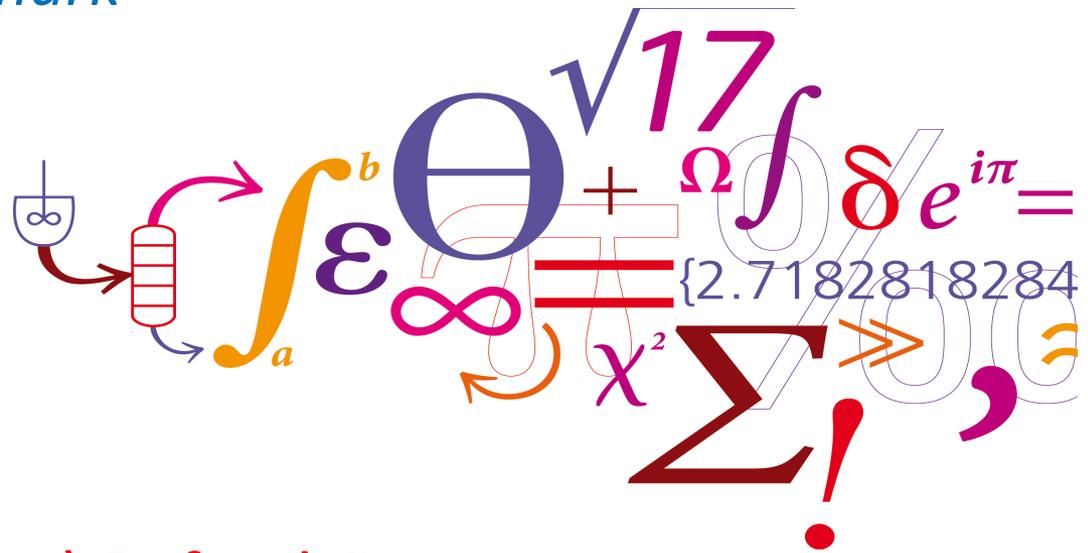


# Computer Aided Design of Complex Products/Fluids And Application to Fuels

Georgios M. Kontogeorgis

*Center for Energy Resources Engineering (CERE) & KT-Consortium  
Department of Chemical and Biochemical Engineering  
Technical University of Denmark*



Big thanks to Professor (ret.) Rafiqul Gani,  
"guru" in this field and his PhD. students (N. Yunus, S. Kalakul)

# Outline

- CERE and KT-Consortium – short introduction
- What is Computer Aided (Product, Molecule, Blend) Design (CAPD)
- Role of Databases (“Big Data”), Property Models and Sustainability
- Two Case Studies on fuels design (gasoline and jet-fuel)
- Outlook to the future

# In brief – two centers/consortia

- CERE – a DTU center (faculty and researchers from 5 Departments) in the areas of energy (petroleum engineering, biofuels), CCS and related fields
- KT-Consortium – a KT unit across two centers focusing on dissemination of results in process design, simulation – broader PSE
- Diverse disciplines involved esp. thermodynamics, separation and process design, mathematical modeling, geosciences
- Both have industrial consortia in energy, chemistry and biotechnology areas with annual (discussion) meetings

# CERE Consortium 2018 (22)

Schlumberger



MAERSK  
OIL

AkzoNobel



NEPTUNE  
ENERGY

Welltec®



NATIONAL  
OILWELL  
VARCO



MOLGROUP  
THINK. CREATE. MOVE.

ConocoPhillips

ExxonMobil



UNION  
ENGINEERING

Reliable solutions by dedicated people

# KT Consortium Members – 2018 (16)



AVEVA



ARKEMA  
INNOVATIVE CHEMISTRY



syngenta



Firmenich

AstraZeneca



novozymes

MITSUBISHI  
CHEMICAL

NESTE



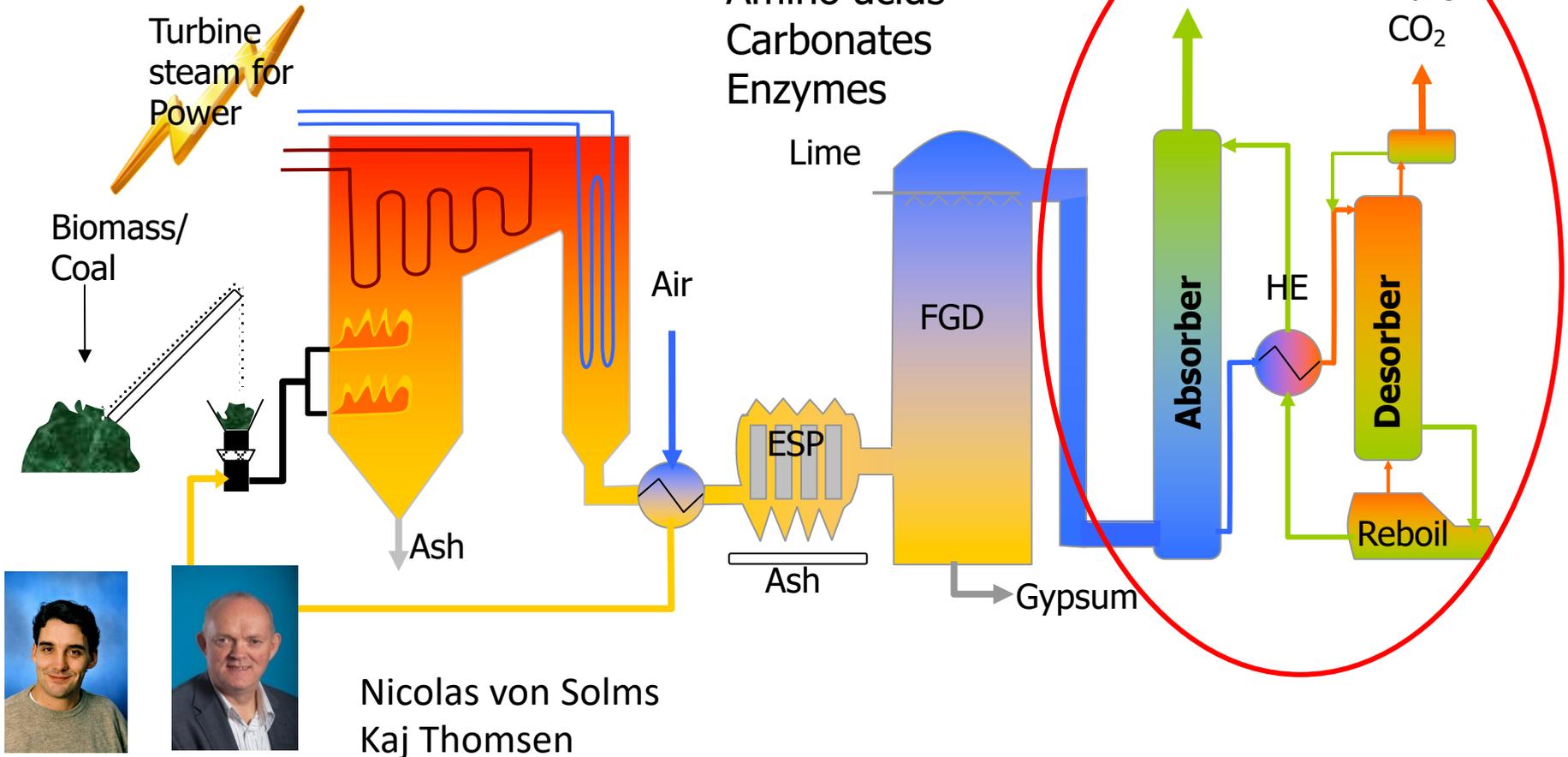
# Post-combustion CO<sub>2</sub> capture



Philip Fosbøl

## Various Solvent Possibilities

- Alkanolamines – mixed amines
- Chilled Ammonia
- Ionic liquids
- Amino acids
- Carbonates
- Enzymes



# Complex Chemical Products

- Chemicals based products are made from a collection of chemicals, which meet specific needs of product functionality and utility.
- Nowadays, more than 70,000 chemicals based products are used in the modern society for its survival



# Chemical Product Design Framework

Problem Definition

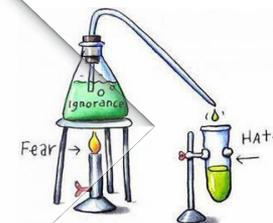
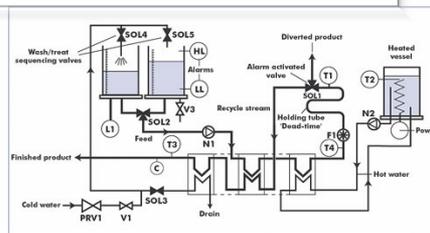
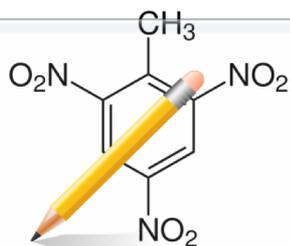
Databases/Models/Algorithms

Experiments

Needs and Targets

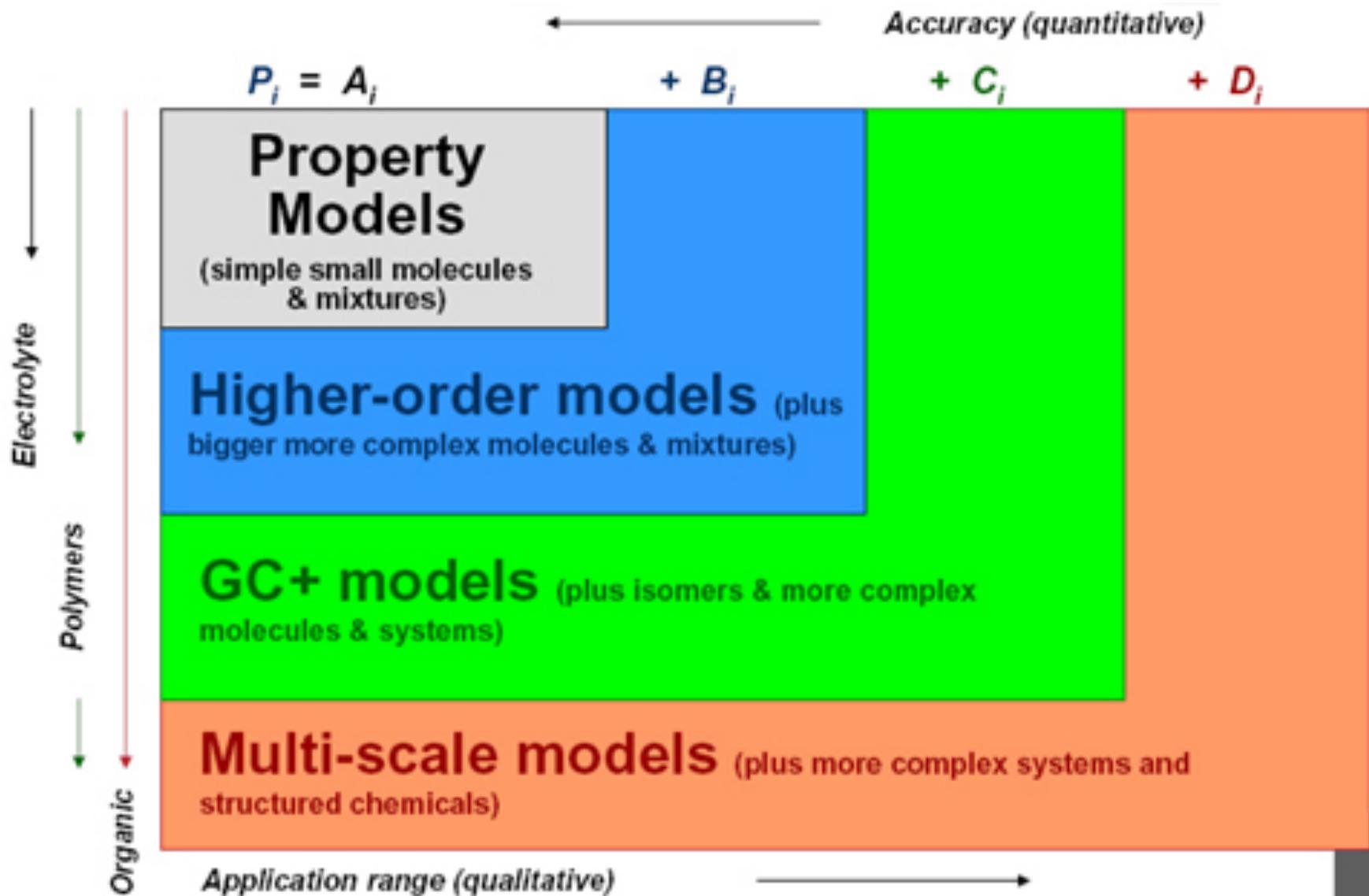
Chemical Product-  
Process Design

Validation

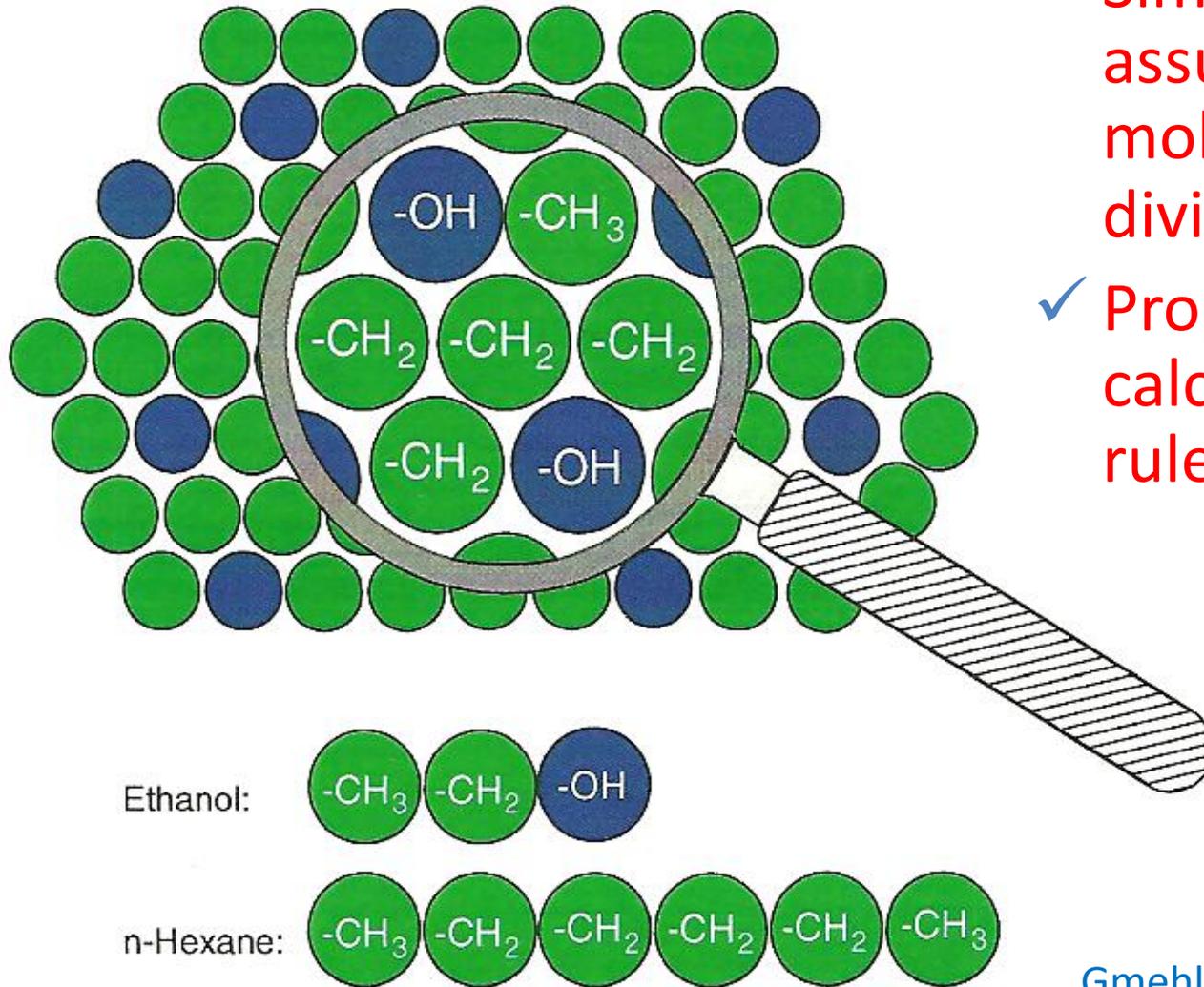


A Computer Framework to ASSIST the design of complex products, molecules, blends,...  
Propose solutions using a Knowledge-base system – to validate with experiments at the end

# Various levels of property models



# The group contribution concept



- ✓ Simple principle: We assume that molecules are divided into groups
- ✓ Properties are then calculated by additive rules

FIGURE 4. Solution of groups-concept.

Gmehling, 2009,  
J.Chem.Thermodynamics,41:731

# CAMD for product design

CAMD can be described as “Reverse Property Prediction”

## Property prediction:

### Given:

Information on compound structure.

### Obtained:

Properties of the compound.

## CAMD:

### Given:

Information on desired properties & type of compound.

### Obtained:

Compound structures having the desired properties.

# CAPD/CAMD studies at DTU

Year	PhD Thesis	Products
2000	Peter Harper	Mixture/Solvent design
2009	Kavitha Satyanarayana	Polymer Design
2010	Elisa Conte	Solvent formulations- lotions (hairspray, insect repellent, paint, sunscreen)
2014	Michele Mattei	Emulsified products (hand-wash, tank-cleaning, sunscreen)
<b>2014</b>	<b>Nor Alafiza Yunus</b>	<b>Blends (gasoline, lubricants)</b>
<b>2016</b>	<b>Sawitree Kalakul</b>	<b>Jet-fuel blends Diesel blends</b>
2017	Spardha Jhamb	Chemical Substitution, Paints
2018	Markus Enekvist	Paints



Professor  
Rafiqul  
Gani

Also  
Professors  
K. Gernaey  
J. Woodley

# Formulated Products

*Formulated products* are obtained by mixing selected components together to get the desired product attributes.



Skin Care Creams



Cosmetics



Detergents



Paints



Inkjet Printer Inks



Adhesives

# Fuels - Blended products

## ❖ Design of Jet-fuel blends



## ❖ Design of Diesel Blends

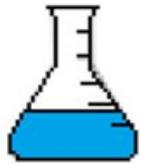
Base Fuel + additives  
(bio-based/renewable sources  
Or diverse chemicals) to enhance  
the quality of base fuel



## ❖ Design of Gasoline Blends

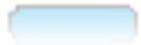


# Chemical Product Design Simulator



## VPPD - Lab

Virtual Product-Process Design Lab

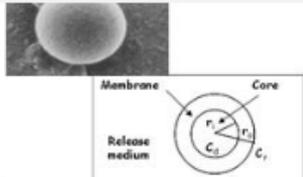


Virtual Product-Process Design Lab

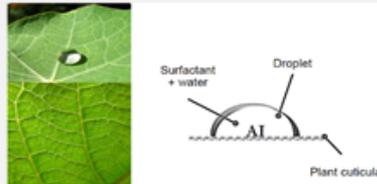
Molecular Design

### Design Templates

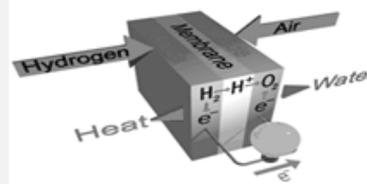
#### Controlled Release



#### Uptake of Pesticides



#### Fuel Cell



#### Formulation



#### Blends



#### Emulsions



Create New Design Template

### Help

Help Documents

Open Solved Example

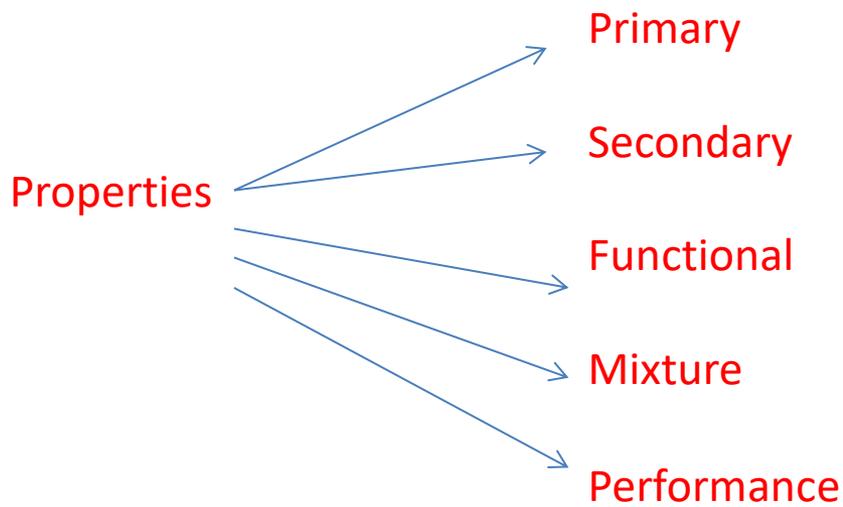
Database Search

### Integrated Tools



# Databases in our software (ICAS/VPPD-Lab)

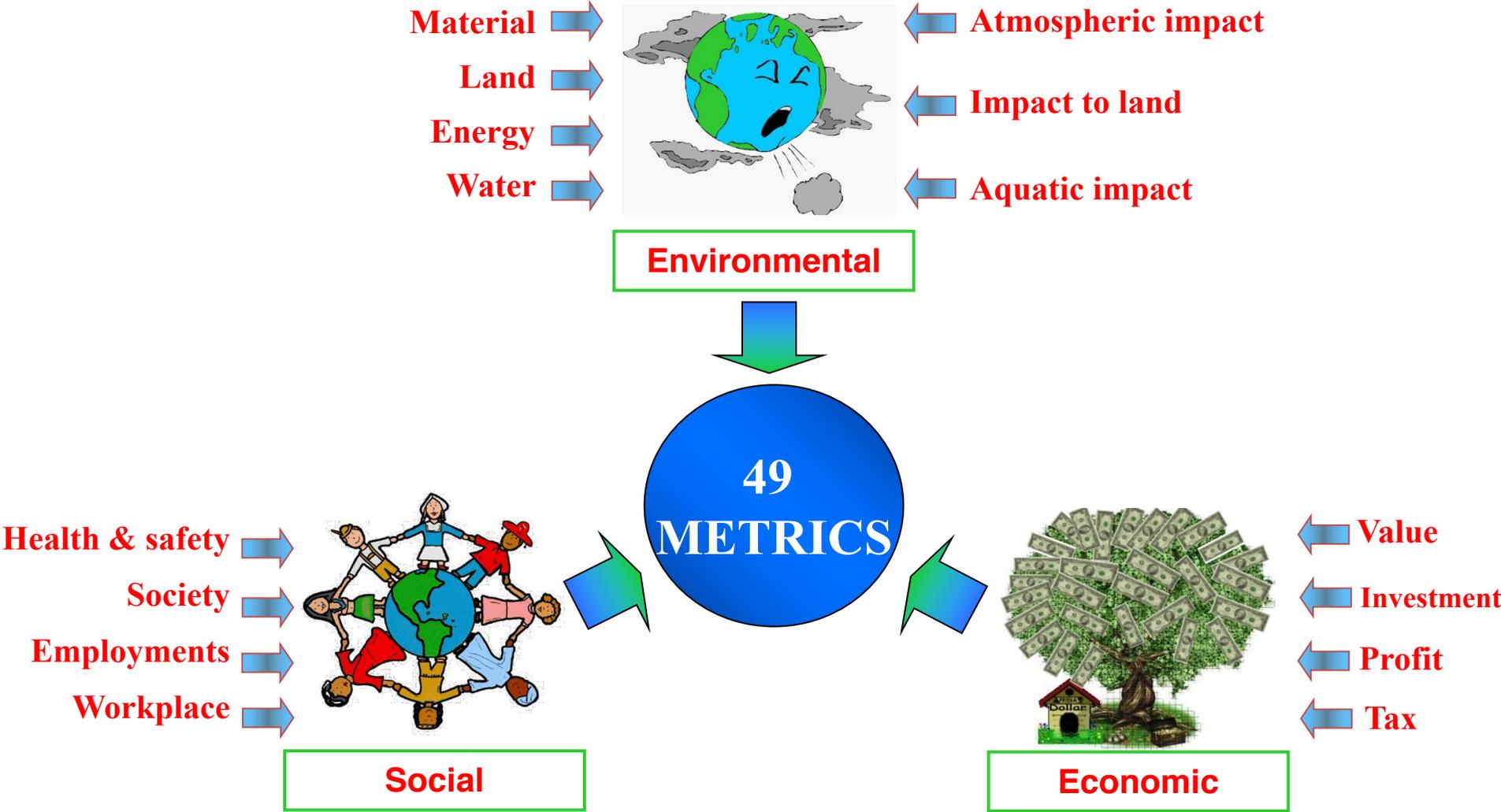
Database	# Compounds	# Properties	Database	# Compounds	# Properties
Combustible compounds (fuel blends)	1725	22	Normal fluids	1664	>60
Lipids	330	25	Polar non-associating	3078	>60
Environmental Compounds	26155	20	Polar associating	2355	>60
Emulsions	472	10	Polymers	23	
Solvents	1350		Electrolytes	124	
Formulations	614	16	Amino acids	104	



# Properties available in ICAS/VPPD-Lab

Type	# Properties	Examples
Primary	"Classical" – critical, transport (about 20) Environmental and combustion (about 50)	Boiling point, BCF, GWP, LC <sub>50</sub> HHV, CO <sub>2</sub> emission in combustion engine, Ozone depletion potential
Secondary	13	Refractive index, Henry's law constant
Functional	14 (depend on T,P)	Viscosity, Evaporation time
Mixture	8 (depend on composition) - Some linear mixing rules - Several non-linear mixing rules	Flash point, distillation curve, RVP
Performance	Solubility check for stability of blends or emulsions Evaporation rate Complex mathematical models	

# Issues: Measure of sustainability



# Property model functions

Many primary properties including environmental and combustion properties

$$f(\mathbf{X}) = \sum_i N_i \mathbf{C}_i + \sum_j M_j \mathbf{D}_j + \sum_k O_k \mathbf{E}_k$$

Examples: Higher Heating Value (HHV) developed by Yunus (2014 PhD thesis)  
GWP, ODP, LC<sub>50</sub>

Fossil-fuel  
Based  
Aviation

$$CO_2E = \frac{44}{12} \sum_i V_i HHV_i C_{content,i} FO_i$$

CO<sub>2</sub> emission in combustion  
engine

Fuels:  
2-3% global  
CO<sub>2</sub> Emission  
(Blakey et al.,2011)

$$P = \sum_i x_i P_i$$

Linear mixing rules

$$RVP = \sum_i x_i \gamma_i P_i^{sat}$$

Reid vapor pressure

$$\sum_i \frac{x_i \gamma_i P_i^{sat}}{P_{i,Tf}^{sat}} - 1 = 0$$

Flash Point

# Case study 1: Gasoline blends

- **Problem statement**

- ✓ The product to be designed is a gasoline blend for car (spark-ignition type) engines to be used in warm climates.
- ✓ Gasoline is the main ingredient in the blends.
- ✓ Other chemicals from renewable and/or non-renewable sources (alcohols, ethers, esters, ketones, aldehydes, acids, furan and amine) are added to gasoline.

## **Objectives**

- ✓ Identify tailor-made gasoline blends that match the desired product attributes
- ✓ Identify the suitable chemicals and their composition

# Mixture/blend design

## Input data

- Chemical database: Gasoline is the main ingredient (MI) or surrogate: A mixture or blend that is a starting estimate of the optimal blend
- 221 chemicals from different family group as additives

Pseudo-components  
Of gasoline to  
Represent the MI

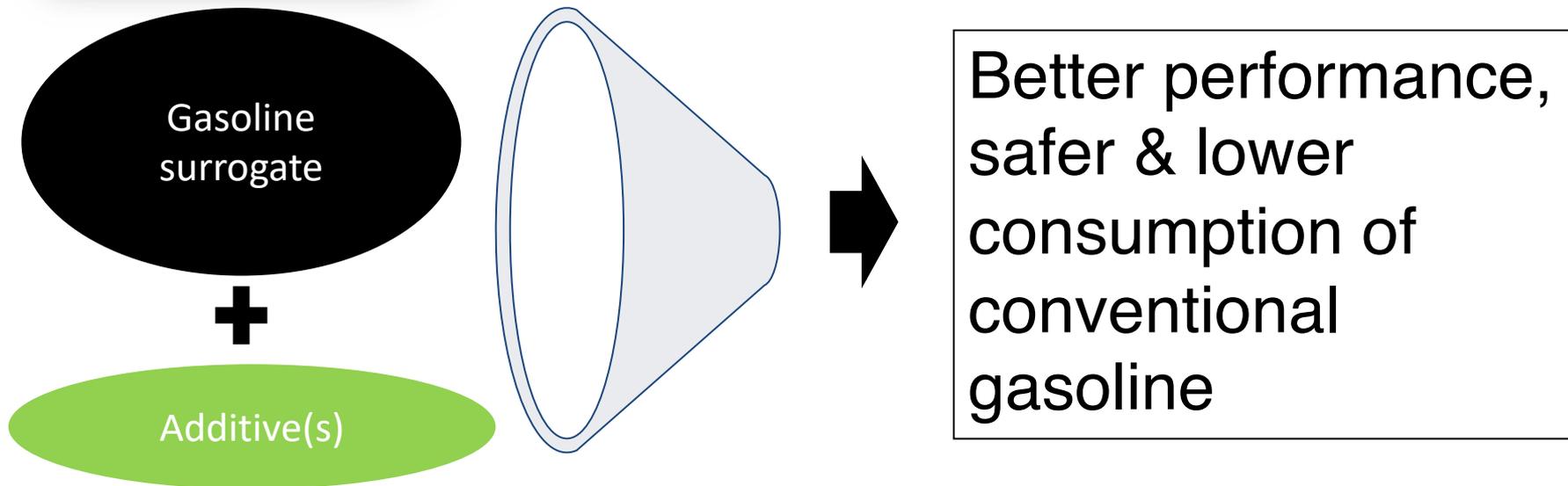
<b>Chemical</b>	<b>Composition (vol%)</b>
<b>Butane</b>	9.99
<b>n-Heptane</b>	10.93
<b>Iso-octane</b>	48.33
<b>1-Pentene</b>	6.7
<b>Methylcyclopentane</b>	8.32
<b>Toluene</b>	15.74

# Gasoline design

S. Kalakul, 2016 PhD Thesis (DTU)



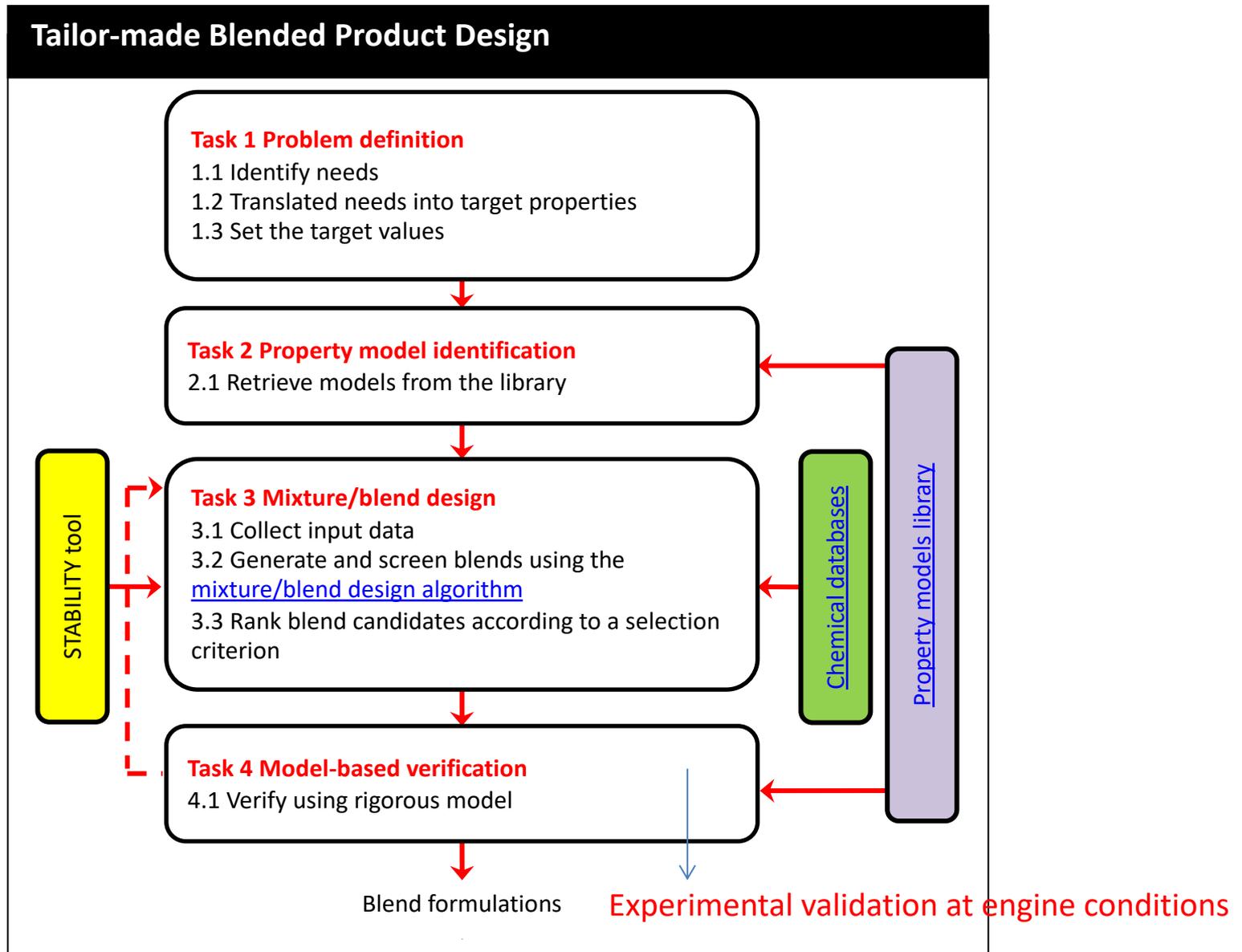
The objective of this work is to improve properties of a gasoline surrogate by adding additives. It is able to help to reduce the conventional gasoline consumption, environmental impacts as well as diesel properties



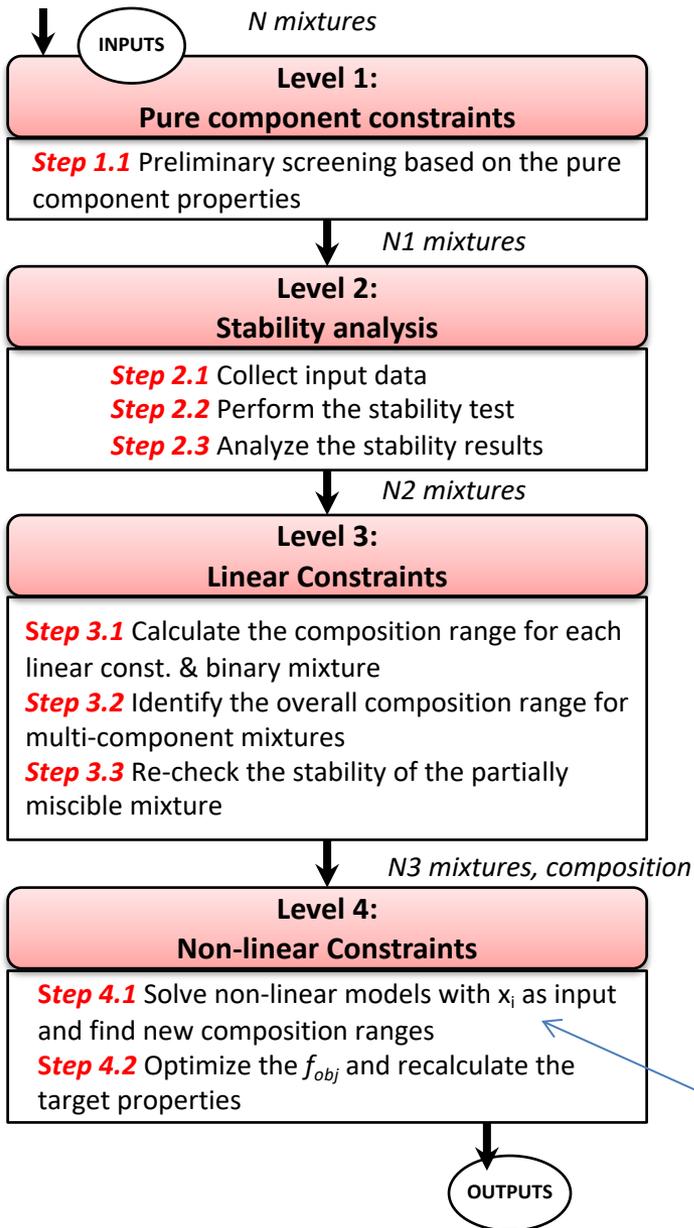
E.g. Alcohols, ethers, ketones, acid/furan derivatives,....)

# Work Flow for Product (Blend) Design

N.A. Yunus, 2014 PhD Thesis



# Mixture/blend design Algorithm

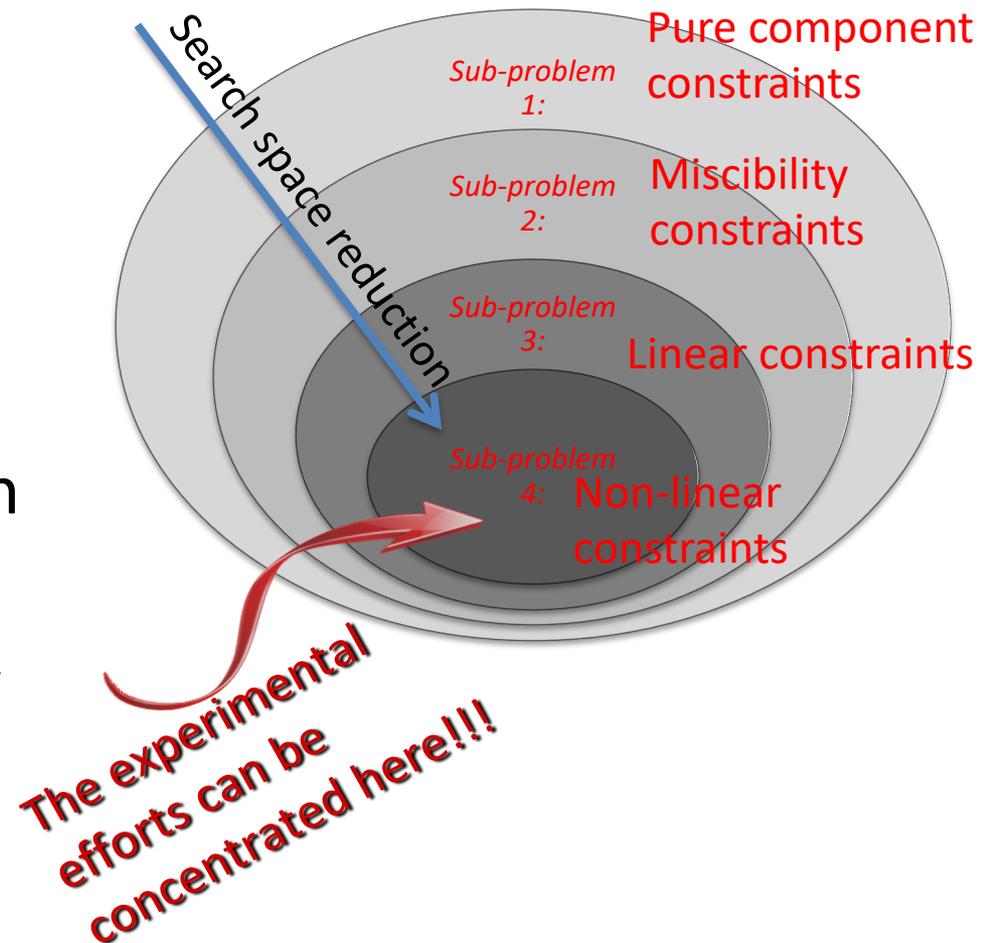


STEP	Method and tools
INPUTS	<ul style="list-style-type: none"> <li>Chemicals database, mixture property models</li> <li>Constraints on the target properties, temperature</li> </ul>
Step 1.1	Compare the pure component properties of mixtures
Step 2.1	UNIFAC-LLE group representation for all chemicals and temperature
Step 2.2	STABILITY tool
Step 2.3	List all the miscible, partially miscible or immiscible mixtures.
Step 3.1 and 3.2	Optimize the composition ranges subject to linear constraints, using <i>linprog</i> solver in MATLAB
Step 3.3	Compare the region of interest with the stable region
Step 4.1	Optimize the composition range subject to non-linear constraints using the function <i>fmincon</i> in MATLAB with the maximum number of iterations set to 1000.
Step 4.2	Optimize the problem according to the defined objective function
OUTPUTS	<ul style="list-style-type: none"> <li>N4 mixtures, composition, property values</li> </ul>

Usually choose one property, and validate for others

# Decomposition Method

- The problem is decomposed into several sub-problems according to their complexity
- Solving the problem this way, allows an efficient, robust and flexible solution of the problem
- This approach sequentially reduces the search space



# Problem Definition

N.A. Yunus, 2014 PhD Thesis

## Product needs:

1. The ability to burn
2. Engine efficiency
3. Consistency of fuel flow
4. Flammability
5. Toxicity
6. Stability
7. Blend regulatory issues and emissions
8. Low oxidation rate

## Target properties:

1. Reid vapor pressure
2. Heating value, Octane Rating
3. Dynamic viscosity
4. Density
5. Flash point
6. Lethal concentration
7. Gibbs energy of mixing
8. Oxygen content
9. Choice of chemicals

# Target Values

*Legislation, existing products, literature, ....*

No.	Target properties:	Symbol:	Unit:	Lower Bound:	Upper Bound:
1	Reid vapor pressure	RVP	kPa	45	60
2	Higher Heating value	HHV	MJ/kg	40	$+\infty$
3	Dynamic viscosity	$\eta$	cP	0.3	0.6
4	Density	$\rho$	g/cm <sup>3</sup>	0.720	0.775
5	Flash point	T <sub>f</sub>	K	$-\infty$	300
6	Lethal concentration	$-\log LC_{50}$	mol/L	$-\infty$	3.08
7	Gibbs energy of mixing	$\Delta G^{mix}$	-	$-\infty$	0
8	Oxygen content	Wt <sub>O<sub>2</sub></sub>	-	2	20

Also  $\frac{d}{dx} \left( \frac{\Delta G^{mix}}{RT} \right) < 0$

Also RON >92 in subsequent studies

# Property models

Five linear (wrt) composition models

No.	Target properties	Symbol	Model	Function
1	Reid vapor pressure	RVP	GC(UNIFAC)	$f(P_{vap,i}, \gamma_i, x_i)$
2	Heating value + RON	HHV	Linear mixing rule	$f(HHV_i, x_i)$
3	Dynamic viscosity	$\eta$	Linear mixing rule	$f(\eta_i, x_i)$
4	Density	$\rho$	Modified Rackett Equation	$f(T, x_i)$
5	Flash point	$T_f$	GC(UNIFAC)	$f(T_{f,i}, \gamma_i, x_i)$
6	Lethal concentration	$-\log LC_{50}$	Linear mixing rule	$f(LC_{50,i}, x_i)$
7	Gibbs energy of mixing	$\Delta G^{mix}$	UNIFAC	$f(GC, x_i)$
8	Oxygen content	$Wt_{O_2}$	Linear mixing rule	$f(O_{2,i}, x_i)$

# Experimental verification of the surrogate conventional gasoline mixture

Gasoline property		Exp.	Model
1	Heating value, HHV (MJ/kg)	---	45
2	Dynamic viscosity, $\eta$ (cP)	0.50	0.51
3	Lethal Conc. $-\log LC_{50}$	---	3.08
4	T10, T90 (K)	345/384	345/382
5	Density, $\rho$ (g/cm <sup>3</sup> )	0.7113	0.7260
6	Reid vapor pressure, RVP (kPa)	55.2	54.0
7	Flash point, $T_f$ (K)	---	257

# MILP/MINLP model formulation at Levels 3 and 4

N.A. Yunus, 2014 PhD Thesis

$$\sum_j y_j = 2$$

$$0.05y_j \leq x_j \leq 0.2y_j$$

$$x_{MI} + \sum_j x_j = 1$$

Candidate selection  
and constraints for  
compositions

$$0.3 \leq \eta = \sum_i x_i \eta_i + \sum_j x_j \eta_j \leq 0.6$$

Viscosity

$$HHV = \sum_i x_i HHV_i + \sum_j x_j HHV_j \geq 35$$

HHV

$$0.72 \leq \rho = \frac{\sum_i x_i MW_i + \sum_j x_j MW_j}{\sum_i \frac{x_i MW_i}{\rho_i} + \sum_j \frac{x_j MW_j}{\rho_j}} \leq 0.775$$

Density

$$2 \leq Wt_{O_2} = \sum_i x_i Wt_{O_2,i} + \sum_j x_j Wt_{O_2,j} \leq 20$$

Oxygen  
content

$$\begin{aligned} & -\log(LC_{50}) \\ & = \sum_i x_i (-\log(LC_{50,i})) + \sum_j x_j (-\log(LC_{50,j})) \\ & \leq 3.08 \end{aligned}$$

Lethal  
concentration, 50%

$$45 \leq RVP = \sum_i x_i \gamma_i P_i^{sat} + \sum_j \quad RVP$$

$$\sum_i \frac{x_i \gamma_i P_i^{sat}(T)}{P_{i,T_f}^{sat}} + \sum_j \frac{x_j \gamma_j P_j^{sat}(T)}{P_{j,T_f}^{sat}} = 1$$

Flash point

$$T_f \leq 27$$

$$\Delta G^{mix}$$

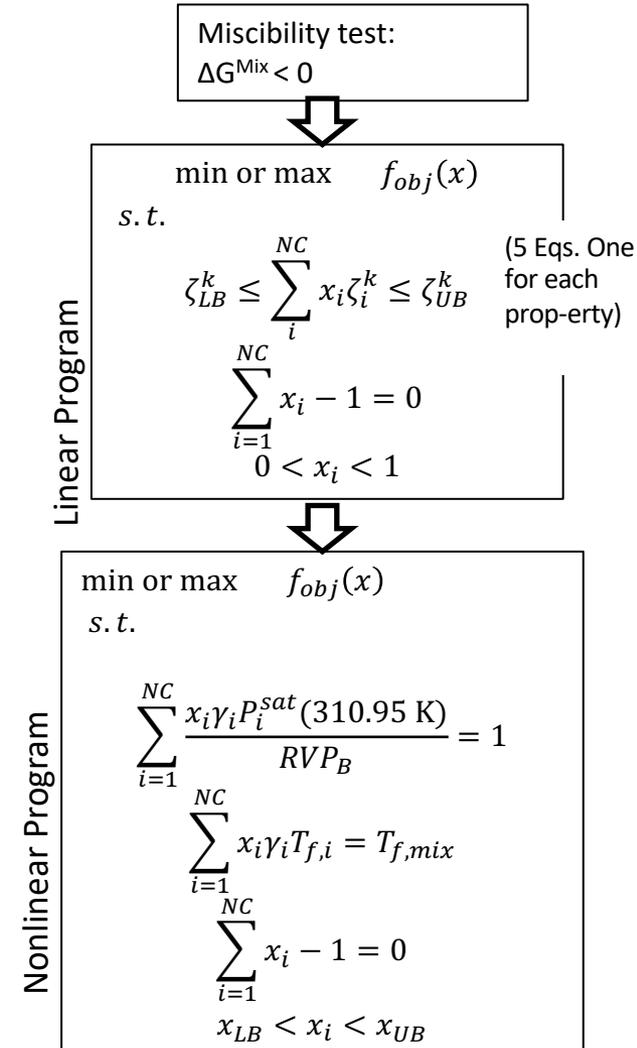
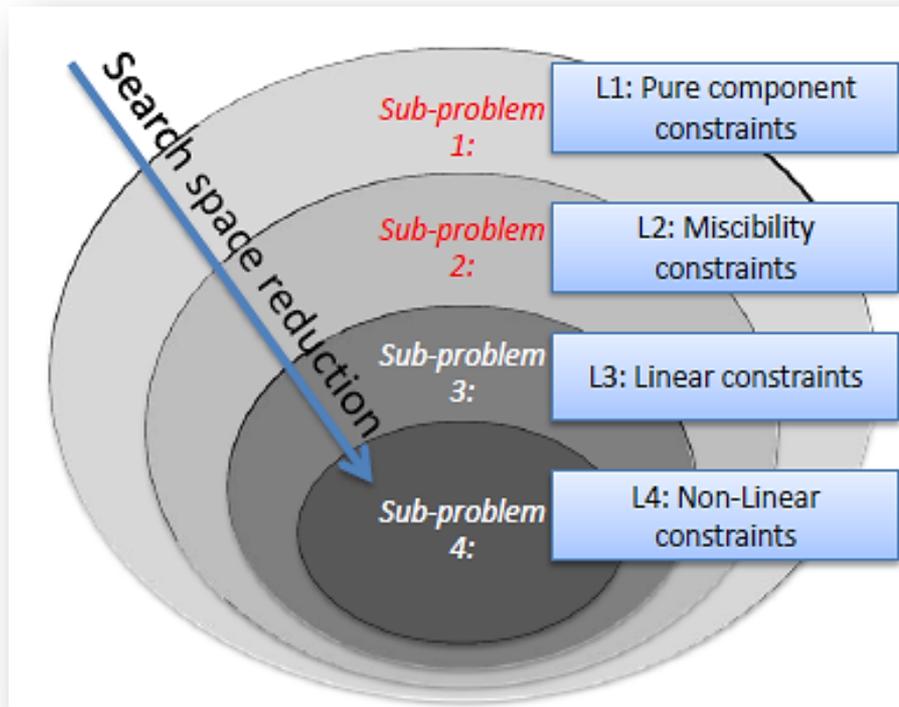
$$= RT \left( \sum_i (x_i \ln x_i + x_i \ln \gamma_i) + \sum_j (x_j \ln x_j + x_j \ln \gamma_j) \right) < 0$$

Stability

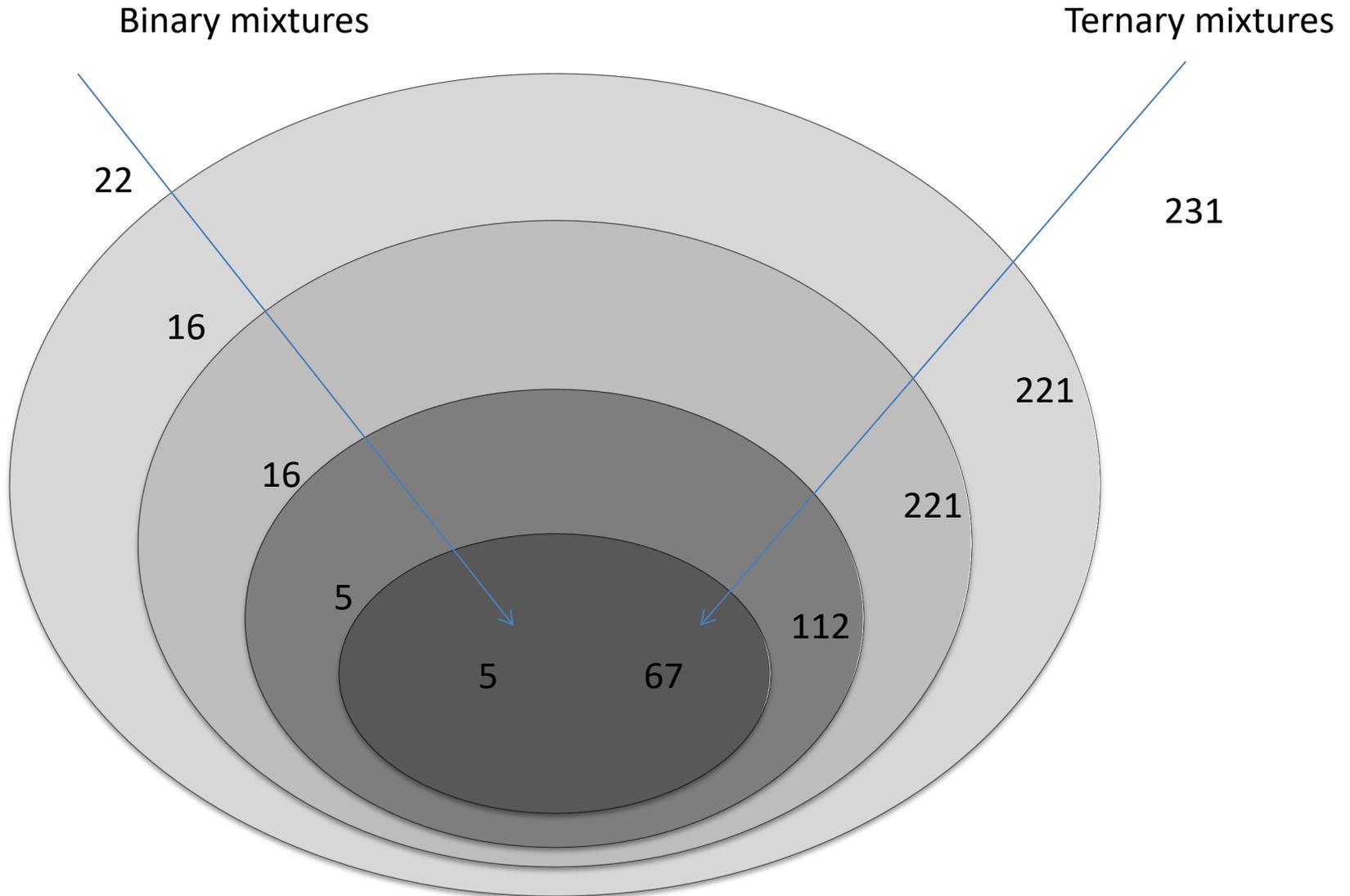
$$\frac{d}{dx} \left( \frac{\Delta G^{mix}}{RT} \right) < 0$$

# Gasoline Blend Design

- 1 Pure component constraints (HHV,  $\rho$ ,  $\eta$ ,  $LC_{50}$ ,  $WtO2$ )
- 2 Miscibility constraint ( $\Delta G^{mix}$ )
- 3 Linear constraints (HHV,  $\rho$ ,  $\eta$ ,  $LC_{50}$ ,  $WtO2$ )
- 4 Non-linear constraints (RVP, Tf)



# Solution – case with bio-based chemicals



# The Results – ternary and binary blends

N.A. Yunus, 2014 PhD Thesis

Blend	Composition (vol%)
Blend 1	MI (69), Tetrahydrofuran (11), 2-Methyl Tetrahydrofuran (20)
Blend 2	MI (67), Acetone (13), 2-Methyl Tetrahydrofuran (20)
Blend 3	MI (72), Acetone (10), 2-Butanone (18)
Blend 4	MI (75), 2-Butanone (13), 2-Methyl Tetrahydrofuran (12)
Blend 5	MI (77), Ethanol (12), 2-Methyl Tetrahydrofuran (11)

## Binary Blends

THF: Tetrahydrofuran; MeTHF: 2-Methyltetrahydrofuran

MI (54) + MTBE (46) or MSBE (46)

MI (75) + MeTHF (25)

MI (81) + THF (19)

MI (92) + Ethanol (8)

Yunus, Gernaey, Woodley and Gani, 2012. 22th ESCAPE, 17-20.6.2012, London

Yunus, Gernaey, Woodley and Gani, 2014. CACE, 66: 201-213

# Properties of the ternary blends

Blend	HHV	WtO <sub>2</sub>	RVP	RON	viscosity	LC <sub>50</sub>
1	41	7.2	46	---	0.48	2.7
2	41	7.8	46	---	0.47	2.7
3	40	7.3	49	---	0.48	2.7
4	43	5.5	45	---	0.50	2.9
5	42	6.7	45	96	0.57	2.8

Very good agreement between these values and recent experimental measurements  
Carried out at TEES Gas & Fuels Research Center, Texas A&M, Qatar – see next slide

Choudhury et al., 2018. J. Nat.Gas.Science & Eng, 55, 585.

Yunus, Germaey, Woodley and Gani, 2012. 22th ESCAPE, 17-20.6.2012, London

Yunus, Germaey, Woodley and Gani, 2014. CACE, 66: 201-213

# The experimental validation

The properties are tested using ProCAPD and experiments

Gasoline blend candidates with their composition and properties ((1): The presented MINLP model; (2): ProCAPD; (3): Experiment)

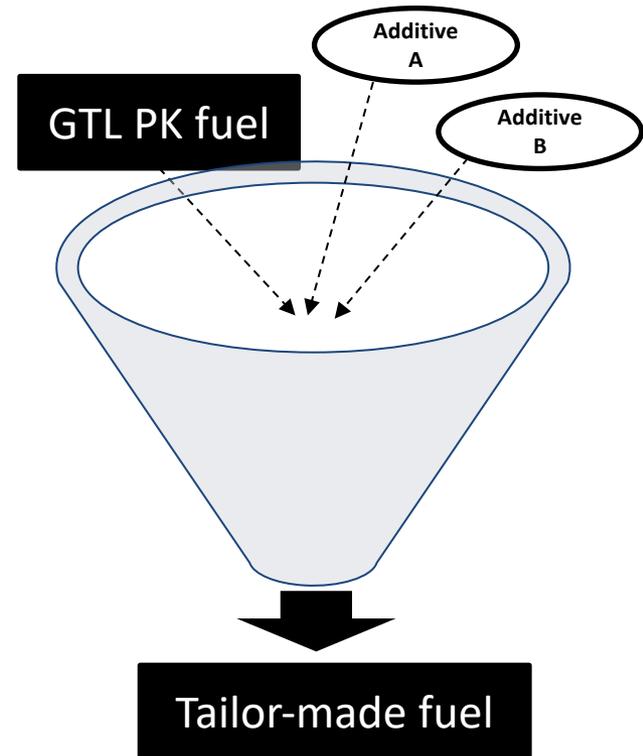
ID	Composition (vol%)	RVP	HHV	$\eta$	$\rho$	Wt <sub>O2</sub>	LC <sub>50</sub>	T <sub>f</sub>
1	MI (69)	(1) 45	(1) 42	(1) 0.50	(1) 0.7424	(1) 6.2	(1) 3.0	(1) -17
	THF (11)	(2) 46	(2) 41	(2) 0.48	(2) 0.7709	(2) 7.2	(2) 2.7	(2) -18
	MeTHF (20)	(3) 46	(3) -	(3) 0.54	(3) 0.7596	(3) -	(3) -	(3) -
2	MI (67)	(1) 45	(1) 40	(1) 0.48	(1) 0.7367	(1) 7.3	(1) 3.0	(1) -18
	ACE (13)	(2) 46	(2) 41	(2) 0.47	(2) 0.7618	(2) 7.8	(2) 2.7	(2) -22
	MeTHF (20)	(3) 60	(3) -	(3) 0.46	(3) 0.7482	(3) -	(3) -	(3) -
3	MI (72)	(1) 46	(1) 40	(1) 0.45	(1) 0.7245	(1) 6.7	(1) 3.0	(1) -18
	ACE (10)	(2) 49	(2) 40	(2) 0.48	(2) 0.7480	(2) 7.3	(2) 2.7	(2) -21
	2BE (18)	(3) 59	(3) -	(3) 0.45	(3) 0.7333	(3) -	(3) -	(3) -
4	MI (75)	(1) 47	(1) 42	(1) 0.48	(1) 0.7288	(1) 5.1	(1) 3.1	(1) -17
	2BE (13)	(2) 45	(2) 43	(2) 0.50	(2) 0.7528	(2) 5.5	(2) 2.9	(2) -18
	MeTHF (12)	(3) 50	(3) -	(3) 0.46	(3) 0.7395	(3) -	(3) -	(3) -
5	MI(77)	(1) 49	(1) 41	(1) 0.58	(1) 0.7234	(1) 6.2	(1) 2.7	(1) -17
	EtOH (12)	(2) 45	(2) 42	(2) 0.57	(2) 0.7487	(2) 6.7	(2) 2.8	(2) -16
	MeTHF (11)	(3) 55	(3) -	(3) 0.61	(3) 0.7357	(3) -	(3) -	(3) -

THF: Tetrahydrofuran; MeTHF: 2-Methyltetrahydrofuran; ACE: Acetone; 2BE: 2-butanone; EtOH: Ethanol

Choudhury et al., 2018. J. Nat.Gas.Science & Eng, 55, 585.

# Case-study 2: Design of a tailor-made jet-fuel blends

- ❑ PK fuels (Paraffinic Kerosene) produced from GTL (Gas to Liquid) via the Fischer-Tropsch process (or CTL: Coal to Liquid)
- ❑ PK fuels lack certain chemical constituents, which although are benign to environment, offer a tradeoff in performance when used in a jet-fuel engine
- ❑ The objective of this work is to improve properties of the GTL PK fuel by blending with feasible additives
- ❑ The main challenge involves how to identify the blends that satisfy the blend target properties with various type of additives



- ✓ Better performance
- ✓ Safer
- ✓ lower consumption of the fuel

Environmental Sustainability

# Blends of jet-fuel should have...

- Low Reid Vapor Pressure (to prevent evaporative losses and fuel system vapor lock)
- High flash-point temperature
- High HHV (to maximize the energy that can be stored in a fixed volume and provide the longest flight range)
- Low melting point (to prevent formation of wax crystals which are difficult to pump into turbine engines)
- Low greenhouse gas (CO<sub>2</sub>) emissions

# Design of a tailor-made jet-fuel blends

S. Kalakul, 2016 PhD Thesis (DTU)

Kalakul et al., 2018, CACE, 116: 37-55

Zhang et al., 2018, IECR, 57: 7008-7020

## □ STEP-1: PROBLEM DEFINITION

Input: Product type is jet-fuel

Tools: Jet-fuel design knowledge base

Output: Target properties and constraints

+Product Standards (ASTM St D1655, 2016)

List of product needs and their corresponding target property constraints for the jet-fuel blend design

Product Need	Target property	Target value	Unit
Low human toxicity	$-\log LC_{50}$	$-\log LC_{50} \leq 4.58$	mol/L
Safety/Flammability	Flash point ( $T_f$ )	$T_f \geq 38$	°C
Ability to be burned	Reid vapor pressure (RVP)	$RVP \leq 1$	kPa
	ASTM distillation temperature	$T_{10} \leq 205$	°C
Consistency of fuel flow	Kinematic viscosity at -20 °C ( $V$ )	$V \leq 8$	mm <sup>2</sup> /s
	Freezing point ( $T_{freez}$ )	$T_{freez} \leq -40$	°C
Engine efficiency	Density at 15 °C ( $\rho$ )	$0.775 \leq \rho \leq 0.840$	g/mL
	Higher heating value (HHV)	$HHV \geq 43$	MJ/kg
Low environmental impacts	CO <sub>2</sub> emission in the combustion engine (CO <sub>2</sub> E)	$CO_2E \leq 25.36$	kgCO <sub>2</sub> /mile

Phase Stability

$$\Delta G_{mix} < 0 \quad \text{and} \quad \frac{d}{dx} \left( \frac{\Delta G^{mix}}{RT} \right) < 0$$

# Design of a tailor-made jet-fuel blends

Kalakul et al., 2018, CACE, 116: 37-55

## STEP-2: PRODUCT INGREDIENT IDENTIFICATION (GTL PK + Additive)

Input: List of target properties and constraints from STEP-1, GTL PK composition

Tools: ProCAPD database, property calculation toolbox

Output: Set of jet-fuel additives, pure component properties of GTL PK and additives

GTL PK fuel composition\*

Name	Formula	Composition (vol%)
Octane, 2-methyl-	C9H20	2.9
Octane, 3-methyl-	C9H20	2.9
Nonane	C9H20	2.8
Heptane, 2,4,6-trimethyl-	C10H22	3.3
Nonane, 4-methyl-	C10H22	3.1
Octane, 2,6-dimethyl-	C10H22	3.2
Octane, 3,6-dimethyl-	C10H22	3.3
Octane, 4-ethyl-	C10H22	3.1
Decane	C10H22	3.0
Nonane, 4-methyl-	C10H22	3.1
Nonane, 2-methyl-	C10H22	3.1
Octane, 3-ethyl-	C10H22	3.1
Nonane, 3-methyl-	C10H22	3.1
Decane, 2-methyl-	C11H23	3.3
Nonane, 2,5-dimethyl-	C11H24	3.5
Nonane, 2,6-dimethyl-	C11H24	3.5
Decane, 3-methyl-	C11H24	3.4
Decane, 5-methyl-	C11H24	3.4
Decane, 4-methyl-	C11H24	3.4
Decane, 3-methyl-	C11H24	3.4
Undecane	C11H24	3.2
Nonane, 5-propyl-	C12H26	3.6
2,3-Dimethyldecane	C12H26	3.7
Decane, 2,5-dimethyl-	C12H26	3.7
Decane, 4-ethyl-	C12H26	3.6
Undecane, 5-methyl-	C12H26	3.6
Undecane, 4-methyl-	C12H26	3.6
Undecane, 2-methyl-	C12H26	3.5
Undecane, 3-methyl-	C12H26	3.6
Decane, 2,6,6-trimethyl-	C13H28	4.0

Gas chromatography (GC)



List of additives for tailor-made jet-fuel blends

Chemical	Formula
Toluene	C7H8
Undecane	C11H24
Benzene, Propyl-	C9H12
2,2-Dimethyloctane	C10H22
2,2,4,4-Tetramethylpentane	C9H20
3,3-Diethylpentane	C9H20
Decane	C10H22
Ethylbenzene	C8H10
2,2-Dimethylheptane	C9H20
2,4,4-Trimethylhexane	C9H20
N-Butyl Ether	C8H18O
2,3,3,4-Tetramethylpentane	C9H20
3-Methyl-3-Ethylpentane	C8H18
4-Methylnonane(DI)	C10H22
5-Methylnonane	C10H22
Nonane	C9H20
2,2-Dimethylhexane	C8H18
2,7-Dimethyloctane	C10H22
2,4-Dimethyloctane	C10H22
3-Ethylheptane	C9H20
4-Methyloctane	C9H20
2,2,4-Trimethylpentane	C8H18
2,2,3-Trimethylpentane	C8H18
N-Octane	C8H18
2,2-Dimethylpentane	C7H16
2,6-Dimethylheptane	C9H20
2-Methylheptane	C8H18
2,2,3-Trimethylbutane	C7H16
Methyl-Isobutyl-Ether	C5H12O
3-Methylheptane	C8H18
2,3,4-Trimethylpentane	C8H18
Methyl-Sec-Butyl-Ether	C5H12O
2,4-Dimethyl-3-Ethylpentane	C9H20
N-Heptane	C7H16
Methylcyclopentane	C6H12
2,2-Dimethylbutane	C6H14
2,5-Dimethylhexane	C8H18
2-Methyl-3-Ethylpentane	C8H18
Diisopropyl-Ether	C6H14O
3-Methylhexane	C7H16
3-Ethylpentane	C7H16

CAMD technique in ProCAPD



50 feasible additives are generated using the CAMD technique in ProCAPD according to the benchmark of the existing jet-fuel characterized by properties such as boiling point, melting point and flash point as well as types of chemicals present

# Design of a tailor-made jet-fuel blends

Kalakul et al., 2018, CACE, 116: 37-55

## □ STEP-3: CAM<sup>b</sup>D SOLUTION

Input: Objective function, mixture type (ternary), GTL PK composition and its property equations, set of additive candidates and their property equations

Tools: ProCAPD database, property calculation toolbox, ProCAPD solvers (GAMS, MATLAB)

Output: List of promising blend candidates

The target property models are formulated as a MINLP problem

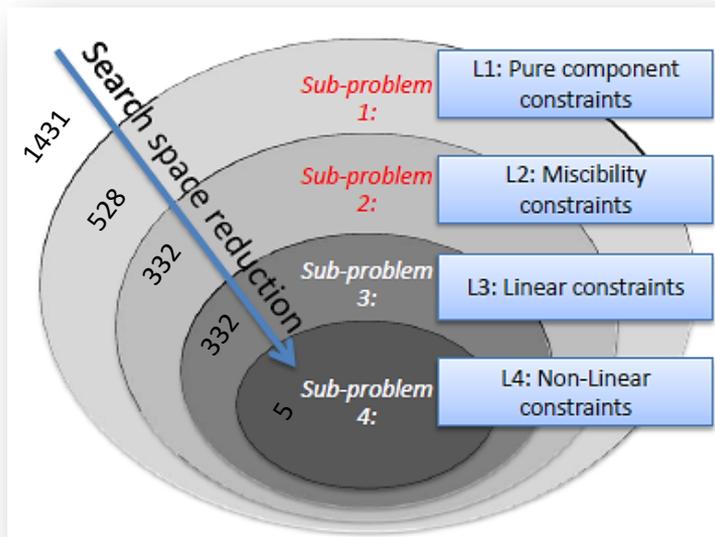
Subject to;	$\max f_{obj} = \sum_{i=2}^{NC} x_i y_i \quad \dots(1)$	Minimize GTL PK (MI) amount Down to a specific limit
Mixture constraints:	$\frac{\Delta G^{mix}}{RT} = \sum_i x_i \ln x_i + \frac{G^E}{RT} \quad \dots(2)$	
	$\frac{d^2 \Delta G^{mix}}{dx^2} > 0 \quad \dots(3)$	Mixture miscibility
Product property constraints:	$\phi_k = \sum_i x_i \phi_{i,k} \quad k = 1, 5 \dots(4)$	
	$\sum \frac{x_i \gamma_i P_i^{sat}(T)}{RVP_B} - 1 = 0 \quad \dots(5)$	Ideal properties (Linear models)
	$\sum_i \frac{x_i \gamma_i P_i^{sat}(T)}{P_{i,FP}^{sat}} - 1 = 0 \quad \dots(6)$	
Process model constraints:	$\sum_i x_i - 1 = 0 \quad \dots(7)$	Non-ideal properties (Non-linear models)
	$0 \leq x \leq 1, \quad y \in \{0,1\}$	

# Design of a tailor-made jet-fuel blends

## ❑ STEP-3: CAM<sup>b</sup>D SOLUTION

ID	Optimization Solution	Composition (vol%)
1	DC	GTL PK (80.2) Decalin (8.3) Butylbenzene (11.5)
2	DC	GTL PK (78.6) Decalin (12.4) Pentylbenzene (9)
3	DC	GTL PK (77) Decalin (6) Hexylbenzene (17)
4	TS	GTL PK (77) Decalin (18) Hexylbenzene (5)

Blend matching the target properties  
(DC: the decomposition-base algorithm;  
TS: The two step solution approach)



decomposition-base algorithm [1]

Kalakul et al., 2018, CACE, 116: 37-55  
Zhang et al., 2018, IECR, 57: 7008-7020

# Equations: 143 (461)  
# Continuous variables: 30099 (85781)  
# Discrete variables: 51 (221)  
(in parenthesis for the Gasoline case study)

Two step solution approach [2]

[1] S. Kalakul, S. Cignitti, L. Zhang, R. Gani, 2017, Chapter 3 – VPPD Lab: The Chemical Product Simulator, Tools For Chemical Product Design, Computer Aided Chemical Engineering, 39, 61-94.

[2] L. Zhang, S. Cignitti, R. Gani, 2015, Generic mathematical programming formulation and solution for computer-aided molecular design, Computers & Chemical Engineering, 78, 79-84.

# Design of a tailor-made jet-fuel blends

Kalakul et al., 2018, CACE, 116: 37-55

## STEP-4: MODEL-BASED VERIFICATION/EXPERIMENTAL VERIFICATION

Input: List of promising candidates from STEP-3

Tools: Property calculation toolbox, Jet-fuel design knowledge base

Output: A set of promising blend candidates and property values calculated by rigorous property models and a set of experimental tests for product design verification

- Rigorous property models to predict  $\eta$  and ASTM distillation temperatures are applied in this step
- Experimental verification is done by TEES Gas & Fuels Research Center, Texas A&M University at Qatar
- It can be noted that the results predicted by ProCAPD are in good agreement with the experimentally measured data

List of Blend matching the target properties and their target property values (ProCAPD-RG: Rigorous models in ProCAPD)

ID		RVP	HHV	V	$\rho$	CO <sub>2</sub> E	$-\log LC_{50}$	T <sub>f</sub>	T <sub>10</sub>	T <sub>50</sub>	T <sub>90</sub>	T <sub>m</sub>	WSD	Small for good lubricity
1	ProCAPD	0.57	46.6	3.55	0.784	21.4	4.41	56	183	197	222			
	ProCAPD-RG			3.56										
	Experiment		46.9	3.83	0.776			56	181	195	220	-55	0.706	
2	ProCAPD	0.55	46.5	4.22	0.786	20	4.32	56	186	202	221			
	ProCAPD-RG			4.18										
	Experiment		46.8	4.19	0.779			58	184	199	219	-55	0.731	
3	ProCAPD	0.52	46.5	4.32	0.784	22	4.51	57	190	209	228			
	ProCAPD-RG			4.21										
	Experiment		46.9	4.24	0.776			60	187	205	222	-55	0.641	
4	ProCAPD	0.50	43.1	4.09	0.780	24	4.42	51	183	197	222			
	ProCAPD-RG			4.1										
	Experiment													
GTL PK	ProCAPD	0.64	47.6	3.22	0.756	23	4.58	58	184	204	228			
	ProCAPD-RG													
	Experiment		47.0	4.11	0.752			56	181	201	223	-49	0.712	



\*wear scar diameter (WSD) (ASTM D7566-12a standard (2013))

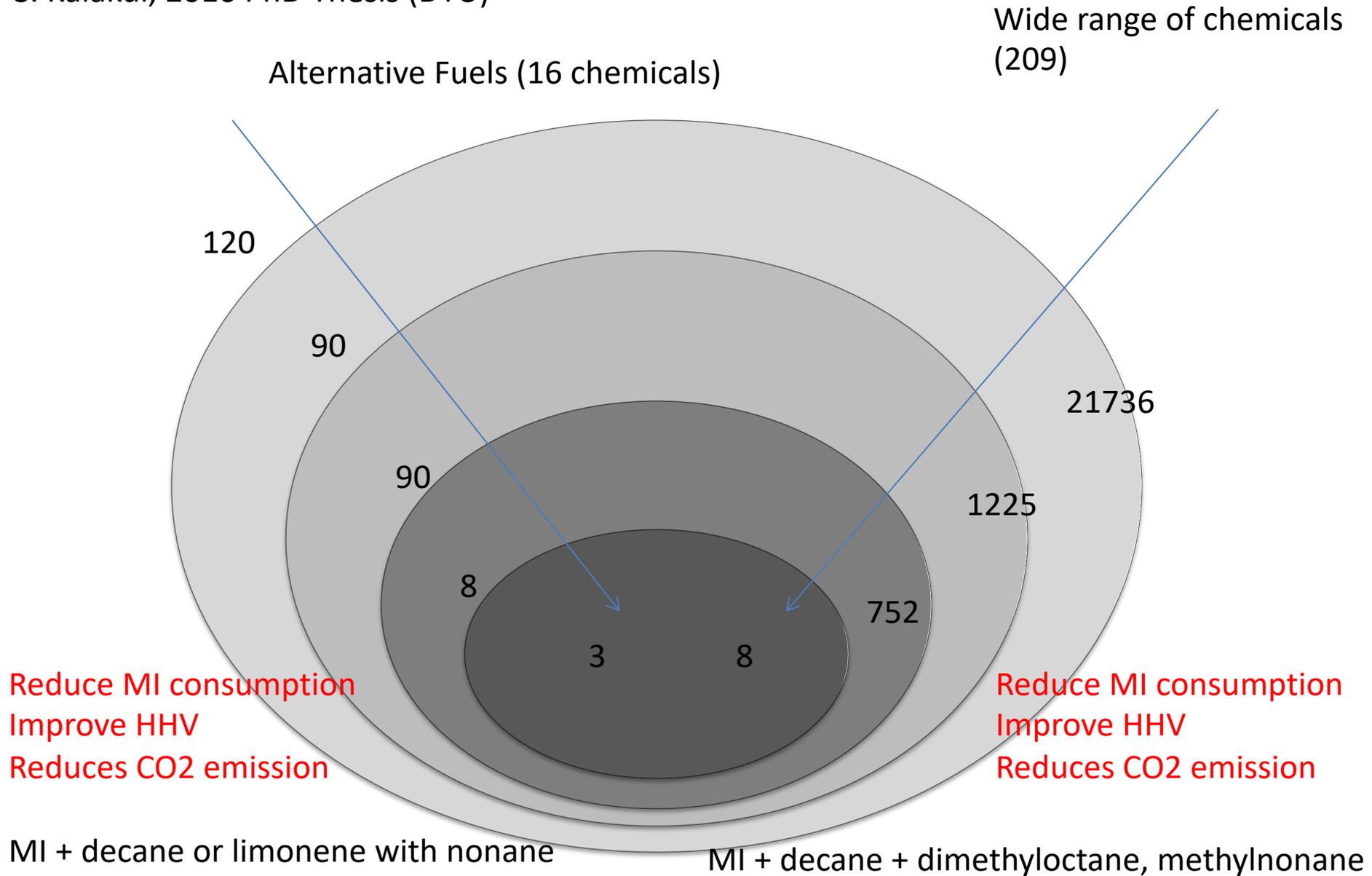
Improve All properties

## The optimum Blend ID1 composition

Octane, 2-methyl-	2.3	2,3-Dimethyldecane	3.4
Octane, 3-methyl-	1.8	Decane, 2,5-dimethyl-	1.2
Nonane	9.3	Decane, 4-ethyl-	1.0
Heptane, 2,4,6-trimethyl-	0.8	Undecane, 5-methyl-	1.4
Nonane, 4-methyl-	1.5	Undecane, 4-methyl-	0.9
Octane, 2,6-dimethyl-	1.5	Undecane, 2-methyl-	1.1
Octane, 3,6-dimethyl-	1.1	Undecane, 3-methyl-	0.8
Octane, 4-ethyl-	2.2	Decane, 2,6,6-trimethyl-	1.3
Decane	13.7		
Nonane, 4-methyl-	2.3	Decalin	18.0
Nonane, 2-methyl-	3.3	Hexylbenzene	5.0
Octane, 3-ethyl-	0.7		
Nonane, 3-methyl-	4.2		
Decane, 2-methyl-	3.0		
Nonane, 2,5-dimethyl-	1.3		
Nonane, 2,6-dimethyl-	1.2		
Decane, 3-methyl-	1.1		
Decane, 5-methyl-	2.6		
Decane, 4-methyl-	2.4		
Decane, 3-methyl-	3.2		
Undecane	4.8		
Nonane, 5-propyl-	1.6		

# Flexibility in the approach e.g. change of database

S. Kalakul, 2016 PhD Thesis (DTU)



# Design of a tailor-made jet-fuel blends

Screenshot of step-1 using Blend Design Template in ProCAPD

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

**Select Product**

Problem Type: BlendDesign Product Type: Jet-fuel Product Name: Information:

Define Needs Select All Translate Needs into Target Properties Specify Target Property Constraints Default

List of Needs and Target Properties

	Need	Use	TargetProperty	TargetpropertyII	TargetpropertyIII
▶	Ability to be burned	<input checked="" type="checkbox"/>	RVP	▼	▼
	Safety	<input checked="" type="checkbox"/>	FlashP	▼	▼
	Engine efficiency1	<input checked="" type="checkbox"/>	HHV	▼	▼
	Engine efficiency2	<input checked="" type="checkbox"/>	Lden_15C	▼	▼
	Consistency of fuel flow1	<input checked="" type="checkbox"/>	KinVis_-20C	▼	▼
	Environmental impacts	<input checked="" type="checkbox"/>	CO2E	▼	▼
	Low toxicity	<input checked="" type="checkbox"/>	MinlogLC50	▼	▼
*		<input type="checkbox"/>		▼	▼

List of Target Property Constraints

	TargetProperty	MinValue	MaxValue
▶	RVP	0	1
	FlashP	311	370
	HHV	43	50
	Lden_15C	775	840
	KinVis_-20C	0	8
	CO2E	0	25.36
	MinlogLC50	0	4.58
*			

# Design of a tailor-made jet-fuel blends

## Screenshot of step-2 using Blend Design Template in ProCAPD

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

Surrogate Additive(s)

Select Surrogate

Jet-fuelSurrogate1  
GTLPK1

Information

The GTL PK composition is obtained from GC analysis provided by TEES Gas & Fuels Research Center, Texas A&M University at Qatar

Surrogate composition

ID	ChemName	CAS	Formula	Xi
149	Octane, 2-methyl-	003221-61-2	C9H20	0.032983212318103375
150	Octane, 3-methyl-	002216-33-3	C9H20	0.025911214981993665
151	Nonane	000111-84-2	C9H20	0.13782375014620382
152	Heptane, 2,4,6-trimethyl-	002613-61-8	C10H22	0.010567443045632093
153	Nonane, 4-methyl-	017301-94-9	C10H22	0.019399932755414143
154	Octane, 2,6-dimethyl-	002051-30-1	C10H22	0.01953136861419066
155	Octane, 3,6-dimethyl-	015869-94-0	C10H22	0.013432744766960198
156	Octane, 4-ethyl-	015869-86-0	C10H22	0.028942176102589388
157	Decane	000124-18-5	C10H22	0.18803213956568751

Accept Surrogate

Surrogate Property

ID	ChemName	CAS	Smile	Formula	Mw	ChemType	ProblemType	IngredientType
149	Octane, 2-methyl-	003221-61-2	CCCCCCC(C)C	C9H20	128.25		BlendDesign	Surrogate
150	Octane, 3-methyl-	002216-33-3	CCCCC(C)CC	C9H20	128.25		BlendDesign	Surrogate
151	Nonane	000111-84-2	CCCCCCCC	C9H20	128.25		BlendDesign	Surrogate
152	Heptane, 2,4,6-trimethyl-	002613-61-8	CC(C)CC(C)CC(C)C	C10H22	142.28		BlendDesign	Surrogate
153	Nonane, 4-methyl-	017301-94-9	CCCCC(C)CCC	C10H22	142.28		BlendDesign	Surrogate

# Design of a tailor-made jet-fuel blends

## Screenshot of step-3 Objective function identification

Blend Design Template
— □ ×

1: Problem Definition
2: Ingredient Selection
3: Mixture Blend Design
4: Summary Results
Help

Objective Function
Level 1
Level 2
Level 3
Level 4

Select Blend Type Max Surrogate molar fraction (0-1)

2 = Binary Blend (Surrogate + 1 Additive)

3 = Ternary Blend (Surrogate + 2 Additives)

4 = Quaternary Blend (Surrogate + 3 Additives)

Select Objective Function

Objective

Minimization or Maximization

Surrogate molar fraction limits

Min

Max

Chemical blends is formulated as a Mixed Integer Non-Linear Programming (MINLP) problem

General blend problem is formulated as:

$$\min \text{ or } \max f_{obj}(X, Y, Q, E, S) \quad (3.1)$$

Subject to:

$$\text{Mixture constraints: } g_1(X, Y) > 0 \quad (3.2)$$

$$\text{Product property constraints: } \zeta_{LB} \leq g_2(X, Y, \zeta) \leq \zeta_{UB} \quad (3.3)$$

$$\text{Process model constraints: } g_3(X, Y) = 0 \quad (3.4)$$

$$\min \text{ or } \max f_{obj}(X, Y, Q, E, S) \quad (3.1)$$

where X = composition, Y = mixture property, Q = process constraints, E = Environmental impact constraints, S = Safety constraints

The MINLP problem is decomposed into 4 sub-levels:

Level1: Screening pure compound properties

Level2: Analysis of mixture miscibility

Level3: Linear target property optimization

Level4: Non-linear target property optimization

Number of generated blends

L1: Pure component constraints

L2: Miscibility constraints

L3: Linear constraints

L4: Non-Linear constraints

# Design of a tailor-made jet-fuel blends

## Screenshot of step-3 Level1: Pure component

Blend Design Template
\_ □ ×

1: Problem Definition
2: Ingredient Selection
3: Mixture Blend Design
4: Summary Results
Help

Objective Function
Level 1
Level 2
Level 3
Level 4
➔

Level 1: Pure Component Constraints

Generate Alternatives

All possible blends will be screened by comparing pure component property values with pre-defined target values

Y = A blend satisfies property linear property constraints  
N = A blend does not satisfy linear Level 1 Results

Select

All possible additives will be identified

	BlendID	AddID_1	AddID_2	AddName_1	AddName_2	HHV	Lden_15C
▶	1	1	2	1-Pentanol	3-PENTANOL	Y	Y
	2	1	3	1-Pentanol	2-PENTANOL	Y	Y
	3	1	4	1-Pentanol	3-METHYL-2-BU...	Y	Y
	4	1	5	1-Pentanol	Toluene	Y	Y
	5	1	6	1-Pentanol	Undecane	Y	Y
	6	1	7	1-Pentanol	Benzene, propyl-	Y	Y
	7	1	8	1-Pentanol	2,2-dimethylocta...	Y	Y
	8	1	9	1-Pentanol	2,2,4,4-tetrameth...	Y	Y
	9	1	10	1-Pentanol	3,3-diethylpentane	Y	Y
	10	1	11	1-Pentanol	Decane	Y	Y
	11	1	12	1-Pentanol	Ethylbenzene	Y	Y
	12	1	13	1-Pentanol	2,2-dimethylhept...	Y	Y
	13	1	14	1-Pentanol	2,4,4-trimethylhe...	Y	Y
	14	1	15	1-Pentanol	n-Butyl ether	Y	Y
	15	1	16	1-Pentanol	2,3,3,4-tetrameth...	Y	Y
	16	1	17	1-Pentanol	3-METHYL-3-ET...	Y	Y

The MINLP problem is decomposed into 4 sub-levels:

- Level1: Screening pure compound properties
- Level2: Analysis of mixture miscibility
- Level3: Linear target property optimization
- Level4: Non-linear target property optimization

Number of generated blends

# Design of a tailor-made jet-fuel blends

## Screenshot of step-3 Level2: Miscibility constraints

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

Objective Function Level 1 Level 2 Level 3 Level 4

Level 2: Stability Analysis

Calculate Miscibility Liquid Miscibility of all possible blends will be analyzed

See Results All possible additive that are miscible with Surrogate are

Miscibility results

	BlendID	AddID_1	AddID_2	AddName_1	AddName_2
▶	1	1	2	1-Pentanol	3-PENTANOL
	2	1	3	1-Pentanol	2-PENTANOL
	3	1	4	1-Pentanol	3-METHYL-2-BUTANOL
	4	1	5	1-Pentanol	Toluene
	5	1	6	1-Pentanol	Undecane
	6	1	7	1-Pentanol	Benzene, propyl-
	7	1	8	1-Pentanol	2,2-dimethyloctane
	8	1	9	1-Pentanol	2,2,4,4-tetramethylpentane
	9	1	10	1-Pentanol	3,3-diethylpentane
	10	1	11	1-Pentanol	Decane
	11	1	12	1-Pentanol	Ethylbenzene
	12	1	13	1-Pentanol	2,2-dimethylheptane
	13	1	14	1-Pentanol	2,4,4-trimethylhexane
	14	1	15	1-Pentanol	n-Butyl ether
	15	1	16	1-Pentanol	2,3,3,4-tetramethylpentane
	16	1	17	1-Pentanol	3-METHYL-3-ETHYLPENTANE
	17	1	18	1-Pentanol	4-Methylnonane(DL)
	18	1	19	1-Pentanol	5-methylnonane

The MINLP problem is decomposed into 4 sub-levels:

- Level1: Screening pure compound properties
- Level2: Analysis of mixture miscibility
- Level3: Linear target property optimization
- Level4: Non-linear target property optimization

Number of generated blends 1431

Search space reduction

- L1: Pure component constraints (528)
- L2: Miscibility constraints (332)
- L3: Linear constraints
- L4: Non-Linear constraints

# Design of a tailor-made jet-fuel blends

## Screenshot of step-3 Level3: Linear optimization

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

Objective Function Level 1 Level 2 Level 3 Level 4

Level 3: Linear Constraints

Screen All Blends Blend composition ranges are calculated for all linear target properties

BlendID	AddID_1	AddID_2	AddName_1	AddName_2	xSurrogate
1	1	2	1-Pentanol	3-PENTANOL	0.7258661215...
2	1	3	1-Pentanol	2-PENTANOL	0.7043697190...
3	1	4	1-Pentanol	3-METHYL-2-...	0.7174351370...
4	1	5	1-Pentanol	Toluene	0.8396402621...
5	1	6	1-Pentanol	Undecane	0.7043697190...
6	1	7	1-Pentanol	Benzene, pro...	0.8313894382...
7	1	8	1-Pentanol	2,2-dimethylo...	0.7043697190...
8	1	9	1-Pentanol	2,2,4,4-tetram...	0.7043697190...
9	1	10	1-Pentanol	3,3-diethylpe...	0.7043697190...
10	1	11	1-Pentanol	Decane	0.7043697190...
11	1	12	1-Pentanol	Ethylbenzene	0.8391779857...
12	1	13	1-Pentanol	2,2-dimethyl...	0.7043697190...
13	1	14	1-Pentanol	2,4,4-trimethyl...	0.7043697190...
14	1	15	1-Pentanol	n-Butyl ether	0.7043697190...
15	1	16	1-Pentanol	2,3,3,4-tetram...	0.7043697190...
16	1	17	1-Pentanol	3-METHYL-3-...	0.7043697190...
17	1	18	1-Pentanol	4-Methylnona...	0.7043697190...
18	1	19	1-Pentanol	5-methylnona...	0.7043697190...

The MINLP problem is decomposed into 4 sub-levels:

- Level1: Screening pure compound properties
- Level2: Analysis of mixture miscibility
- Level3: Linear target property optimization
- Level4: Non-linear target property optimization

Number of generated blends

Search space reduction

- 528 L1: Pure component constraints
- 332 L2: Miscibility constraints
- 332 L3: Linear constraints
- L4: Non-Linear constraints

# Design of a tailor-made jet-fuel blends

## Screenshot of step-3 Level4: Non-linear optimization

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

Objective Function Level 1 Level 2 Level 3 Level 4

Level 4: Non-Linear Constraints

Screen All Blends Blend composition ranges are calculated for all linear and non-linear target properties

Level 4 Results

	BlendID	AddName_1	AddName_2	xSurro	xAdd1	xAdd2	HHV	Lden_1
	208	Decalin	Benzene, propyl-	0.834...	0.0614...	0.1040...	46.892457700...	775
	213	Decalin	Ethylbenzene	0.839...	0.0276...	0.1330...	46.880978206...	775
	252	Decalin	Butylbenzene	0.833...	0.0716...	0.0953...	46.909562191...	775
	253	Decalin	Hexylbenzene	0.830...	0.0756...	0.0943...	46.854586056...	775
	255	Decalin	Pentylbenzene	0.830...	0.0747...	0.0951...	46.920496343...	775

The MINLP problem is decomposed into 4 sub-levels:

- Level1: Screening pure compound properties
- Level2: Analysis of mixture miscibility
- Level3: Linear target property optimization
- Level4: Non-linear target property optimization

Number of generated blends 1431

528 L1: Pure component constraints

332 L2: Miscibility constraints

332 L3: Linear constraints

5 L4: Non-Linear constraints

# Design of a tailor-made jet-fuel blends

## Screenshot of summary results

Blend Design Template

1: Problem Definition 2: Ingredient Selection 3: Mixture Blend Design 4: Summary Results Help

**View Summary Results**

Product

Product: Jet-fuel

Other Name:

Information:



Mixture Properties

	BlendID	AddID_1	AddID_2	AddName_1	AddName_2	xSurrogate	xAdd1	xAdd2	HHV	Lden_15C
▶	252	5	51	Decalin	Butylbenzene	0.83302879...	0.07163083...	0.09534036...	46.9095621...	775
*										

Experimental Verification List

	Performance	TargetProperty	Considered	ExperimentalVerification
▶	Ability to be burned	RVP	<input checked="" type="checkbox"/>	Reid vapor pressure measurement
	Safety	FlashP	<input type="checkbox"/>	Flash point measurement
	Engine efficiency1	HHV	<input checked="" type="checkbox"/>	Higher heating value measurement
	Engine efficiency2	Lden_15C	<input checked="" type="checkbox"/>	Density measurement
	Consistency of fuel flow1	KinVis_-20C	<input checked="" type="checkbox"/>	Kinematic viscosity measurement
	Consistency of fuel flow2	Tm	<input checked="" type="checkbox"/>	Freezing point measurement
	Environmental impacts	CO2E	<input checked="" type="checkbox"/>	
	Low toxicity	MinlogLC50	<input checked="" type="checkbox"/>	
	Ability to be burned	Distillation curve	<input type="checkbox"/>	ASTM distillation temperature
	Lubricity		<input type="checkbox"/>	Wear Scar Diameter ASTM D5001

# CHEMICAL PRODUCT DESIGN (CPD)

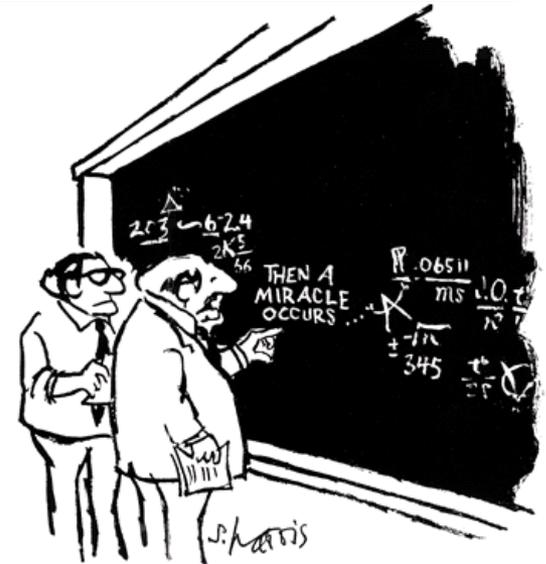
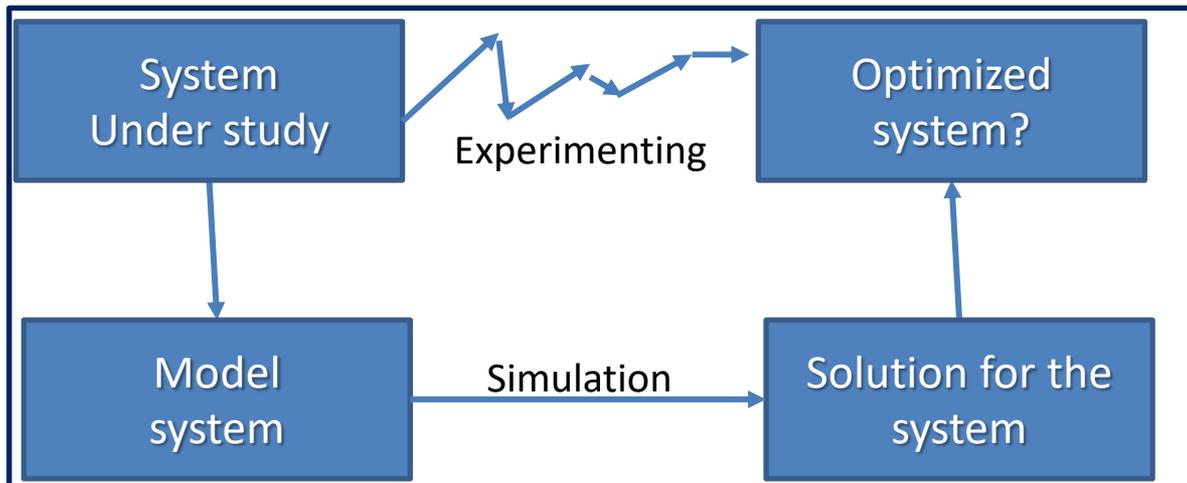
## Why CPD

Synthesize and design chemical products that exhibit desirable target behaviour and test for their performance



## CPD approaches

- Experimental-based trial and error approach
- **Computer-aided model-based approach**
- **Integrated experimental-modeling approach**



"I think you should be more explicit here in step two."