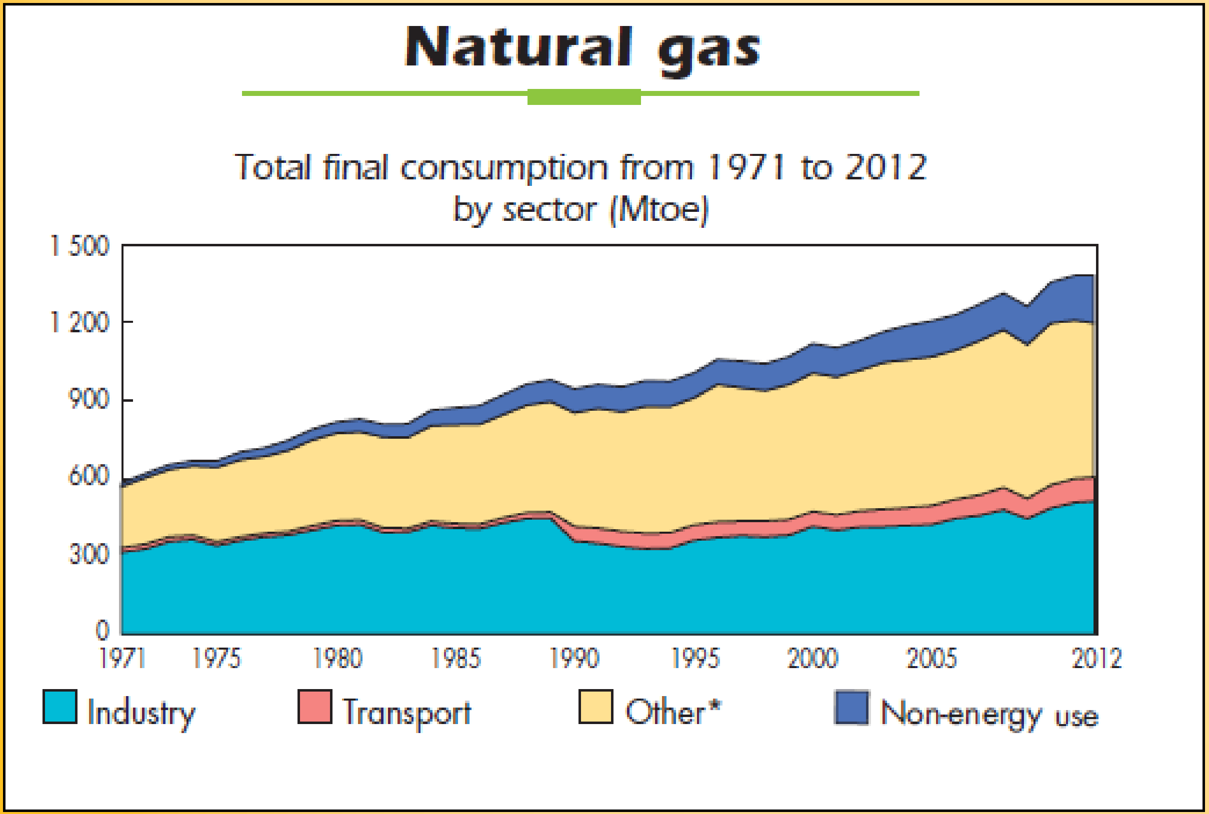
Total Oil Consumption:
3,652 Mtoe

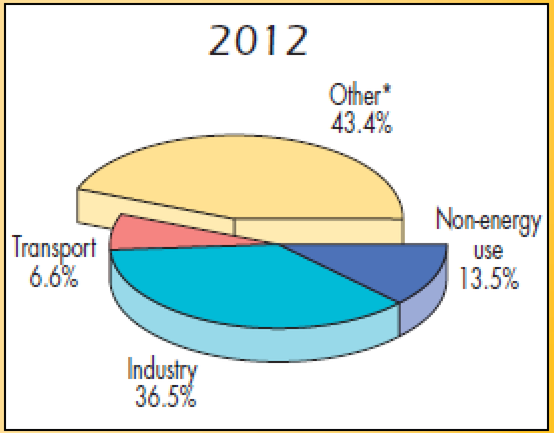




World Energy: Gas Consumption

Total Gas Consumption:
1,366 Mtoe





Natural Gas Utilization

- About $\frac{2}{3}$ of oil products are used for transportation vs less than $\frac{1}{10}$ of Natural Gas.
- Opportunity for GTL products to tap into that large slice.
- Almost half of the Natural Gas utilization is towards agriculture, commercial, residential and public services. Alternative energy resources will free that portion for innovative processing.

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Carbon Footprint

S. Blakey et al. / Proceedings of the Combustion Institute 33 (2011) 2863–2885

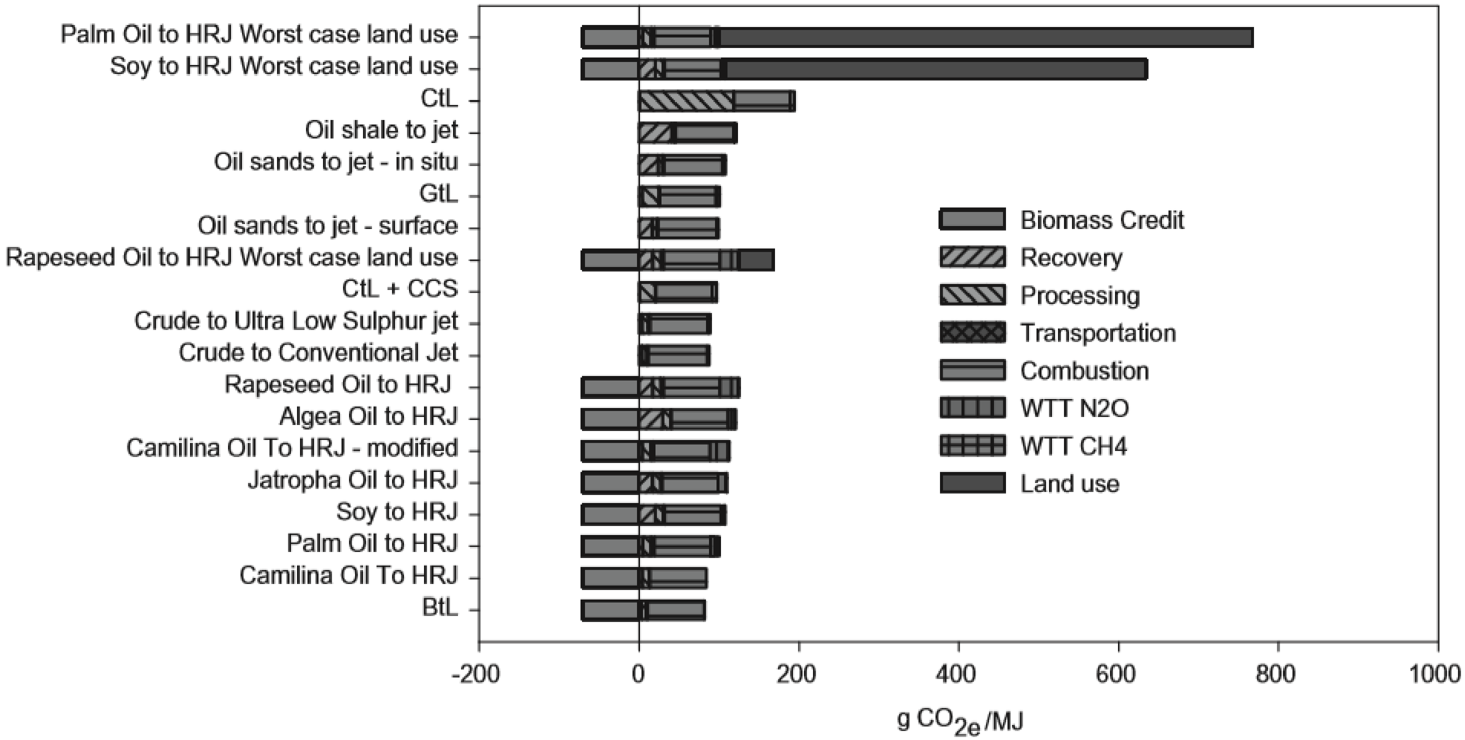

Fig. 12. CO_2 equivalent lifecycle data for a range of conventional and alternative fuels. [40–43,46].

Cleaner Skies

- In 2013, Qatar Airways makes 1st journey from Doha to London utilizing locally produced GTL fuel from the Pearl plant.

Consortium

Funding Agencies

- A unique collaboration between industry and academia partners.
- Each partner works on specific topics and collaborate towards the overall objective.
- The testing is split up as follows:

Technical Guidance

Properties Testing | **Combustion Testing** | **Performance Review**

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- Introduction: World Energy
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- **Fuel Characterization Laboratory**
- Synthetic Fuel Challenges
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Overview of TAMUQ Fuel Characterization Lab

Built a world class research lab to support the development of the Fuel Technology Capabilities of Qatar for Gas-to-Liquid (GTL) processes.

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- Fuel Characterization Laboratory
- **Synthetic Fuel Challenges – the Jet Fuel case**
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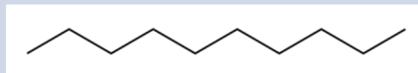
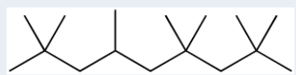
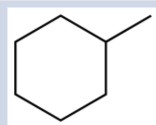
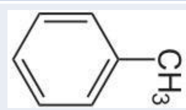
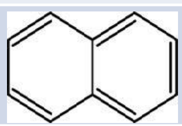
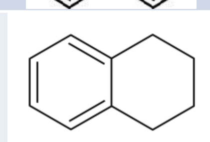
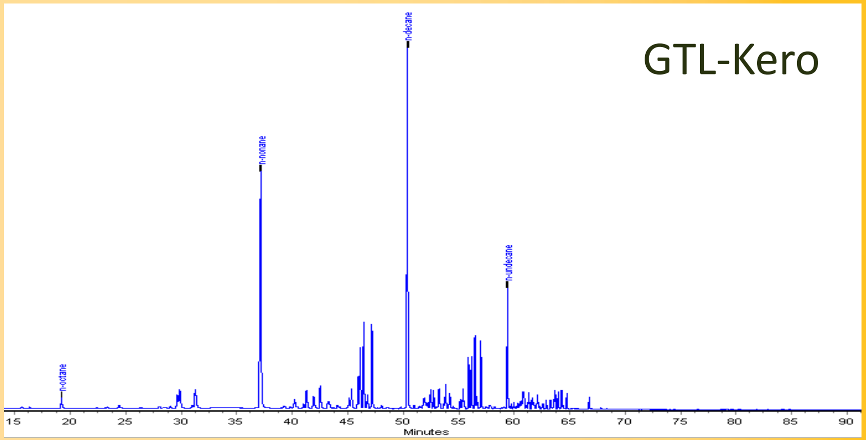
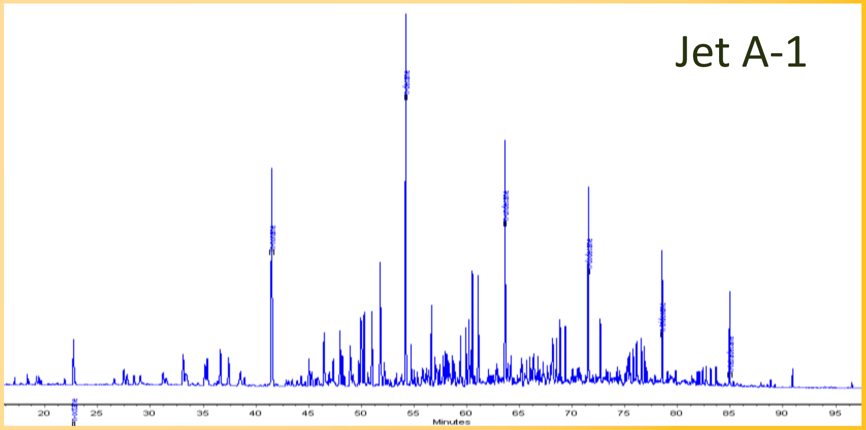
Hydrocarbon Groups

Group	Structure
normal-Paraffins	
iso-Paraffins	
Naphthenes (cyclo-Paraffins)	
mono-Aromatics	
di-Aromatics	
Naphthenic-mono-Aromatics	





Building Blocks

Hydrocarbon	Density (g/mL)	Freezing Point (°C)	Boiling Point (°C)	Flash Point (°C)	Net Heat
(n-) Octane					++
(n-) Decane					++
(n-) Undecan					+
(n-) Hexadeca					+
(Cyclo-) Deca					-
(Ar-) Toluene					-
(Ar-) P-Xylene					-
(Cyclo Ar-) Tetralin	970	-35.8	206	77	--
(Di Ar-) Naphthalene	1140	80.26	218	87	--

Figure 4.4 Table from Chevron's Aviation Fuels Technical Review

Potential Contribution* of Each Hydrocarbon Class to Selected Jet Fuel Properties
(For hydrocarbons in the jet fuel carbon number range)

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

* "+" indicates a beneficial effect, "0" a neutral or minor effect, and "–" a detrimental effect.

ASTM D1655 & D7566

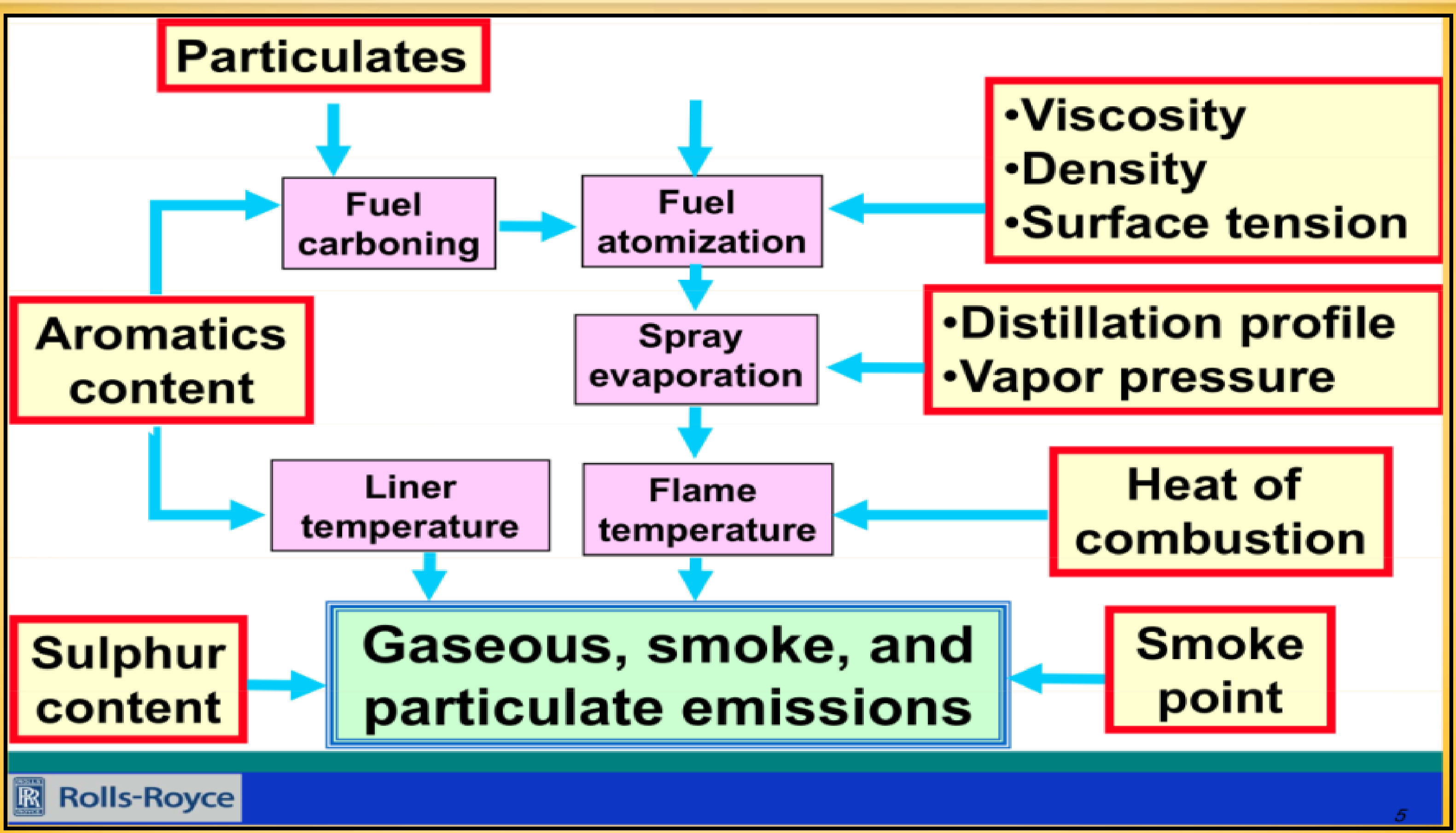
TABLE A1.1 Detailed Batch Requirements; Fischer–Tropsch Hydroprocessed SPK[A]

Property		FT–SPK	ASTM Test Method[B]
COMPOSITION			
Acidity, total mg KOH/g	Max	0.015	D3242
VOLATILITY			
Distillation—both of the following requirements shall be met:			
1. Physical Distillation			D86[C]
Distillation temperature, °C:			
10 % recovered, temperature (T10)	Max	205	
50 % recovered, temperature (T50)		report	
90 % recovered, temperature (T90)		report	
Final boiling point, temperature	Max	300	
T90-T10, °C	Min	22	
Distillation residue, %	Max	1.5	
Distillation loss, %	Max	1.5	
2. Simulated Distillation			D2887
Distillation temperature, °C:			
10 % recovered, temperature (T10)		report	
50 % recovered, temperature (T50)		report	
90 % recovered, temperature (T90)		report	
Final boiling point, temperature		report	
Flash point, °C	Min	38[D]	D56 or D3828[E]
Density at 15°C, kg/m³		730 to 770	D1298 or D4052
Freezing point, °C	Max	−40	D5972, D7153, D7154, or D2386
Thermal Stability (2.5 h at control temperature)			
Temperature, °C	Min	325[F]	D3241
Filter pressure drop, mm Hg	Max	25[G]	
Tube deposit rating less than		3[H] No peacock or abnormal color deposits	
ADDITIVES			
Antioxidants, mg/L[I]	Min	17	
	Max	24	

COMPOSITION
Acidity, total mg K
1. Aromatics, vol %
2. Aromatics, vol %
Sulfur, mercaptan,
Sulfur, total mass
VOLATILITY
Distillation tempera
10 % recovered,
50 % recovered,
90 % recovered,
Final boiling poi
Distillation residue
Distillation loss, %
Flash point, °C
Density at 15°C, k
FLUIDITY
Freezing point, °C
Viscosity −20°C, m
COMBUSTION
Net heat of combu
One of the followir
ments shall be
(1) Smoke point
(2) Smoke point
Naphthalene
CORROSION
Copper strip, 2 h a
THERMAL STABIL
(2.5 h at control te
Filter pressure d
Tube deposi
CONTAMINANTS
Existent gum, mg/
Microseparometer,
Without electrica
With electrical c
ADDITIVES
Electrical conducti

thod[B]
, D4294, or D5453
G
52
, D7154, or D2386
, or D4809

Property Interlinks



Courtesy of Dr. John Moran from Rolls-Royce

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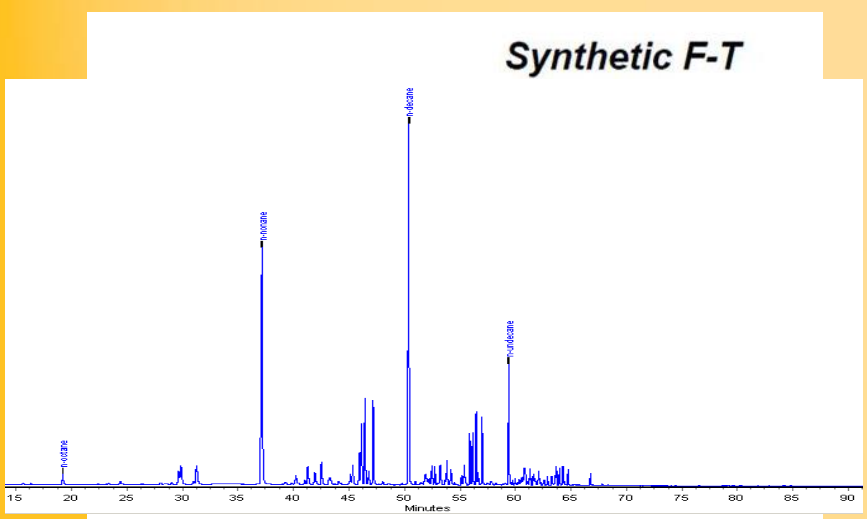
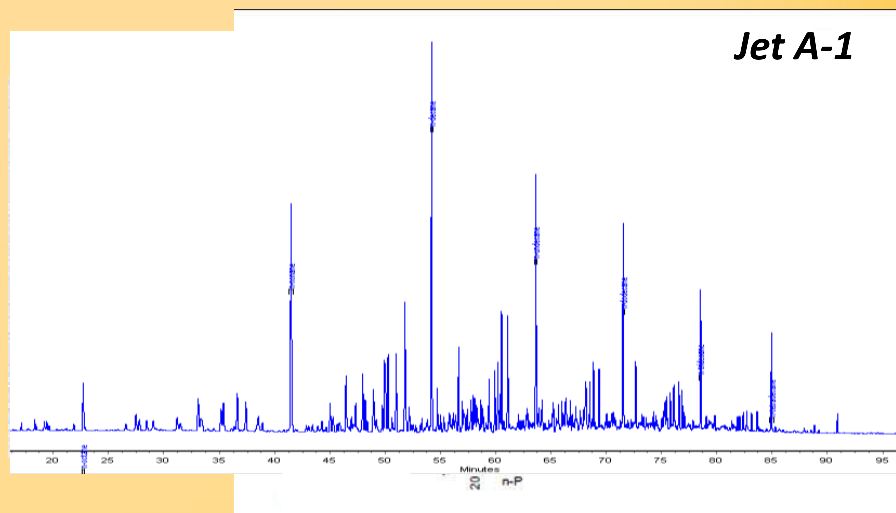
Hydrocarbon Groups

Species & carbon number distribution in a conventional jet fuel (Jet A-1) versus a GTL Synthetic Paraffinic Kerosene (SPK) .





*GCxGC data provided by Shell

Blending

The Blends were made using 3 pure solvents, representing three paraffinic composition classes:

***normal*-paraffin:** ***n*-decane**
***iso*-paraffin:** **Sol-T**
***cyclo*-paraffin:** **Decalin**

However, initially some blends were made using other solvents such as (D60, D70, DSC, SPK). Unlike the pure solvents these have a broad carbon spread.

Terminology:

Pure Axis Blends:

All blends made using only pure solvents on ends of axis (i.e. *n*-decane)

Mixed Solvent Blends:

Certain blends were made with mixed solvents (i.e D60)

Solvent	Composition (%)			Carbon Range	Main Carbon Number
	n-paraffin	*i*-paraffin	*cyclo*-paraffin		
SPK	43.4	55.7	0.84	8 - 13	10 (41%)
D-60	23.52	26.74	49.74	10 - 14	11 (55%)
D-70	24.5	27.83	47.68	10 - 16	12 (27%)
DSC	24.88	29.21	45.91	10 – 13	11 (75%)

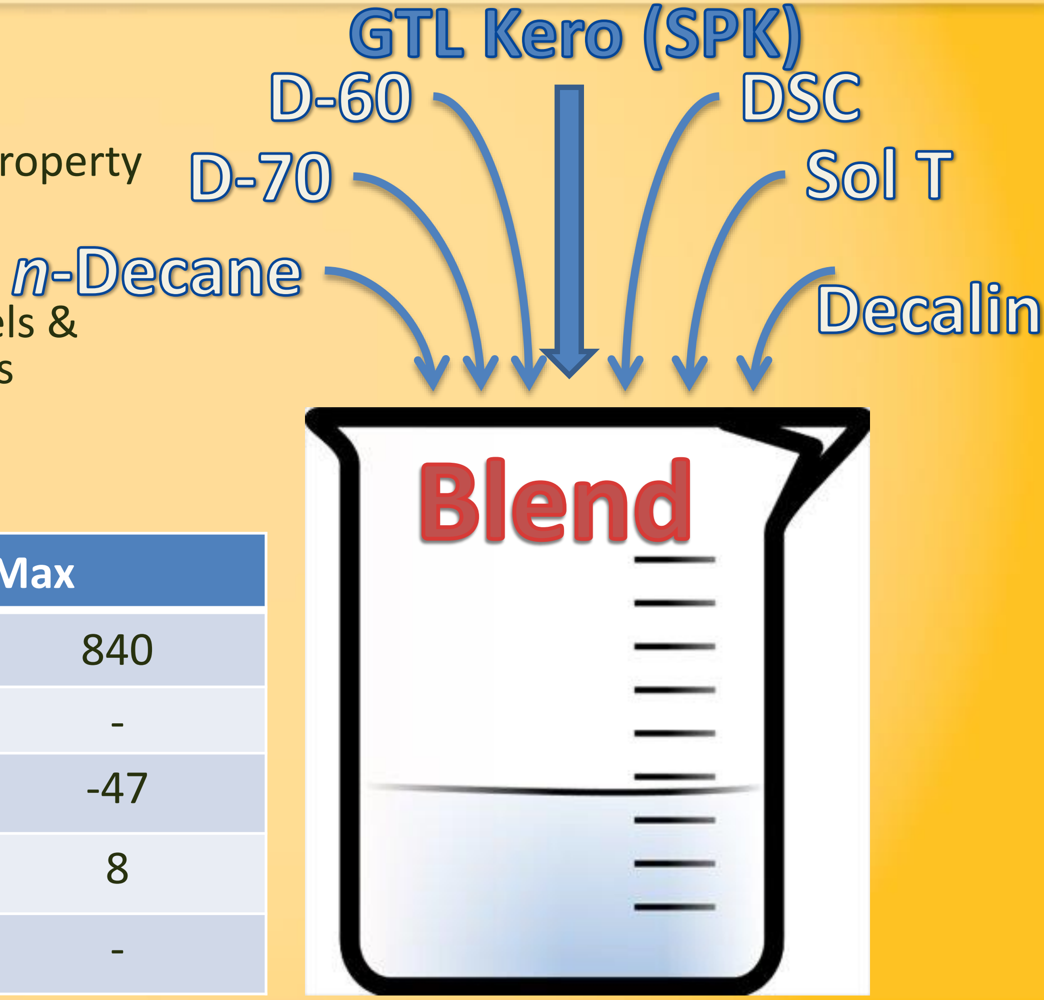
Broad cut (SPK, D-60)

Narrow cut (D-70)

Experimental

Objectives:

- To develop correlation between the property and the hydrocarbon structure
- Blending of SPK with conventional fuels & solvents to alter its physical properties

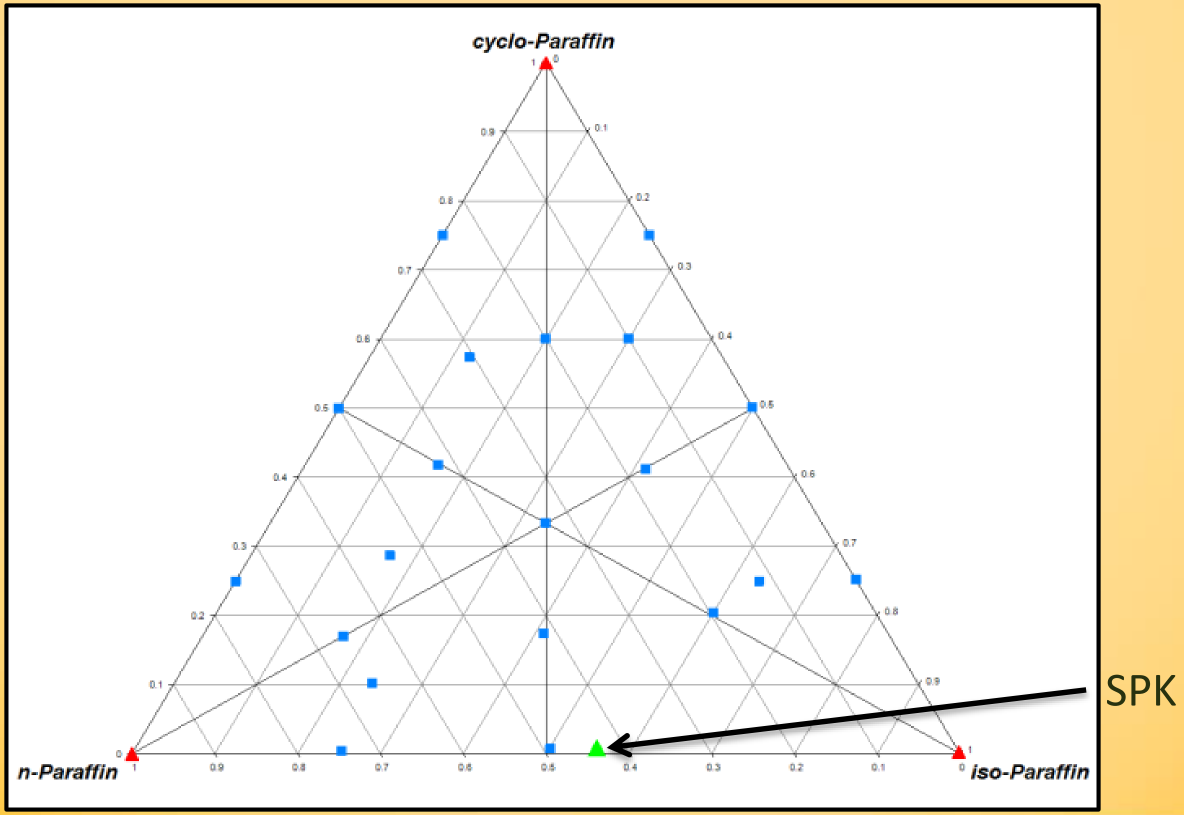


ASTM D1655 Property Limits

Property	Min	Max
Density (g/L)	775	840
Flash Point (°C)	38	-
Freezing Point (°C)	-	-47
Viscosity @ (cSt)	-	8
Heat Content (MJ/Kg)	42.8	-

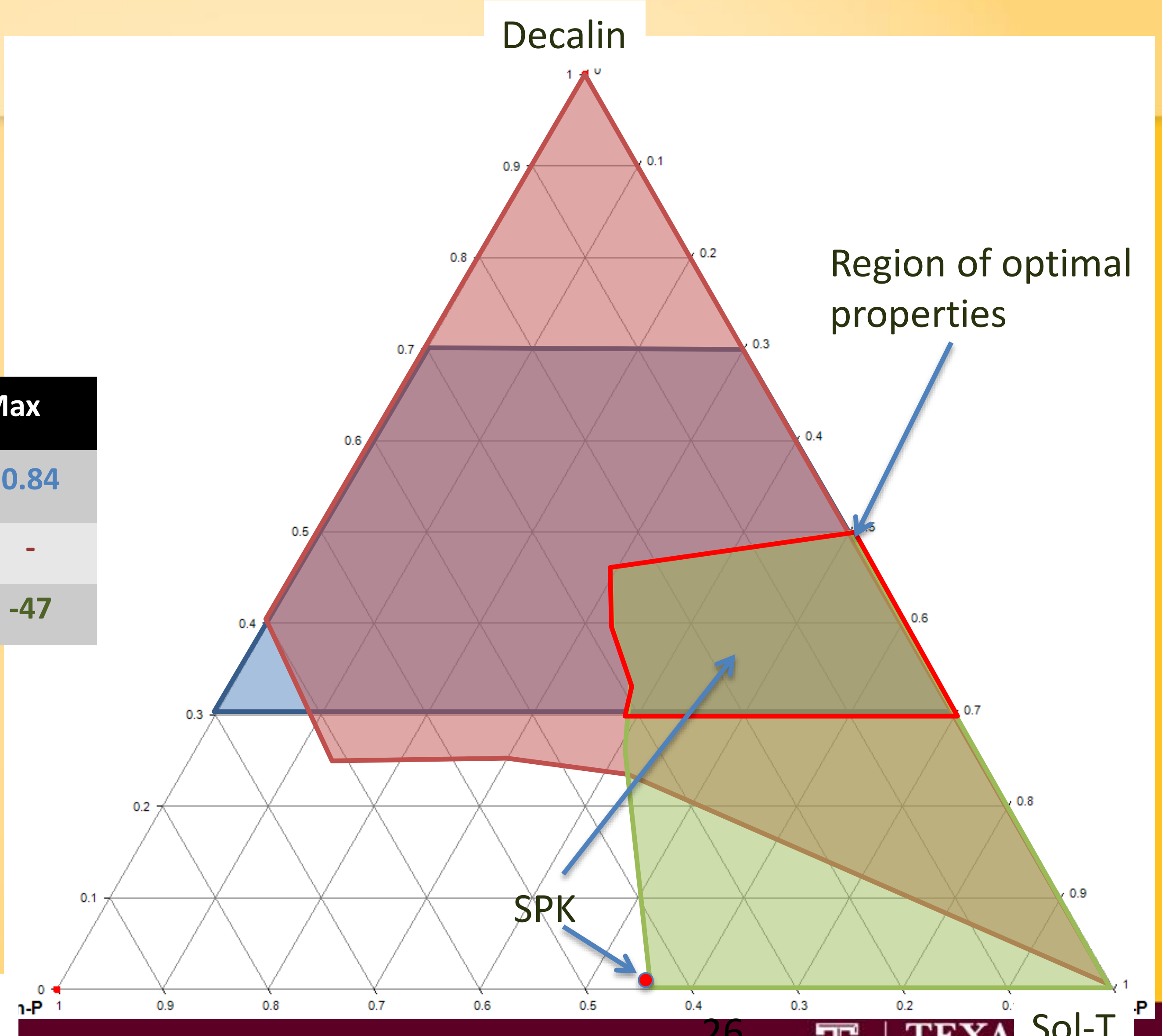
Blend Formulation

- 21 Blends were formulated, chosen compositions were to provide a large spread across the ternary diagram:

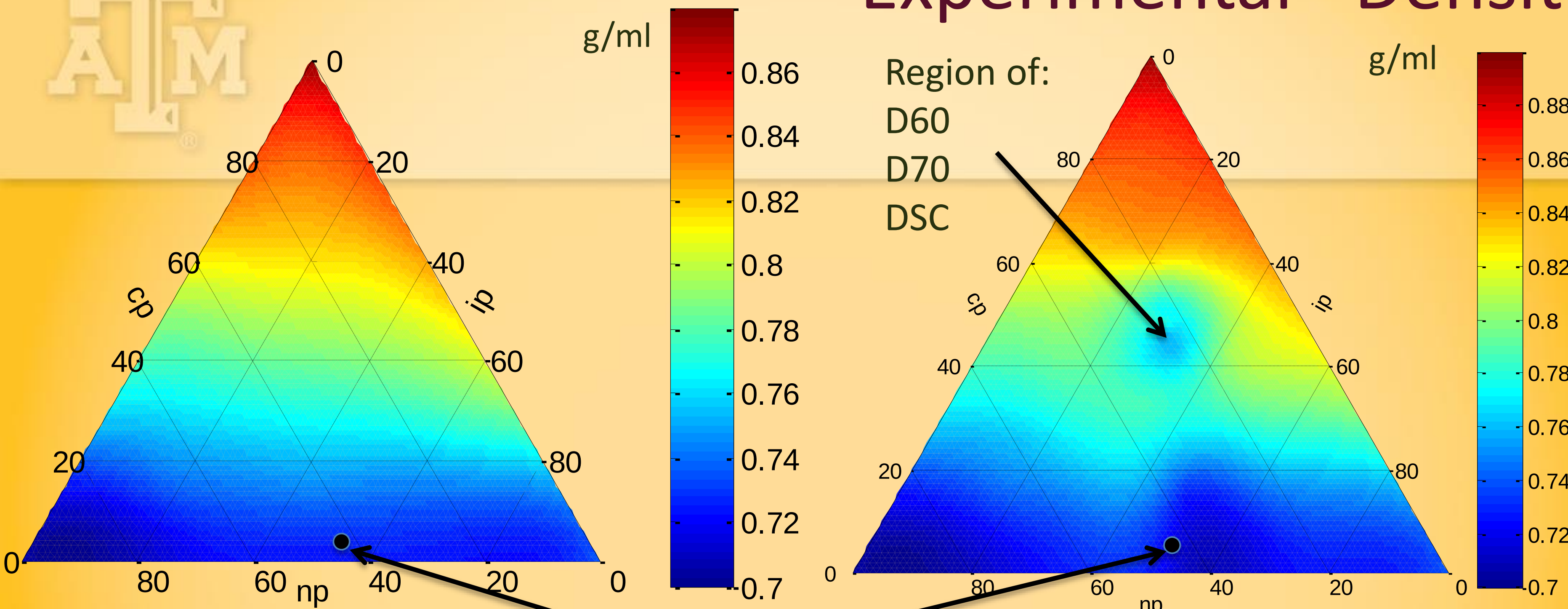


Initial Assessment

Property	Min	Max
Density (g/ml)	0.775	0.84
Flash Point (°C)	38	-
Freezing Point (°C)	-	-47



Experimental - Density



Pure Axis Blends

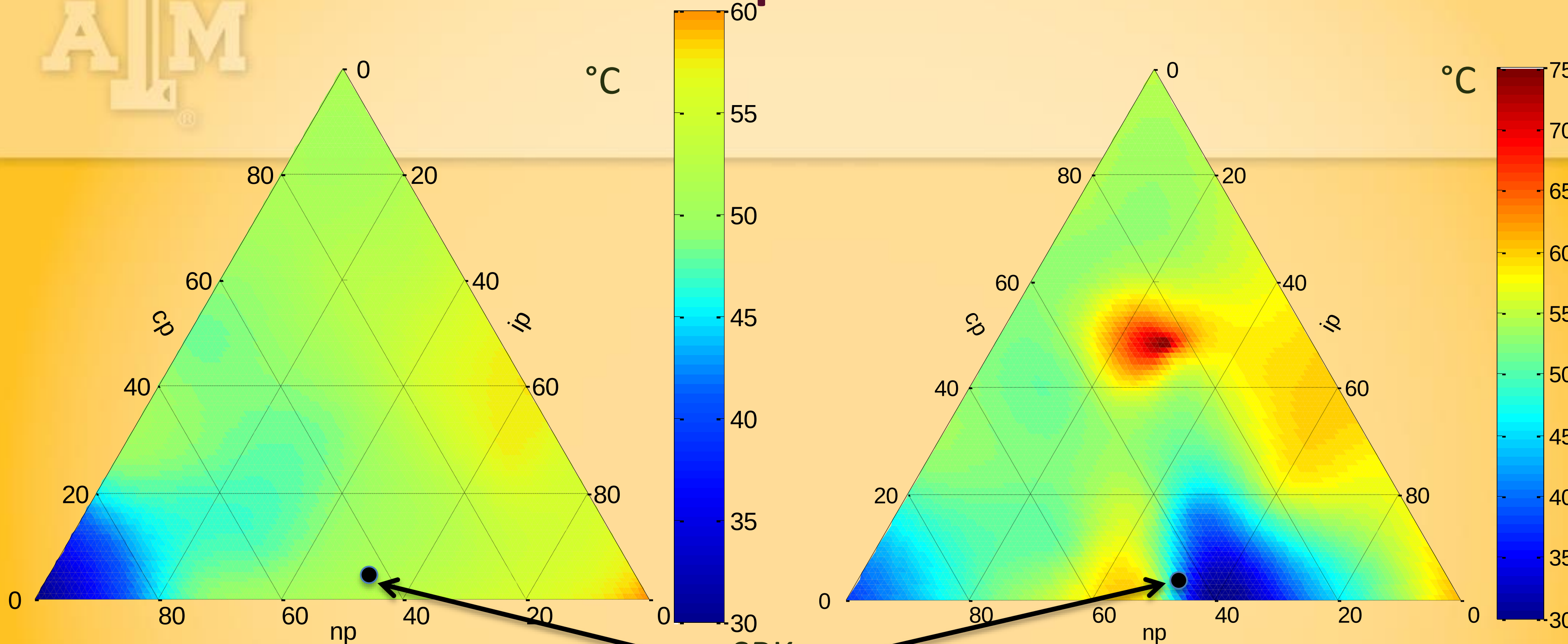
Mixed Solvent Blends

- <u>**Density Results**</u>
  - Strongly linear results observed
  - Density strongly effected by the cyclo-paraffin composition
  - *normal*- and *iso*- paraffins have low densities, less than the aviation requirements

When including blends made with other solvents:

- Linear results still observed
- No significant changes to the results
- Indicates that the density is not strongly influenced by carbon number

Experimental - Flash Point

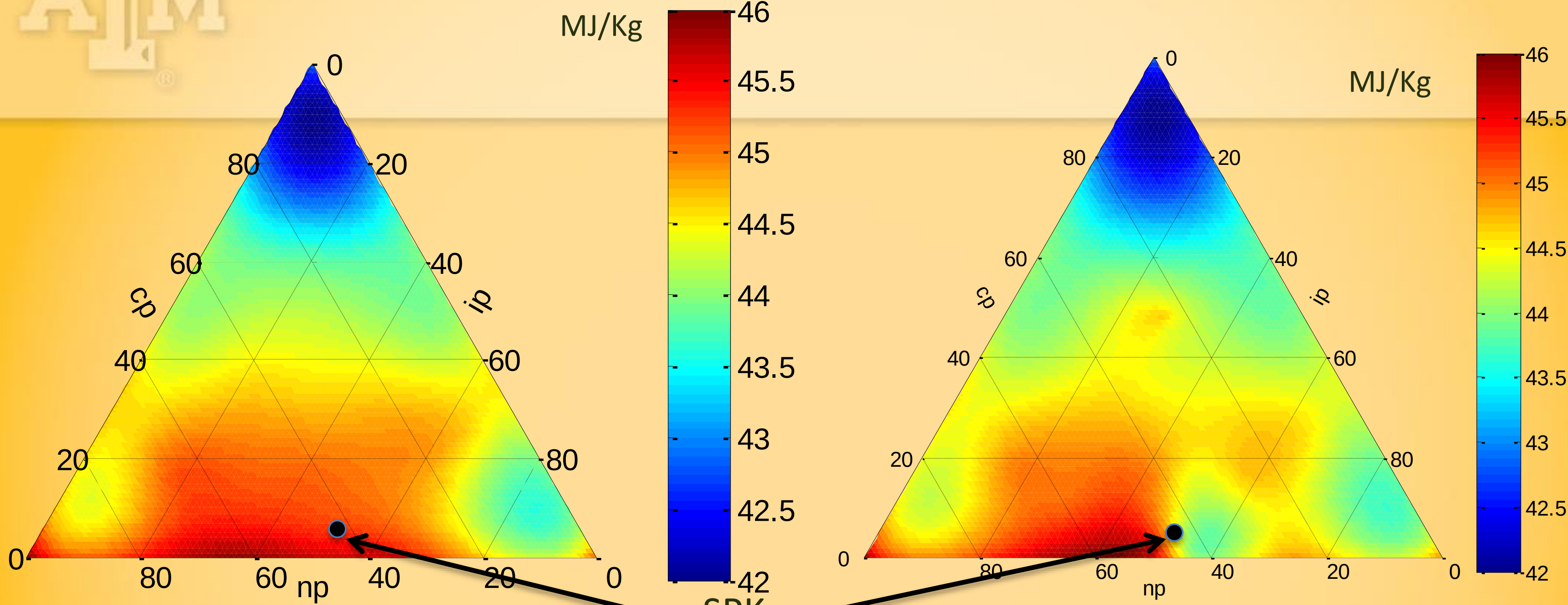


Pure Axis Blends

Mixed Solvent Blends

- **Flash Point Results**
  - Relatively linear results observed
  - All of points meet the target flash point of 38 °C
- Carbon number influence of the different solvents is notable
- The SPK sample has a lower flash point than the pure axis blends

Experimental - Heat Content



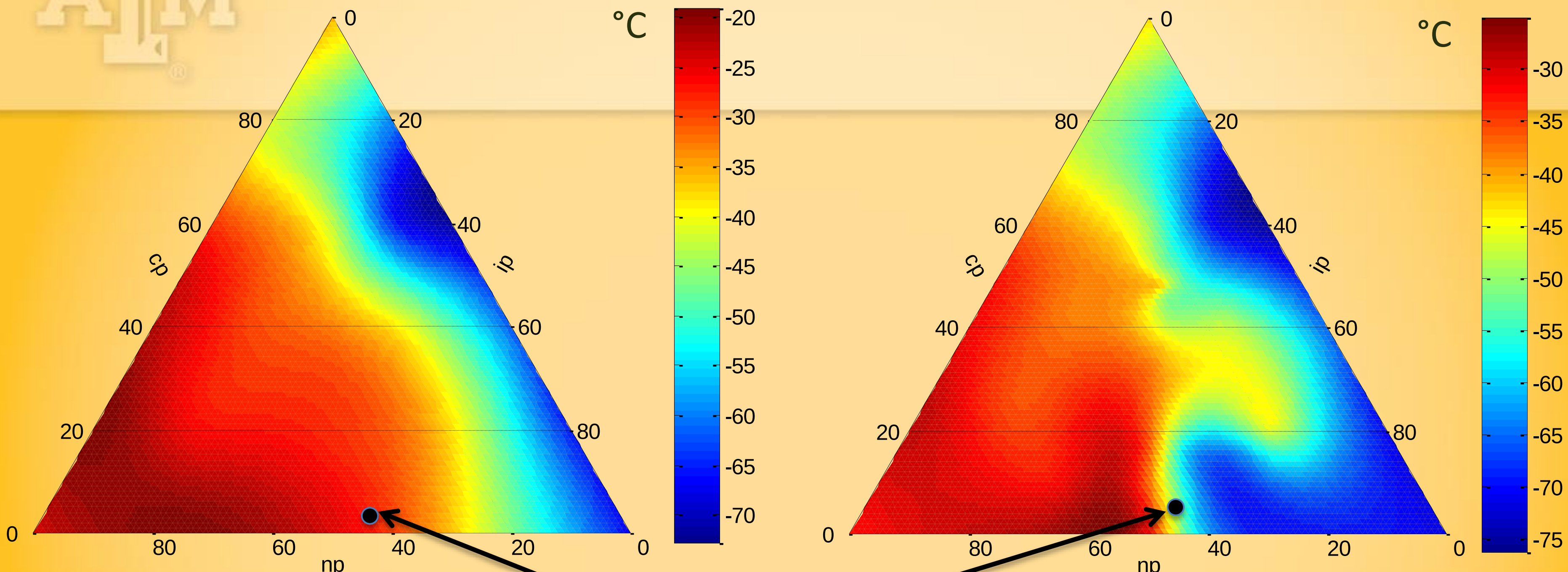
Pure Axis Blends

Mixed Solvent Blends

- **Heat Content Results**
  - Mainly Linear Results observed
    - Along the *iso*-paraffin axis there appears to some non-linearity
  - All areas meet the jet fuel limits for heat content

- The results remain relatively the same with the inclusion of the mixed solvent data
- This indicates that heat content is not greatly effected by the carbon number, but more so by the structure

Experimental - Freezing Point



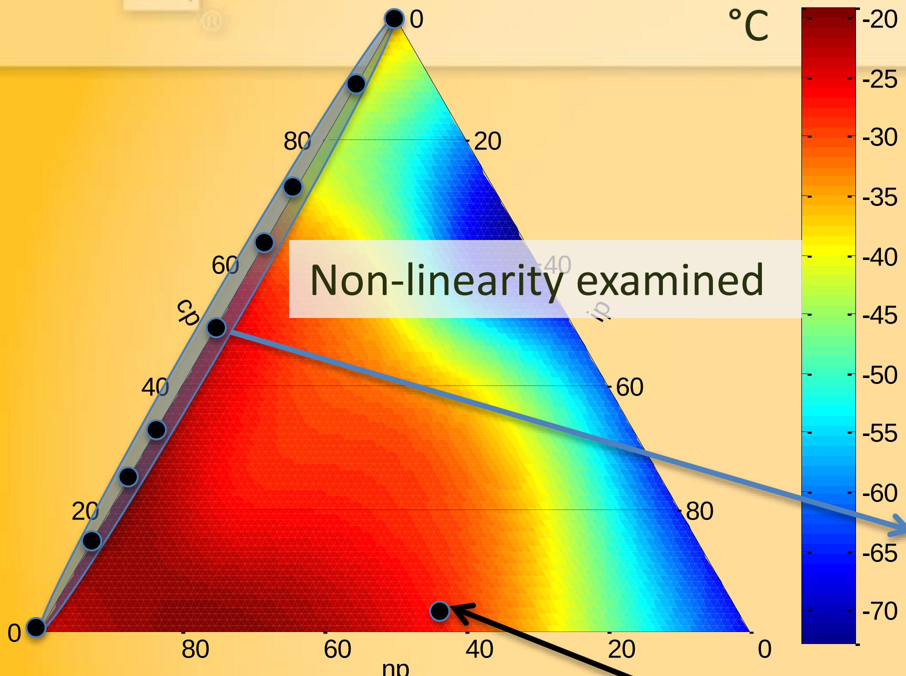
Pure Axis Blends

SPK

Mixed Solvent Blends

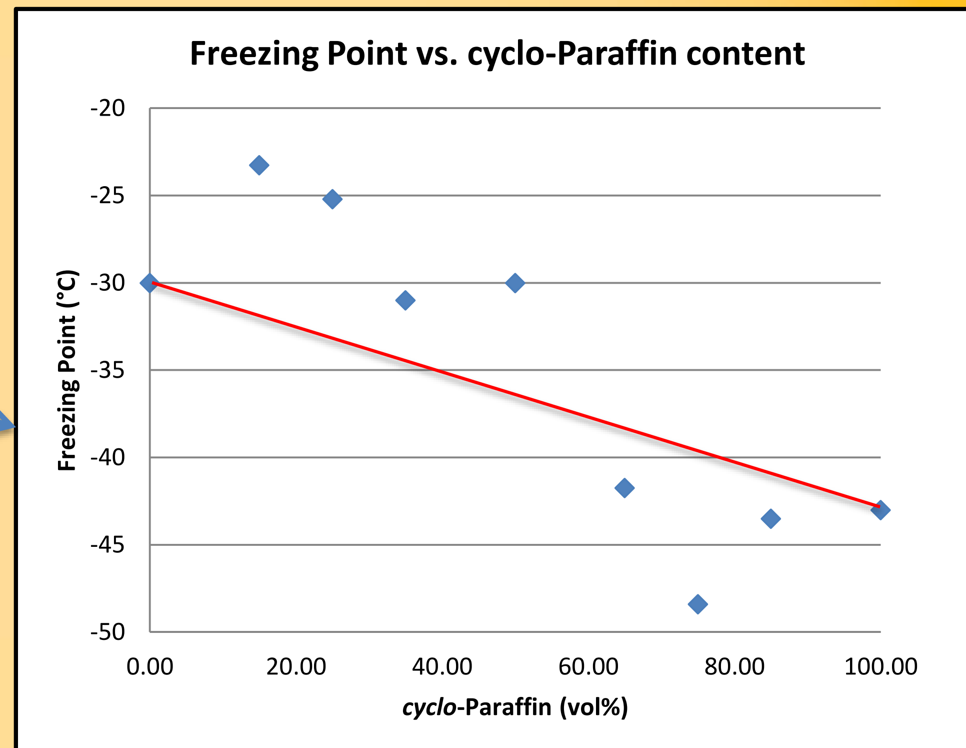
- The use of other solvents causes significant changes in the freezing point
- This indicates that carbon number may have a larger influence on the freezing point than previously discussed

Results – Freezing Point



Pure Axis Blends

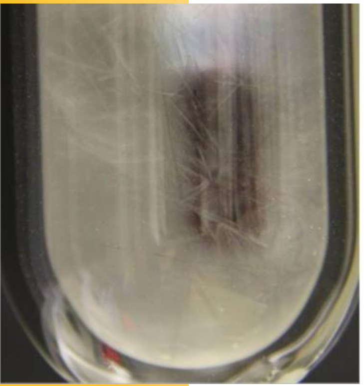
SPK



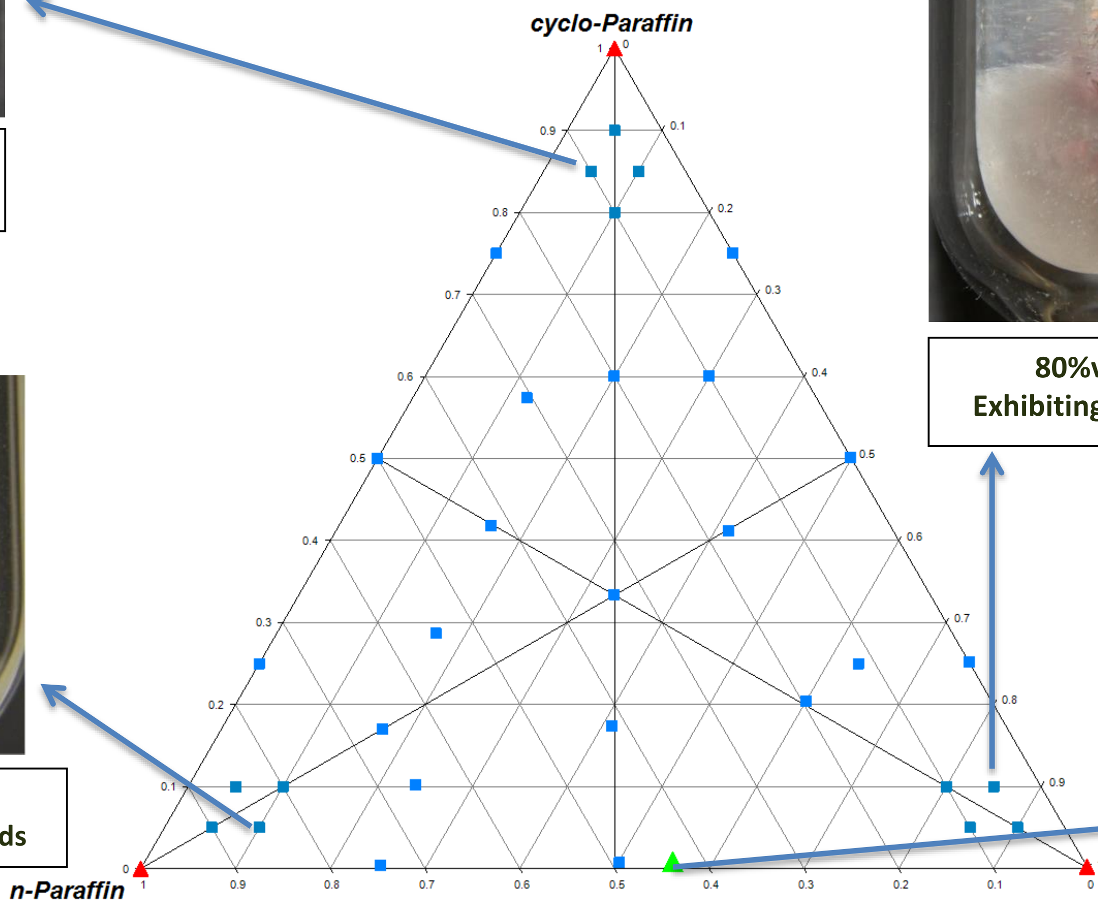
- **Freezing Point Results**
  - Non-linear results observed
  - Red areas represent warmer freezing points (-30)
  - Blue areas represent cooler freezing points (-70)

Crystallization Images

85%v/v *cyclo-*
Exhibiting fine crystals



85%v/v *normal-*
Exhibiting fine & clear rods

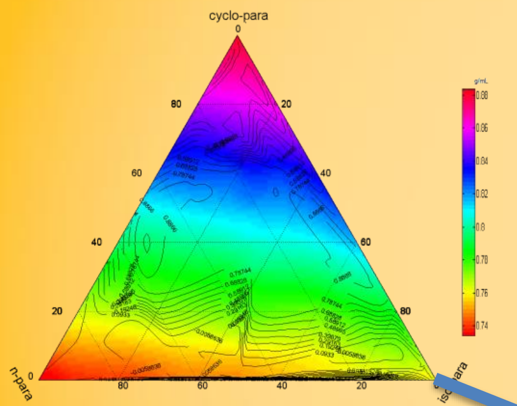


80%v/v *iso-*
Exhibiting a hazy mix

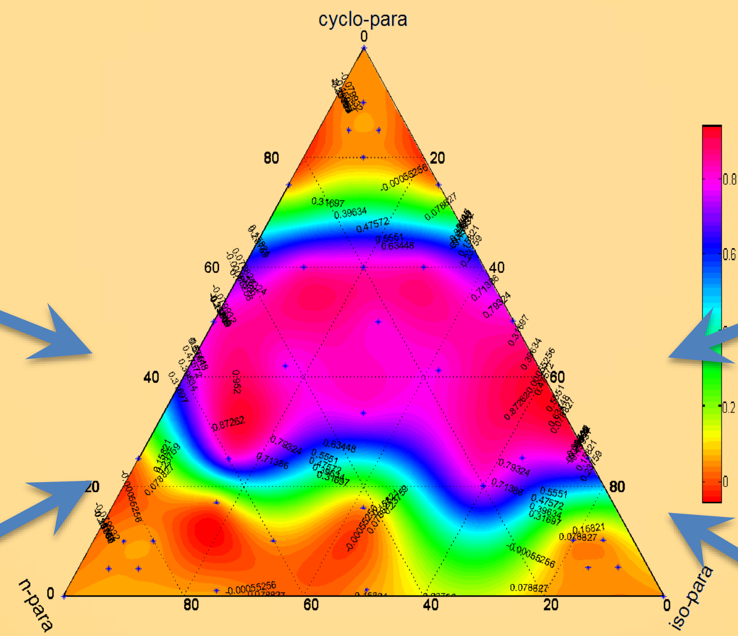
SPK (GTL-Kero)
Exhibiting a cottony haze

Region of Optimum Properties

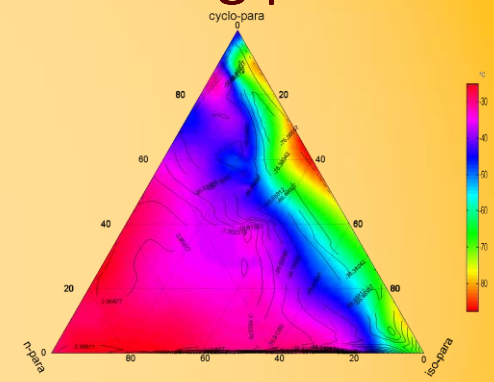
Density



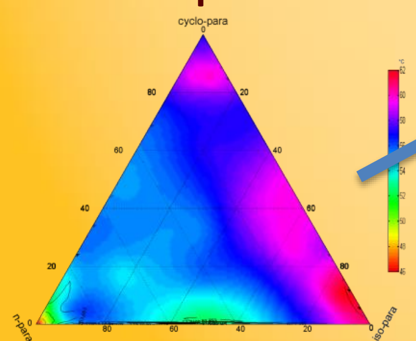
Overlap



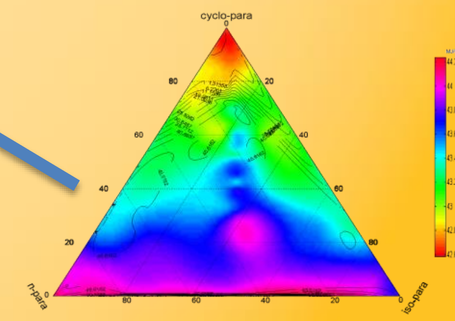
Freezing point



Flash point



Heat content



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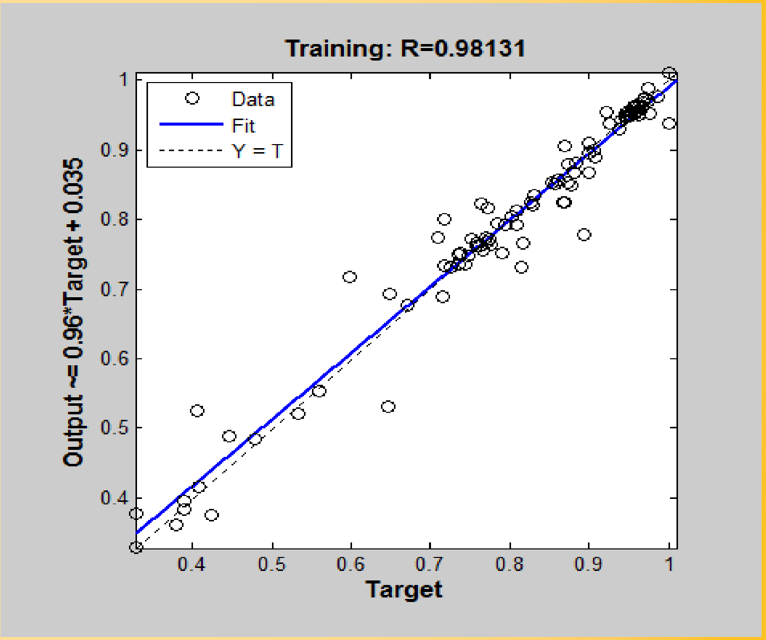
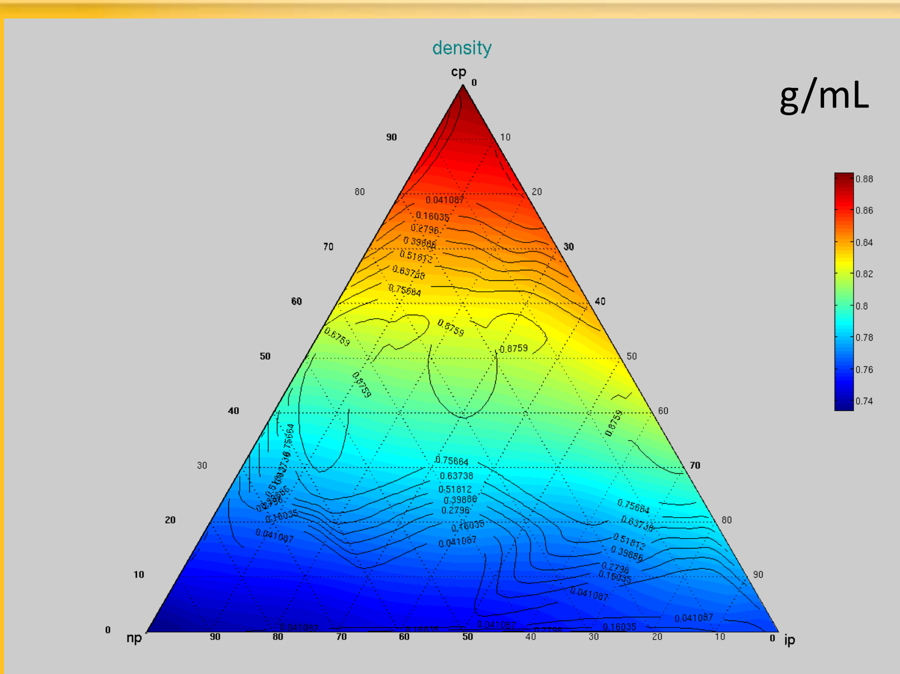
Artificial Neural Network

- Neural network analysis is used to develop a link between input and output values.
- In this study the input values are the 3 compositions, and the output values are the properties.
- The network developed was trained using the results from experimental data.
- The network was able to make strong linkages between the inputs and outputs for most of the properties.

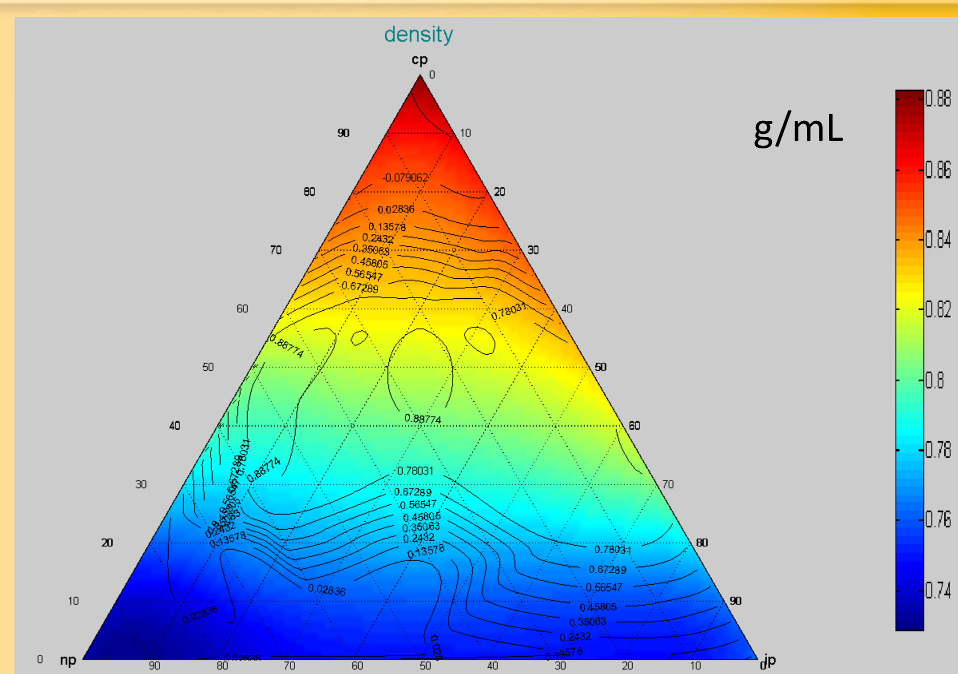


Neural Network Regression

Results - Density



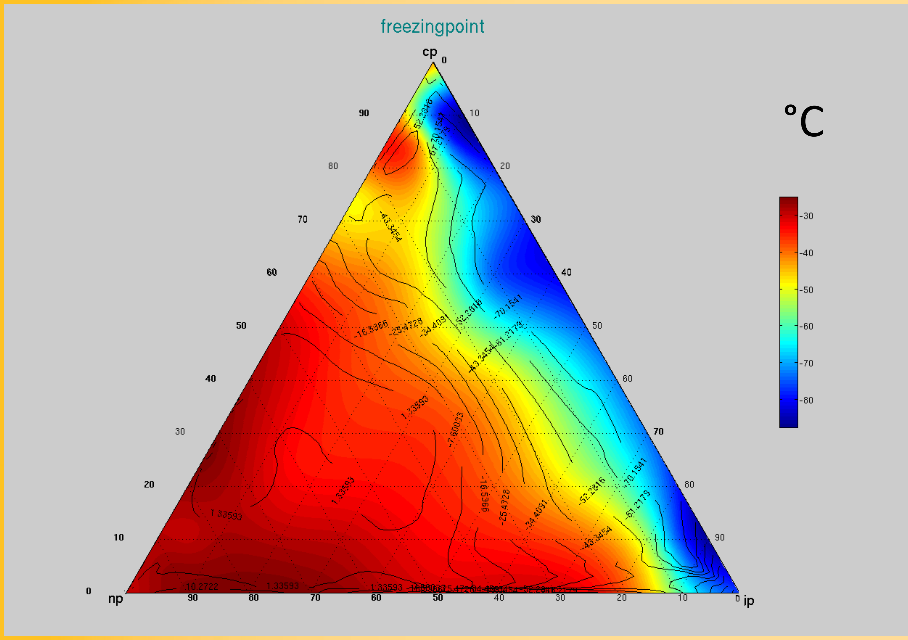
Experimental Results



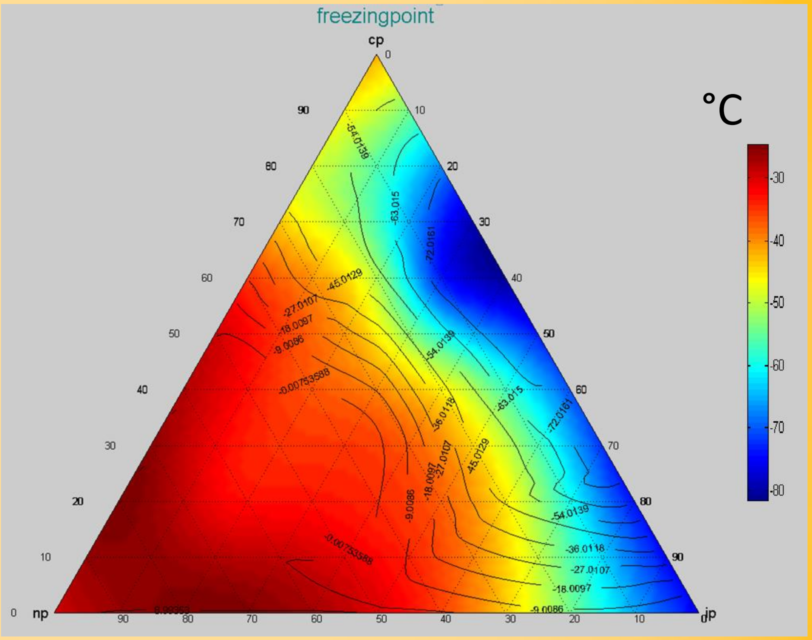
Neural Network Results

Density Results: ANN shows excellent predictability

Results – Freezing Point



Experimental Results



Neural Network Results

Freezing Results: ANN shows excellent predictability

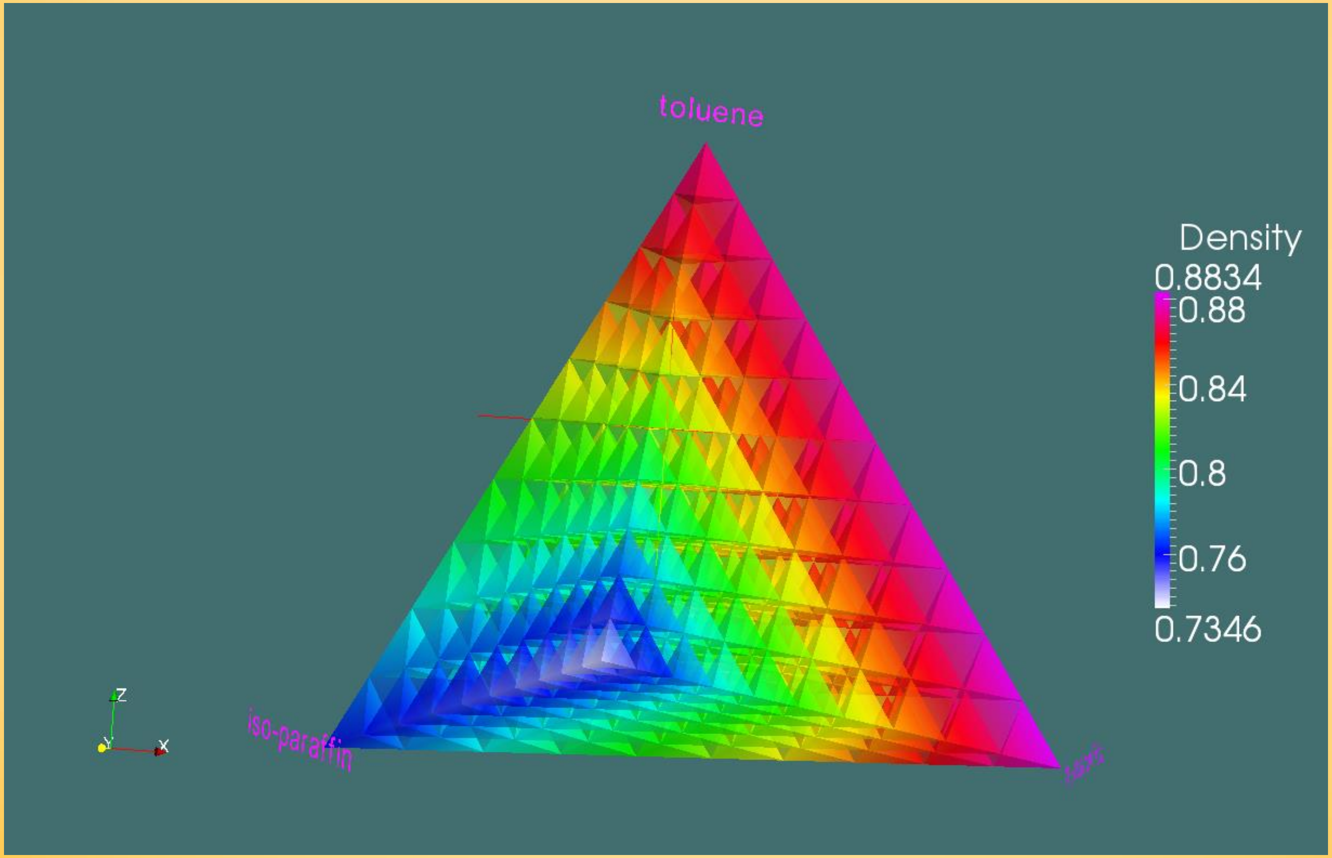
Visualization

3-D visualization supports two types of analysis:

- ❑ Surface or area analysis (2-D analysis of the four surfaces of the pyramid)
- ❑ Depth or volumetric analysis (3-D analysis or “slices” within the pyramid)

Both are unique analysis tools, with the 3-D pyramid being crucial in incorporating extra inputs.

3-D Visualization



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Summary

- It has been empirically demonstrated that it is possible to predict key physical properties of a fuel, given its building blocks.
- For the lab scale, replacement or swapping of certain molecular structures with carbon length is a viable option in order to boost certain properties or lower the negative impact of others.
- The visualization techniques developed make it easier to isolate regions of interest for a given blend.

Future Work

- The methodology and the programing developed as the outcome of this contentious research is being extended to look at different synthetic fuel compositions of different carbon numbers (Gasoline & Diesel fractions).

- Collaborations with centers of computational expertise (DTU, TAMU) are yielding good early results in terms of fuel property predictions.

- TAMUQ FCL is actively engaged in database building and archiving for various fuel cuts, blending compounds, and additives.

Acknowledgements

Dr. Nimir Elbashir

Prof. Iqbal Mujtaba

Mr. Mansoor Al-Shamri

Funding:

الصندوق القطري لرعاية البحث العلمي
Qatar National Research Fund
Member of Qatar Foundation

Thank you for your attention!

Questions?

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CHEMICAL ENGINEERING PROGRAM

336F Texas A&M Engineering Building
Education City
PO Box 23874
Doha, Qatar

Tel. +974.4423.0017
Fax +974.4423.0065

chen@qatar.tamu.edu

http://chen.qatar.tamu.edu