Computer Aided Design of Complex Products/Fluids

And Application to Fuels

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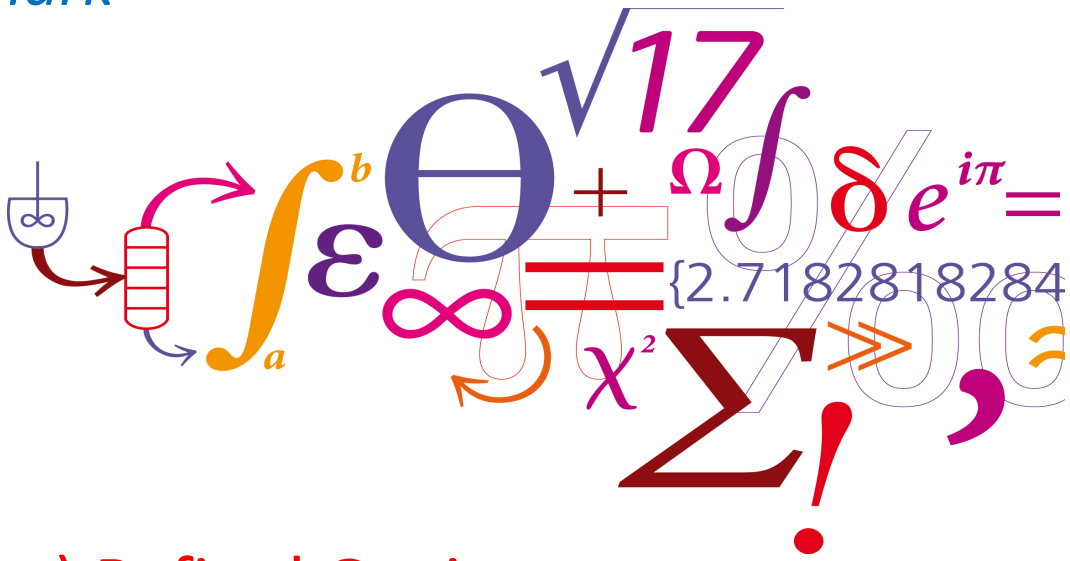


Big thanks to Professor (ret.) Rafiqul Gani,
”guru” in this field and his PhD. students (N. Yunus, S. Kalakul)

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)

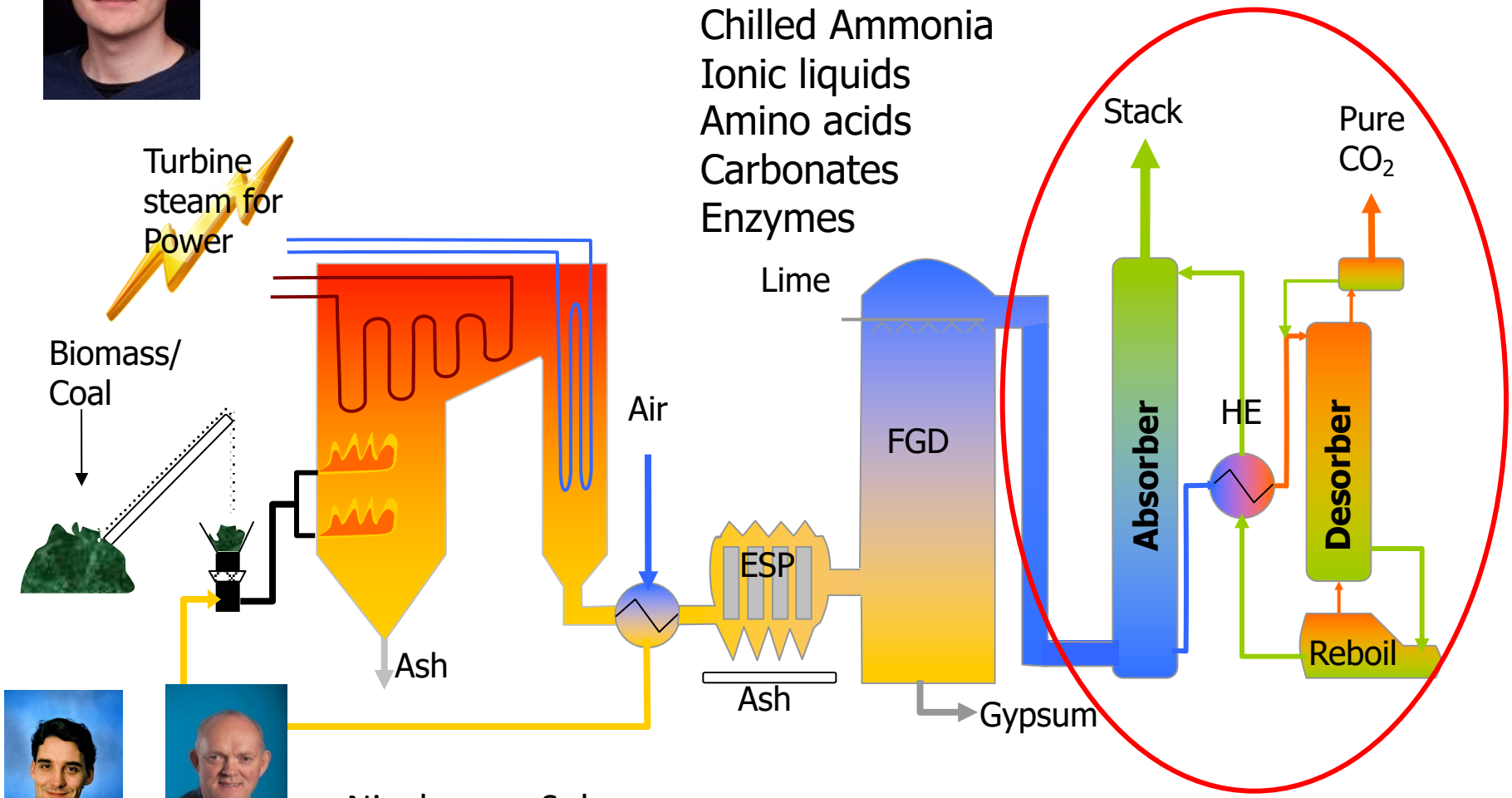
KT Consortium Members – 2018 (16)

Post-combustion CO_2 capture

Philip Fosbøl

Various Solvent Possibilities

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



Nicolas von Solms
Kaj Thomsen

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

Zhang, L.; Babi, D. K.; Gani, R. New Vistas in Chemical Product and Process Design. *Annual Review of Chemical and Biomolecular Engineering*. **2016**, *7*(1), 557-582.

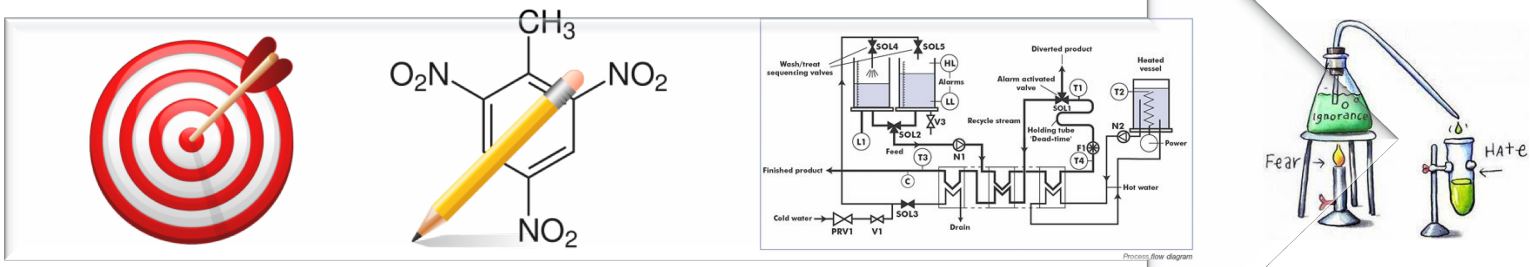
Chemical Product Design Framework

Problem Definition **Databases/Models/Algorithms** **Experiments**

Needs and Targets

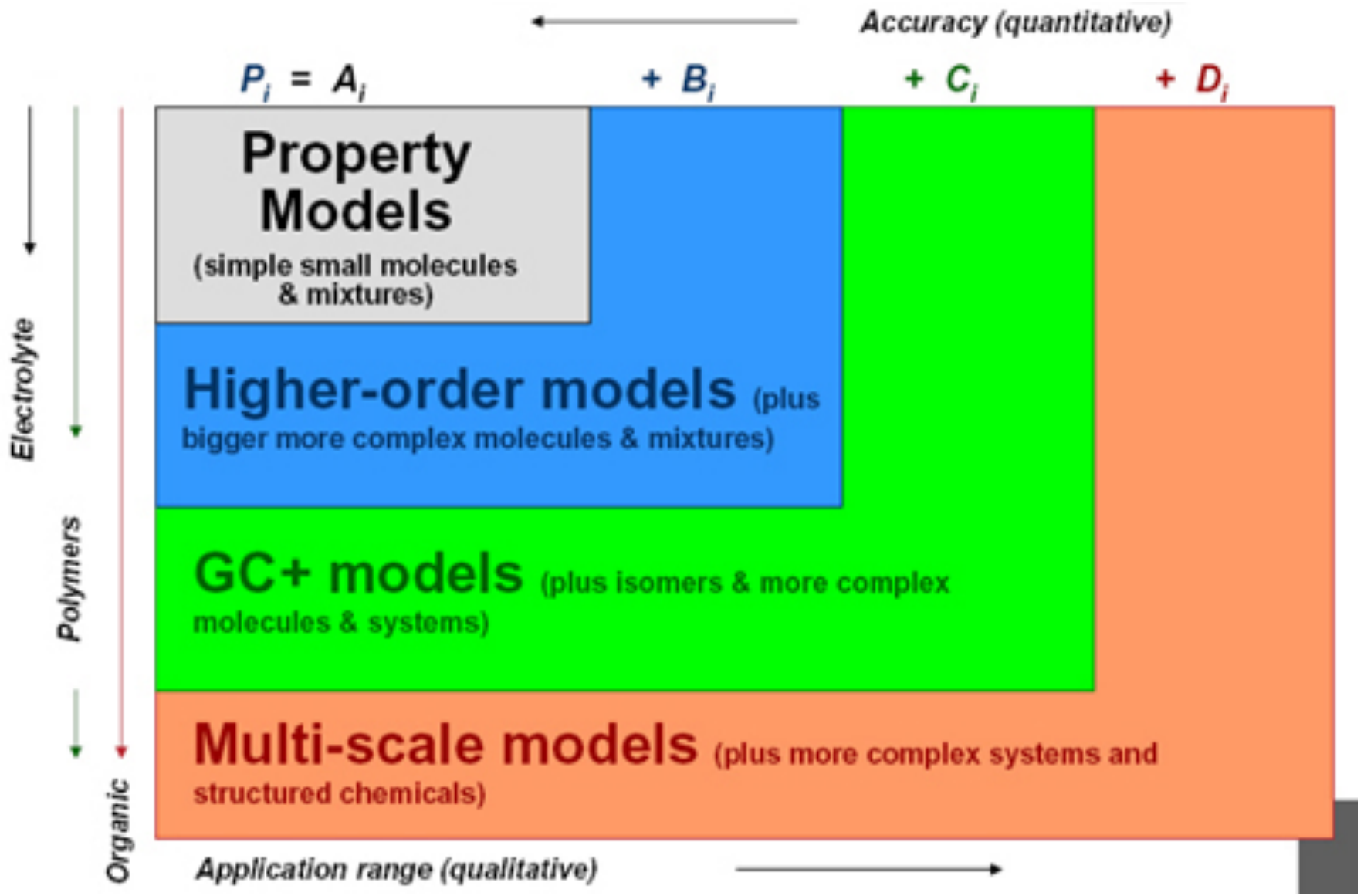
Chemical Product-Process Design

Validation

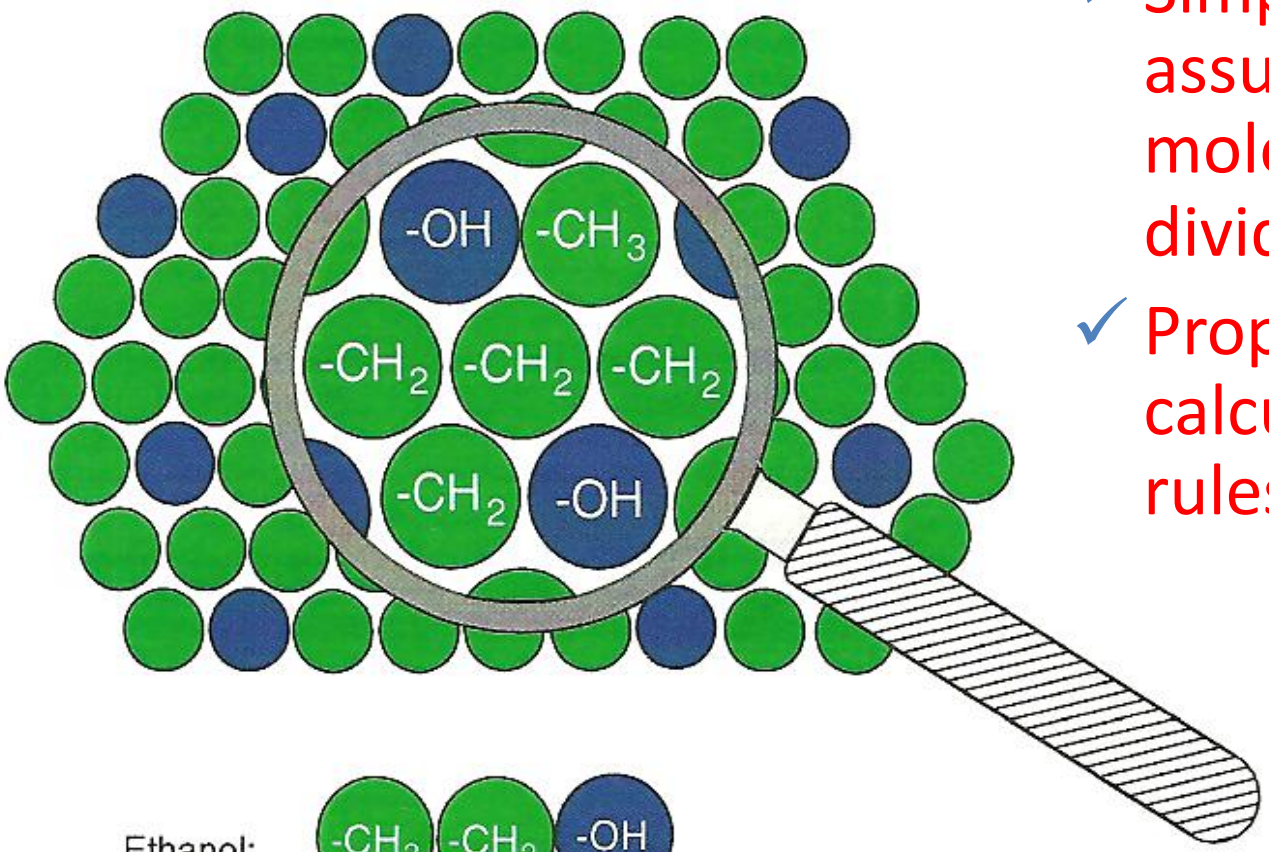


A Computer Framework to ASSIST the design of complex products, molecules, blends,…
Propose solutions using a Knowledge-base system – to validate with experiments at the end

Various levels of property models



The group contribution concept



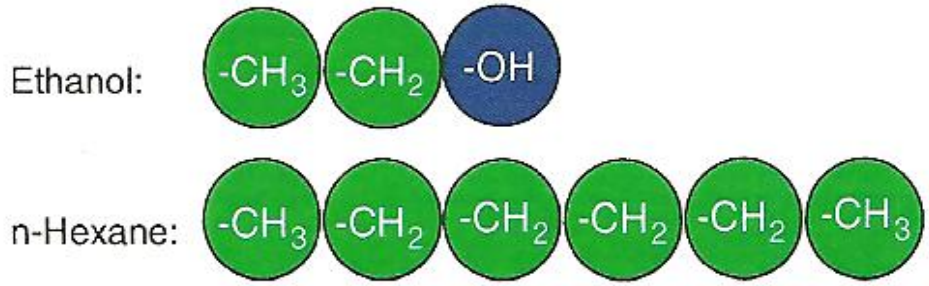


FIGURE 4. Solution of groups-concept.

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

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)
2014	**Nor Alafiza Yunus**	**Blends (gasoline, lubricants)**
2016	**Sawitree Kalakul**	**Jet-fuel blends Diesel blends**
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

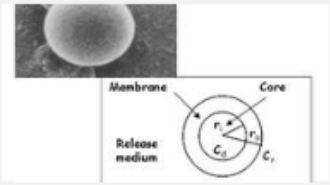
VPPD - Lab

Virtual Product-Process Design Lab

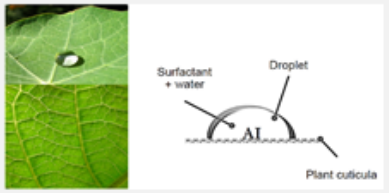
Molecular Design

Design Templates

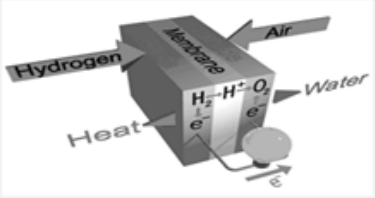
Controlled Release



Uptake of Pesticides



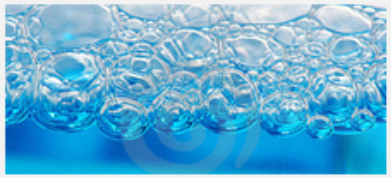
Fuel Cell



Formulation

Blends

Emulsions



Create New Design Template

Help

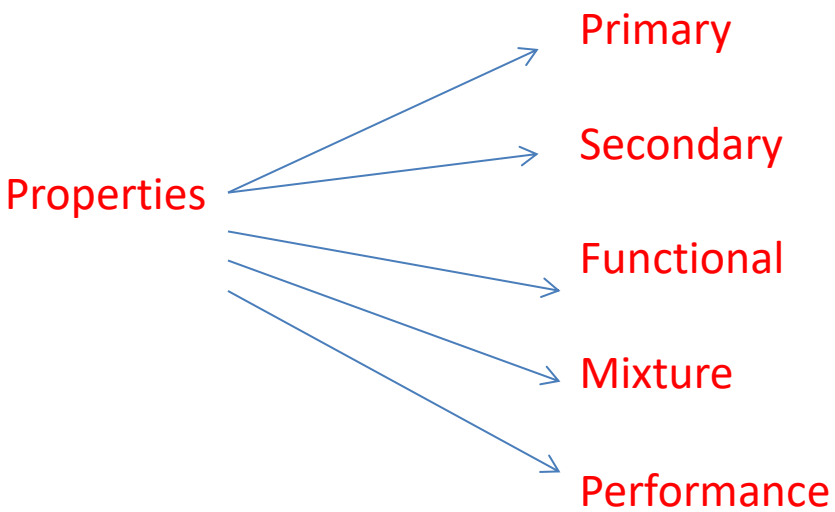
- Help Documents
- Open Solved Example
- Database Search

Integrated Tools

M PRO PRED CAMD

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	



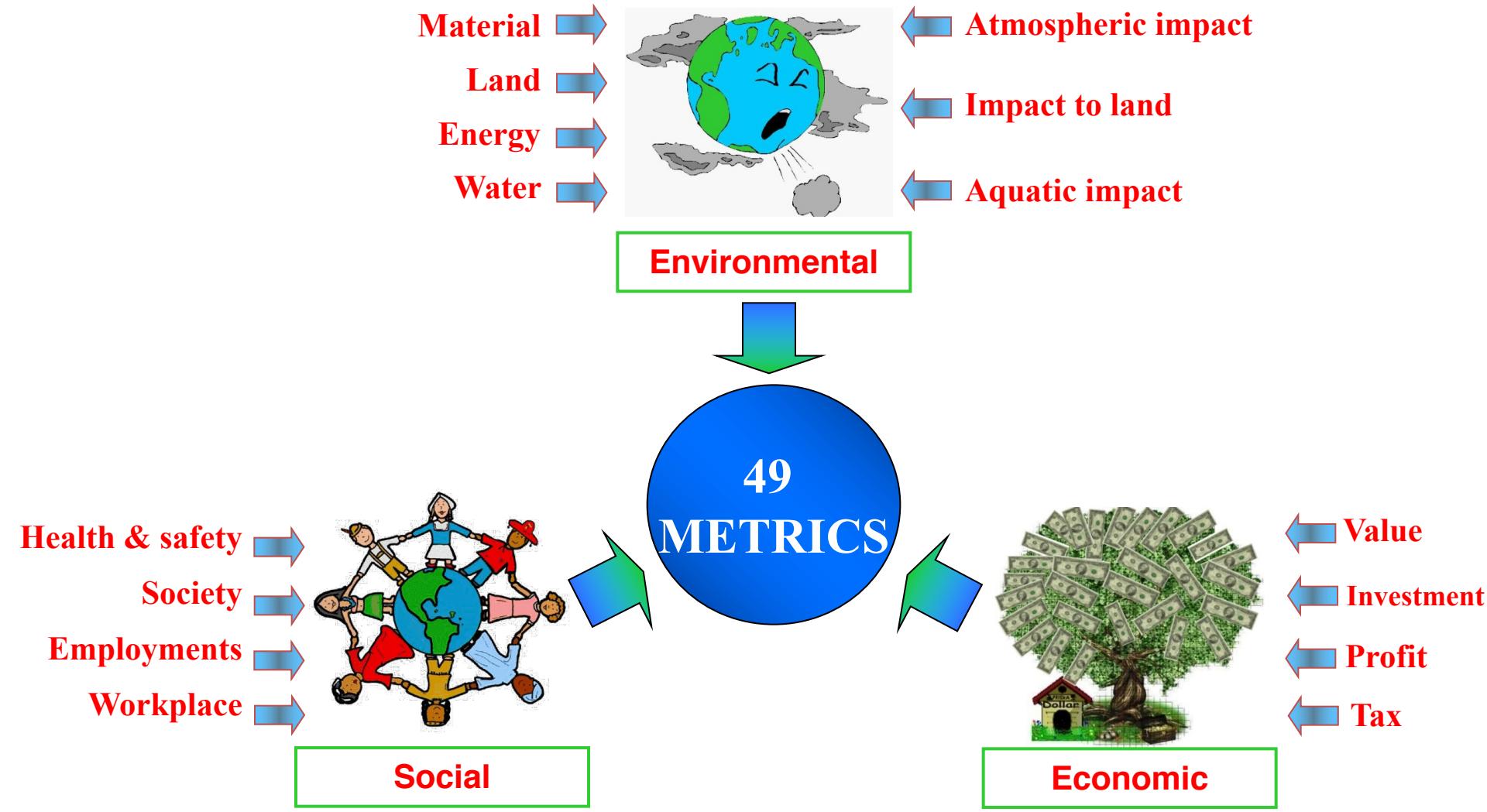
S. Kalakul, 2016 PhD Thesis (DTU)

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_{50} HHV, CO_2 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	

S. Kalakul, 2016 PhD Thesis (DTU)

Issues: Measure of sustainability



Property model functions

Many primary properties including environmental and combustion properties

$$f(X) = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$$

Examples: Higher Heating Value (HHV) developed by Yunus (2014 PhD thesis)
GWP, ODP, LC_{50}

Fossil-fuel Based Aviation Fuels: 2-3% global CO2 Emission (Blakey et al.,2011)

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

CO_2 emission in combustion engine

$$P = \sum_i x_i P_i$$

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

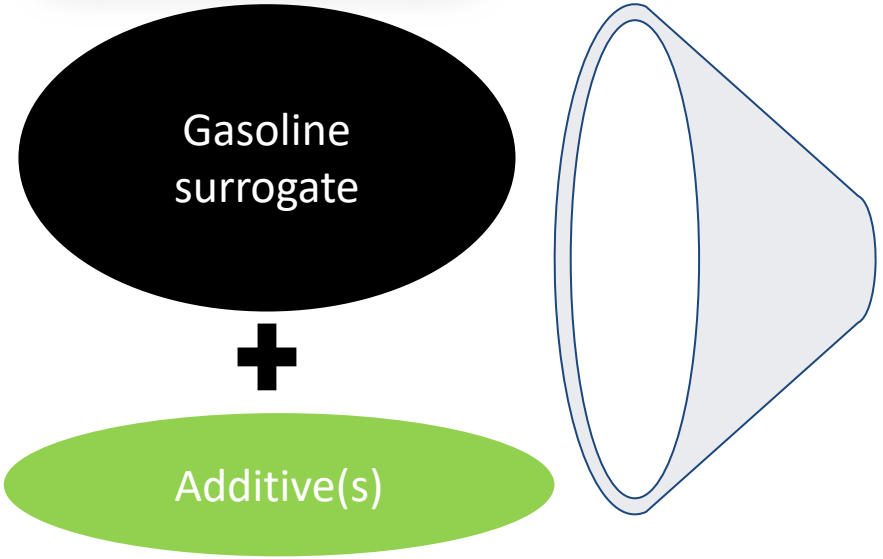
Pseudo-components Of gasoline to Represent the MI

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

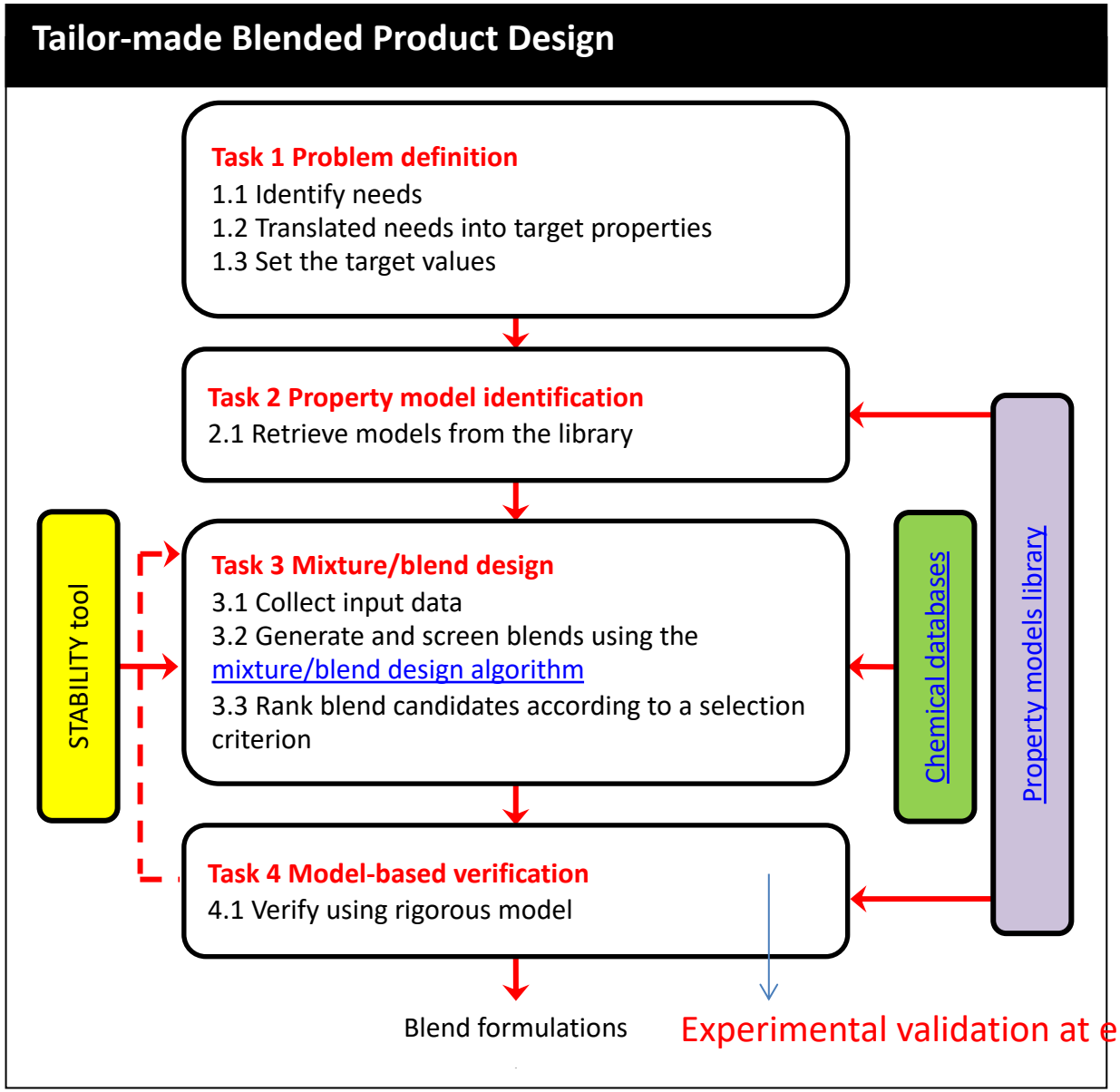


Better performance, safer & lower consumption of conventional gasoline

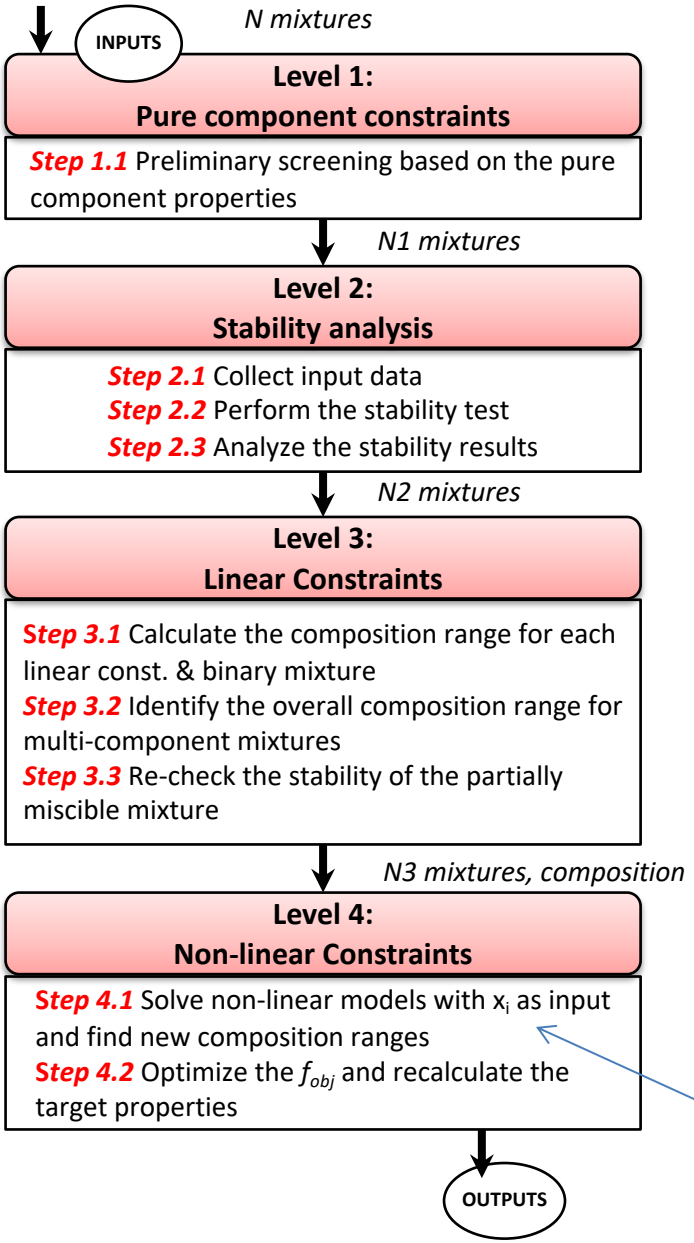
E.g. Alcohols, ethers, ketones, acid/furan derivatives,….)

Work Flow for Product (Blend) Design

N.A. Yunus, 2014 PhD Thesis



Mixture/blend design Algorithm

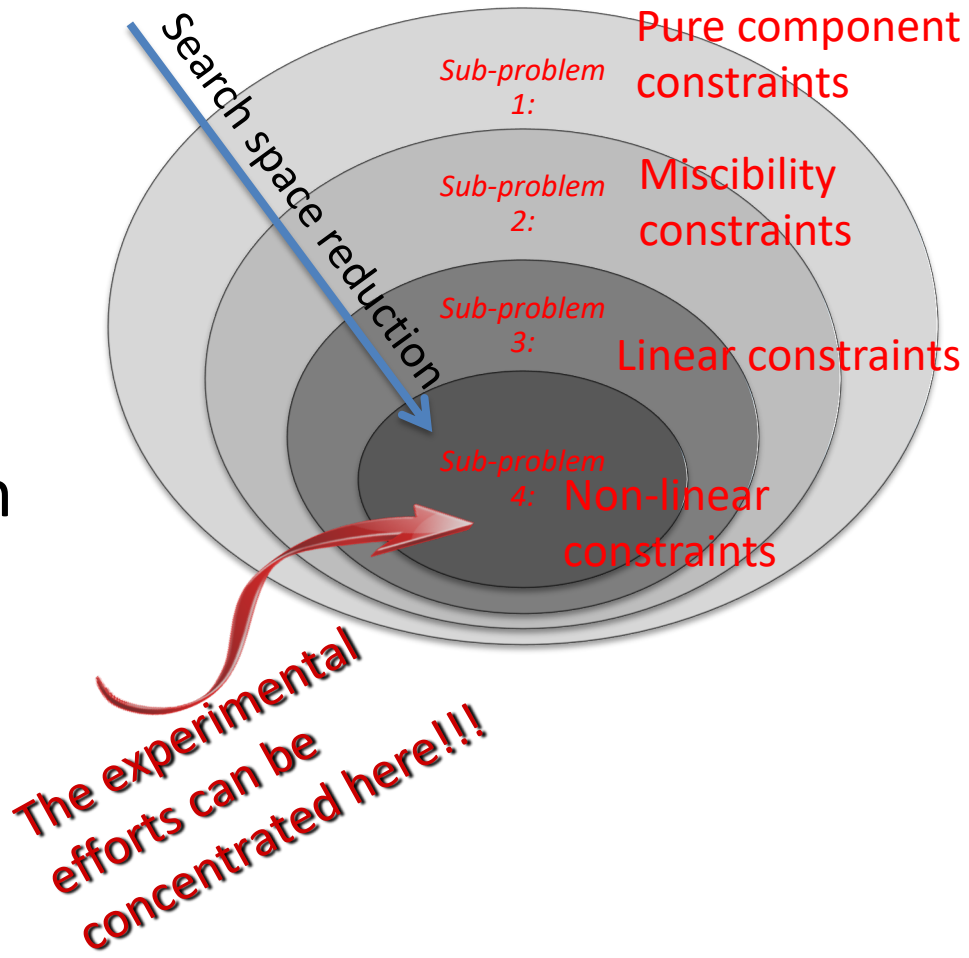


STEP	Method and tools
INPUTS	• Chemicals database, mixture property models • Constraints on the target properties, temperature
Step 1.1	Compare the pure component properties of mixtures
Step 2.1	UNIFAC-LLE group representation for all chemicals and temperature
Step 2.2	STABILITY tool
Step 2.3	List all the miscible, partially miscible or immiscible mixtures.
Step 3.1 and 3.2	Optimize the composition ranges subject to linear constraints, using *linprog* 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 *fmincon* in MATLAB with the maximum number of iterations set to 1000.
Step 4.2	Optimize the problem according to the defined objective function
OUTPUTS	• N4 mixtures, composition, property values

Usually choose one property, and validate for others

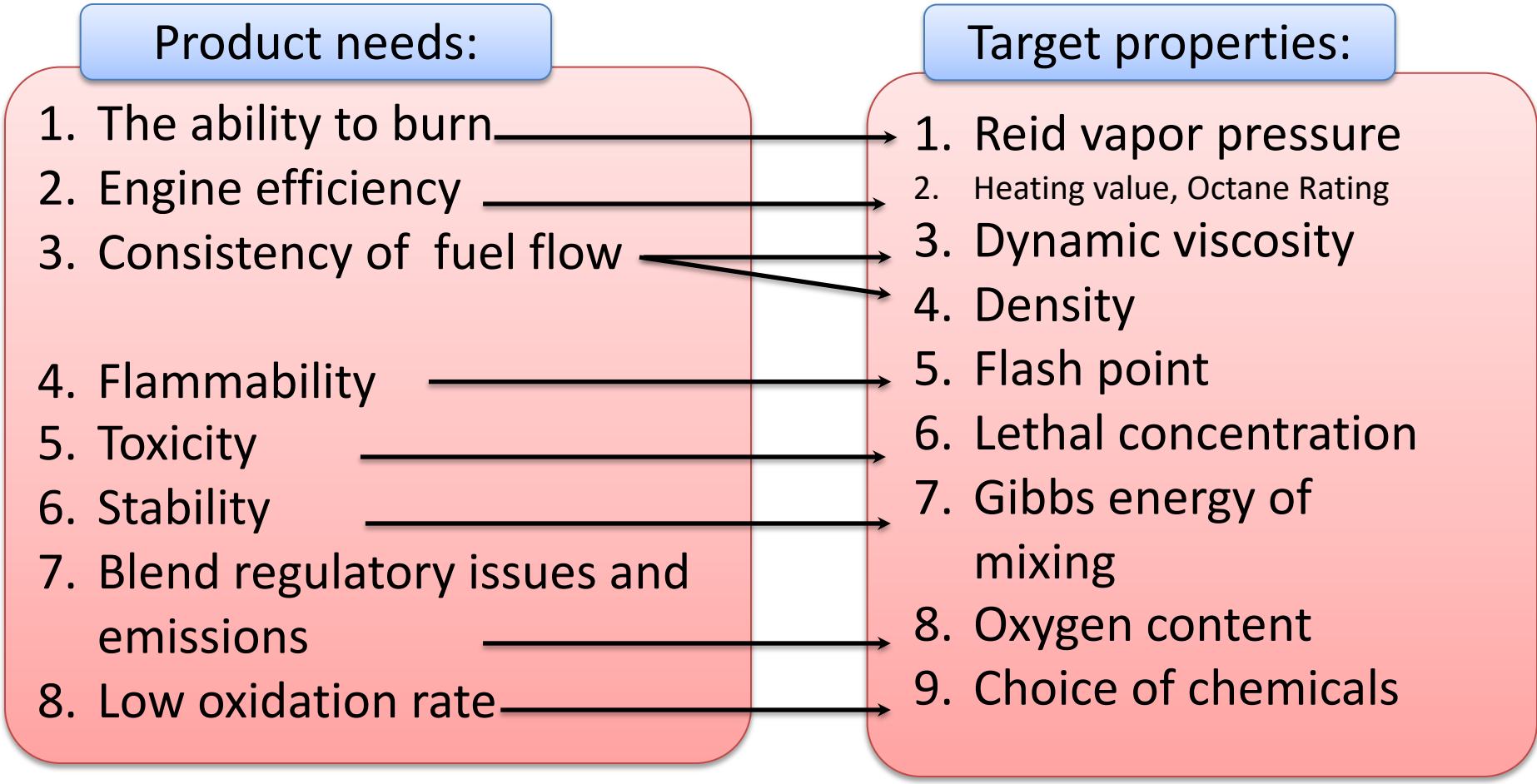
Decomposition Method

- 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



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	η	cP	0.3	0.6
4	Density	ρ	g/cm^3	0.720	0.775
5	Flash point	T_f	K	$-\infty$	300
6	Lethal concentration	$-\log LC_{50}$	mol/L	$-\infty$	3.08
7	Gibbs energy of mixing	ΔG^{mix}	-	$-\infty$	0
8	Oxygen content	Wt_{O2}	-	2	20

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

Also RON >92 in subsequent studies

N.A. Yunus, 2014 PhD Thesis

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	η	Linear mixing rule	$f\,(\eta_i, x_i)$
4	Density	ρ	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	ΔG^{mix}	UNIFAC	$f(GC, x_i)$
8	Oxygen content	Wt_{O2}	Linear mixing rule	$f\,(O_{2,i}, x_i)$

N.A. Yunus, 2014 PhD Thesis

Experimental verification of the surrogate conventional gasoline mixture

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

S. Kalakul, 2016 PhD Thesis (DTU)

MILP/MINLP model formulation at Levels 3 and 4

N.A. Yunus, 2014 PhD Thesis

$$\sum_j y_j = 2$$

$$0.05y_j \le x_j \le 0.2y_j$$

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

Candidate selection and constraints for compositions

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

Viscosity

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

HHV

$$0.72 \le \rho = \frac{\sum_i x_i Mw_i + \sum_j x_j Mw_j}{\sum_i \frac{x_i Mw_i}{\rho_i} + \sum_j \frac{x_j Mw_j}{\rho_j}} \le 0.775$$

Density

$$2 \le Wt_{O2} = \sum_i x_i Wt_{O2,i} + \sum_j x_j Wt_{O2,j} \le 20$$

Oxygen content

$$-\log(LC_{50}) = \sum_i x_i\left(-\log\left(LC_{50,i}\right)\right) + \sum_j x_j\left(-\log\left(LC_{50,j}\right)\right) \le 3.08$$

Lethal concentration, 50%

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

RVP

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

$$T_f \le 27$$

Flash point

$$\Delta G^{mix} = RT\left(\sum_i (x_i \ln x_i + x_i \ln \gamma_i) + \sum_j \left(x_j \ln x_j + x_j \ln \gamma_j\right)\right) < 0$$

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

Stability

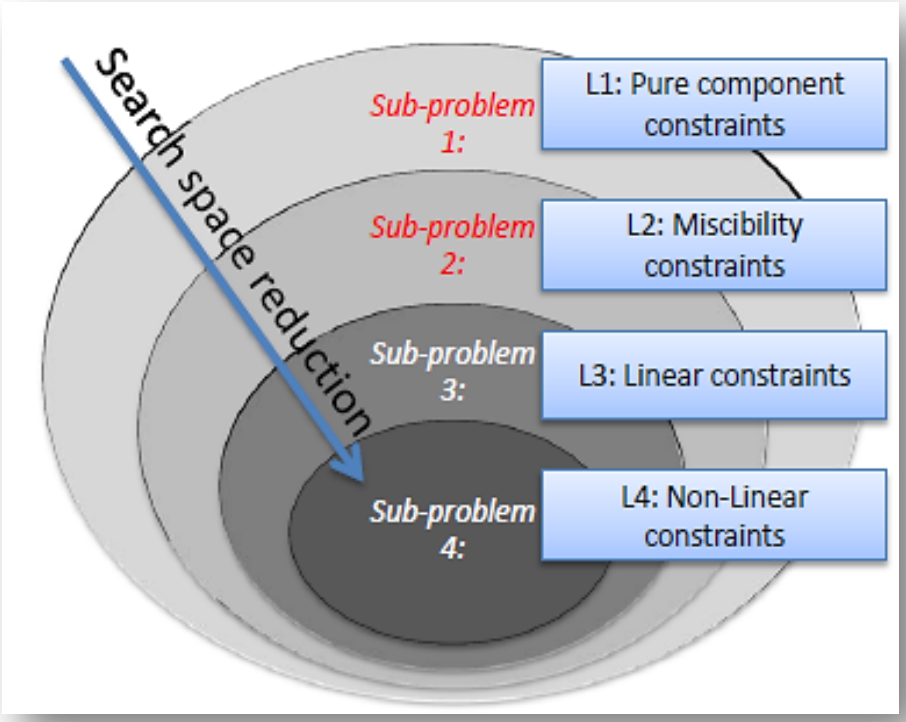
Gasoline Blend Design

1 Pure component constraints (HHV, ρ, η, LC_{50}, $WtO2$)

2 Miscibility constraint (ΔG^{mix})

3 Linear constraints (HHV, ρ, η, LC_{50}, $WtO2$)

4 Non-linear constraints (RVP, Tf)



Miscibility test:
$\Delta G^{Mix} < 0$

Linear Program

$$\min \text{ or } \max \quad f_{obj}(x)$$

$$s.t.$$

$$\zeta_{LB}^{k} \le \sum_{i}^{NC} x_i \zeta_i^k \le \zeta_{UB}^{k}$$

(5 Eqs. One for each prop-erty)

$$\sum_{i=1}^{NC} x_i - 1 = 0$$

$$0 < x_i < 1$$

Nonlinear Program

$$\min \text{ or } \max \quad f_{obj}(x)$$

$$s.t.$$

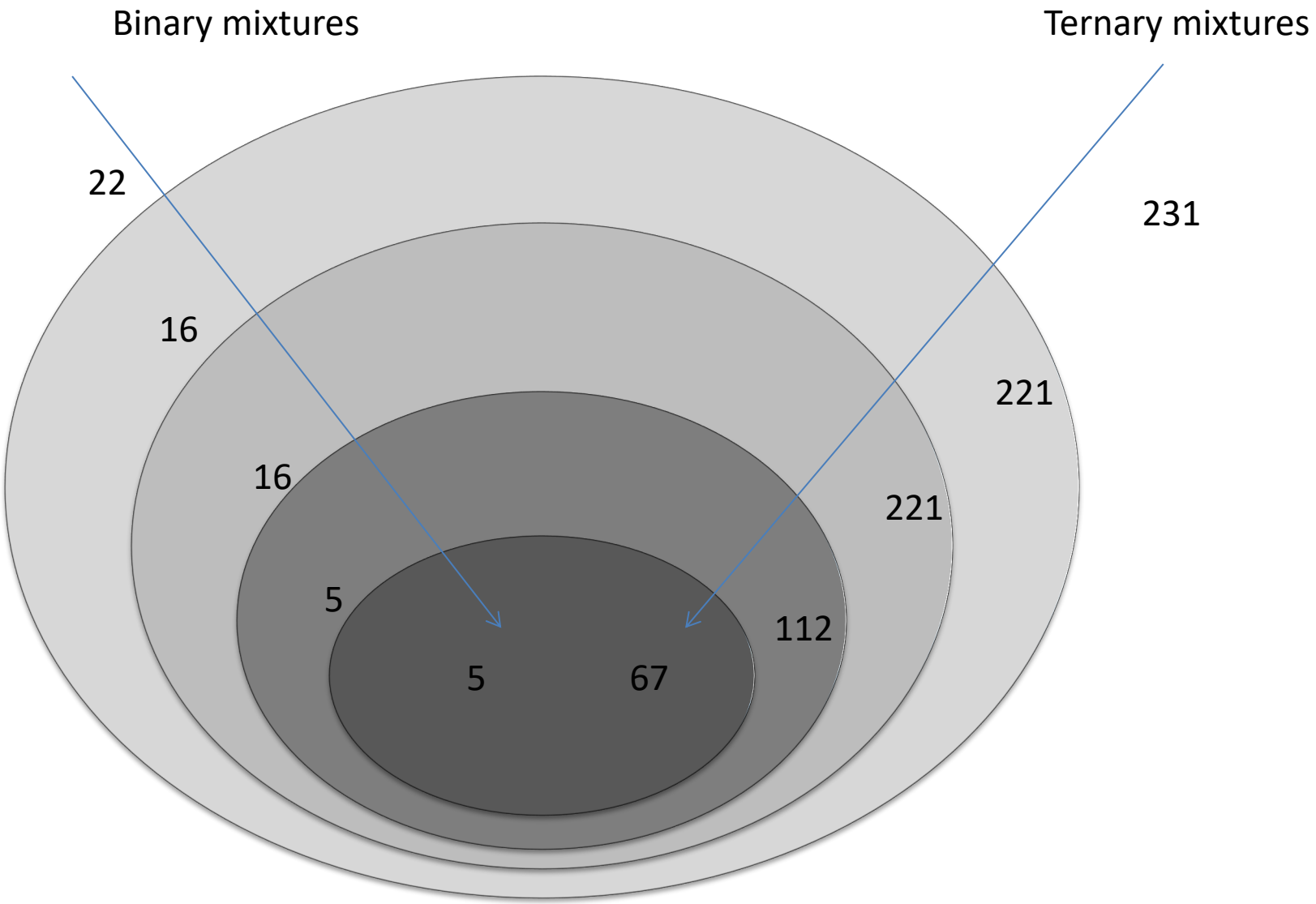
$$\sum_{i=1}^{NC} \frac{x_i \gamma_i P_i^{sat}(310.95\ \text{K})}{RVP_B} = 1$$

$$\sum_{i=1}^{NC} x_i \gamma_i T_{f,i} = T_{f,mix}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0$$

$$x_{LB} < x_i < x_{UB}$$

Solution – case with bio-based chemicals



The Results – ternary and bimary 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_2	RVP	RON	viscosity	LC_{50}
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, Gernaey, Woodley and Gani, 2012. 22th ESCAPE, 17-20.6.2012, London

Yunus, Gernaey, 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)

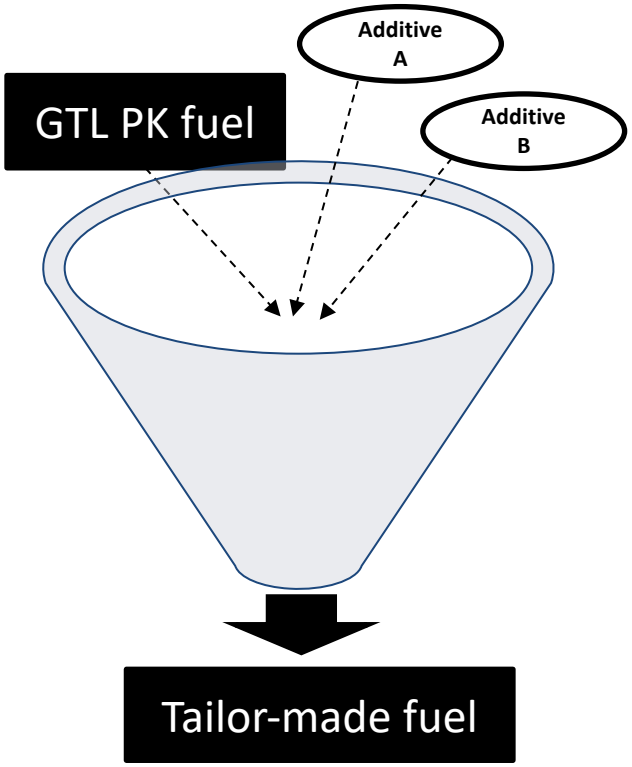
ID	Composition (vol%)	RVP	HHV	η	ρ	Wt_{O2}	LC_{50}	T_f
1	MI (69) THF (11) MeTHF (20)	(1) 45 (2) 46 (3) 46	(1) 42 (2) 41 (3) -	(1) 0.50 (2) 0.48 (3) 0.54	(1) 0.7424 (2) 0.7709 (3) 0.7596	(1) 6.2 (2) 7.2 (3) -	(1) 3.0 (2) 2.7 (3) -	(1) -17 (2) -18 (3) -
2	MI (67) ACE (13) MeTHF (20)	(1) 45 (2) 46 (3) 60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

S. Kalakul and R. Gani

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_2) emissions

Kalakul et al., 2018, CACE, 116: 37-55; Gammon, 2004. ASTM Manual Series, MNL 5.

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	-logLC_{50}	-logLC50 ≤ 4.58	mol/L
Safety/Flammability	Flash point (T_f)	$T_f \geq 38$	°C
Ability to be burned	Reid vapor pressure (RVP) ASTM distillation temperature	RVP ≤ 1 $T_{10} \leq 205$	kPa °C
Consistency of fuel flow	Kinematic viscosity at -20 °C (V) Freezing point (T_{freez})	V ≤ 8 $T_{freez} \leq -40$	mm^2/s °C
Engine efficientcy	Density at 15 °C (ρ) Higher heating value (HHV)	0.775 ≤ ρ ≤ 0.840 HHV ≥ 43	g/mL MJ/kg
Low environmental impacts	CO_2 emission in the combustion engine (CO_2E)	$CO_2E \leq 25.36$	$kgCO_2$/mile

Phase Stability

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

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 properites of GTL PK and additives

GTL PK fuel composition*

Gas chromatography (*GC*)

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

*TEES Gas & Fuels Research Center, Texas A&M University at Qatar

List of additives for tailor-made jet-fuel blends

CAMD technique in ProCAPD

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(Dl)	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

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: CAMbD 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;

$$\max f_{obj} = \sum_{i=2}^{NC} x_i y_i \qquad \cdots(1)$$

Minimize GTL PK (MI) amount
Down to a specific limit

Mixture constraints:

$$\frac{\Delta G^{mix}}{RT} = \sum_i x_i \ln x_i + \frac{G^E}{RT} \qquad \cdots(2)$$

$$\frac{d^2 \Delta G^{mix}}{dx^2} > 0 \qquad \cdots(3)$$

Mixture miscibility

Product property constraints:

$$\phi_k = \sum_i x_i \phi_{i,k} \qquad k = 1,5 \cdots(4)$$

Ideal properties (Linear models)

$$\sum_i \frac{x_i \gamma_i P_i^{sat}(T)}{RVP_B} - 1 = 0 \qquad \cdots(5)$$

$$\sum_i \frac{x_i \gamma_i P_i^{sat}(T)}{P_{i,FP}^{sat}} - 1 = 0 \qquad \cdots(6)$$

Non-ideal properties (Non-linear models)

Process model constraints:

$$\sum_i x_i - 1 = 0 \qquad \cdots(7)$$

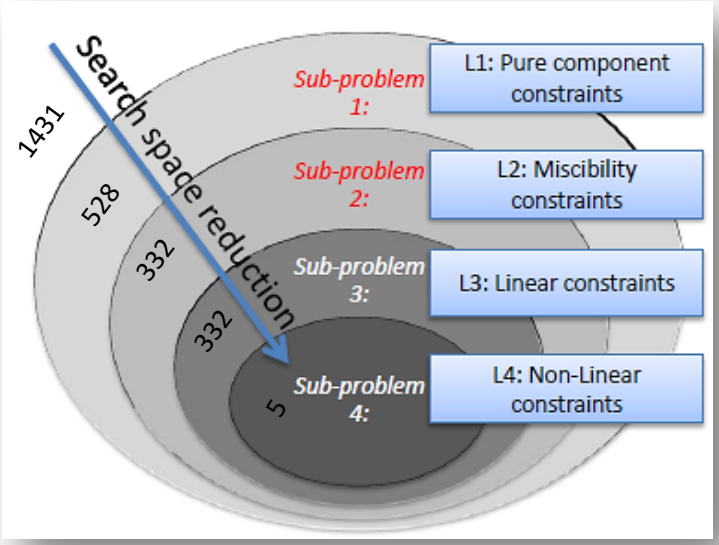
$$0 \le x \le 1, \qquad y \in \{0,1\}$$

Design of a tailor-made jet-fuel blends

❑ STEP-3: CAMbD 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]

[2] 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

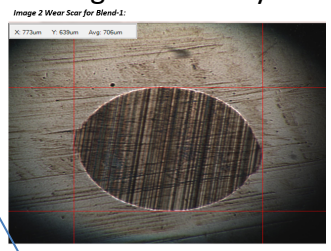
Input: List of promising candidates from STEP-3
Tools: Property calculation toolbox, Jet-fuel design knowledge base
Output: A set of promising blend candidates and property values calculated by rigorous property models and a set of experimental tests for product design verification

- ❑ Rigorous property models to predict η 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*	ρ	CO_2E	$-logLC_{50}$	T_f	T_{10}	T_{50}	T_{90}	T_m	*WSD*
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

Small for good lubricity



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

Improve
All properties

The optimum Blend ID1 composition

Octane, 2-methyl- 2.3
Octane, 3-methyl- 1.8
Nonane 9.3
Heptane, 2,4,6-trimethyl- 0.8
Nonane, 4-methyl- 1.5
Octane, 2,6-dimethyl- 1.5
Octane, 3,6-dimethyl- 1.1
Octane, 4-ethyl- 2.2
Decane 13.7
Nonane, 4-methyl- 2.3
Nonane, 2-methyl- 3.3
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

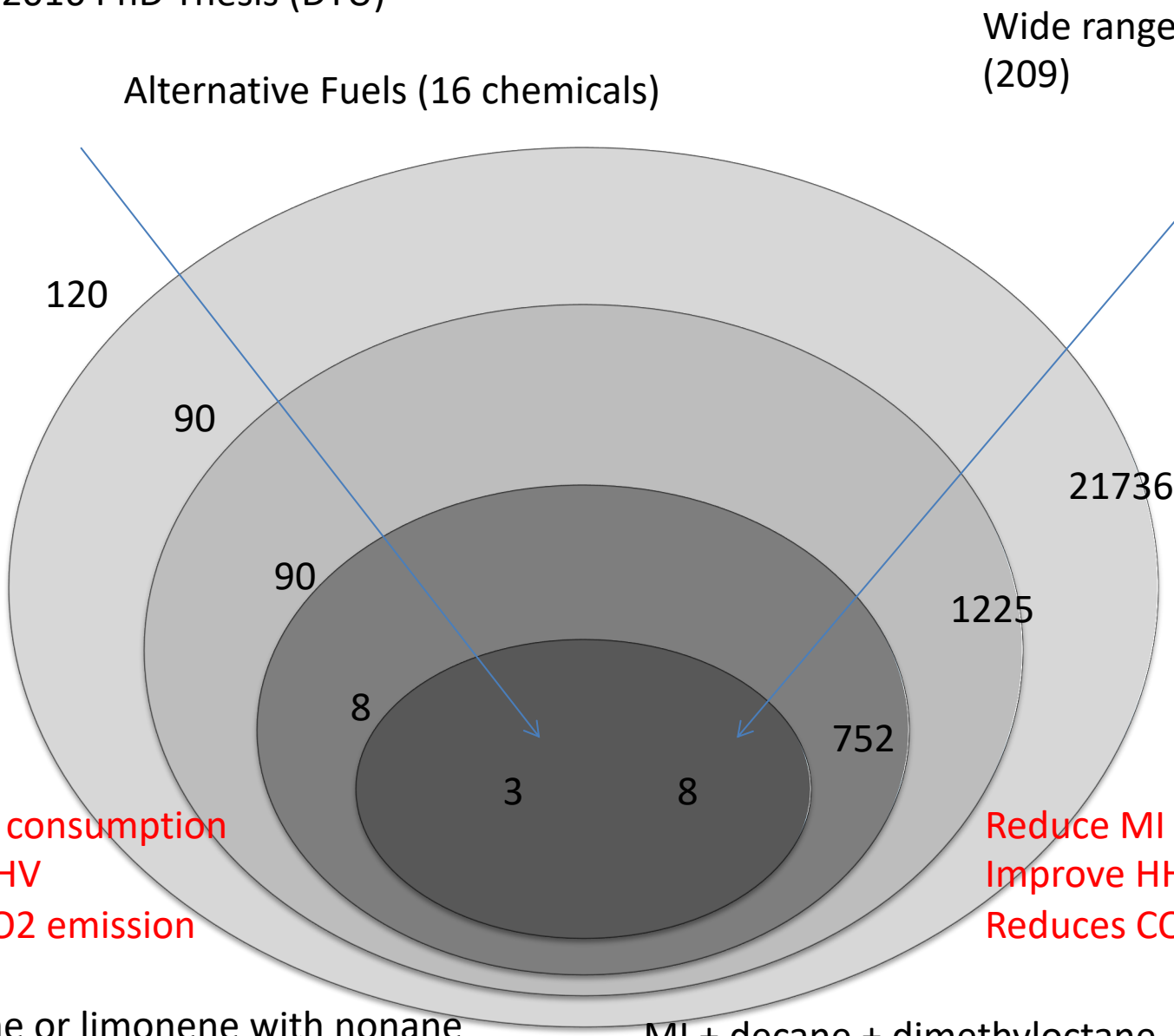
2,3-Dimethyldecane 3.4
Decane, 2,5-dimethyl- 1.2
Decane, 4-ethyl- 1.0
Undecane, 5-methyl- 1.4
Undecane, 4-methyl- 0.9
Undecane, 2-methyl- 1.1
Undecane, 3-methyl- 0.8
Decane, 2,6,6-trimethyl- 1.3

Decalin 18.0
Hexylbenzene 5.0

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

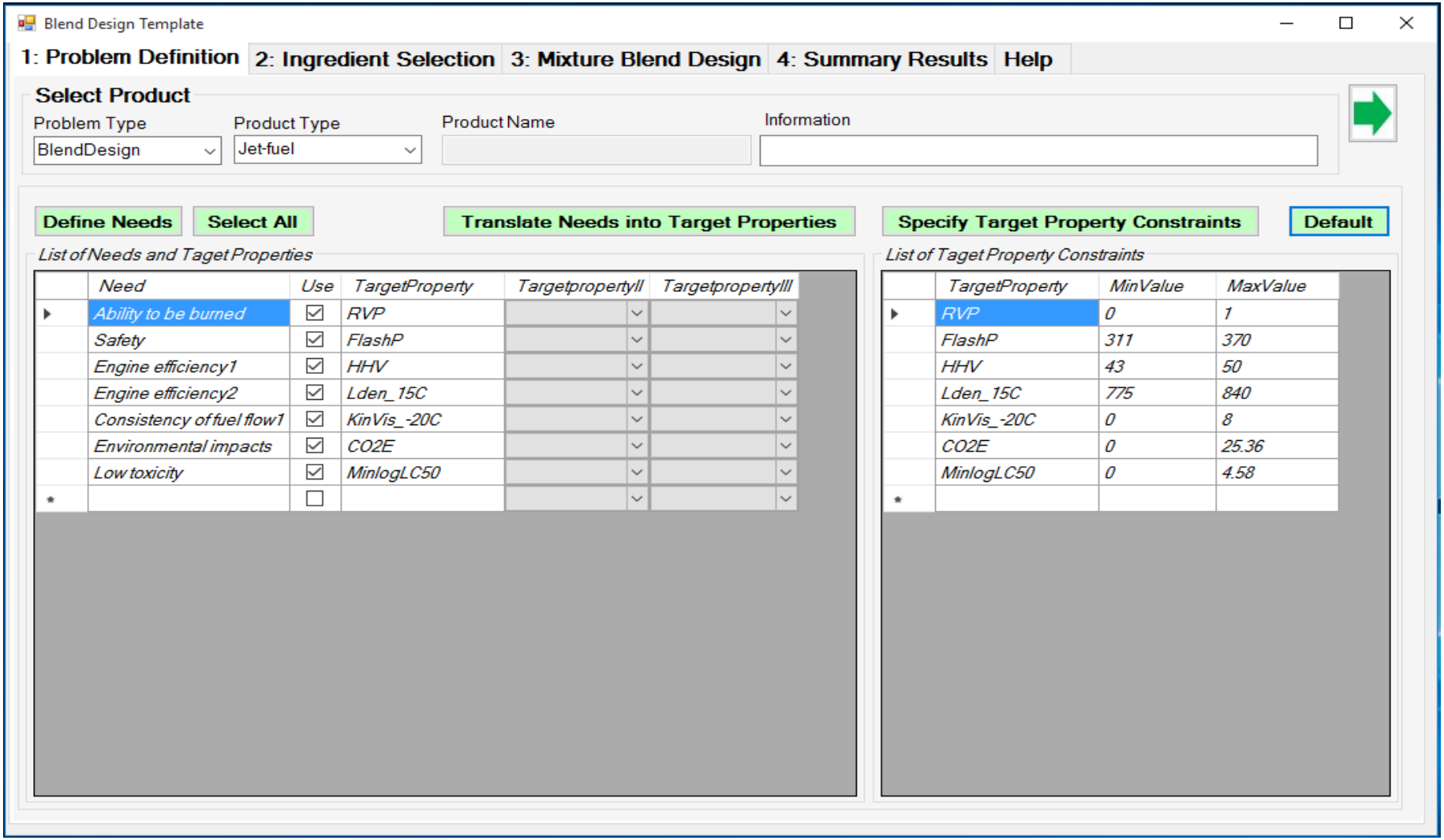
Flexibility in the approach e.g. change of database

S. Kalakul, 2016 PhD Thesis (DTU)



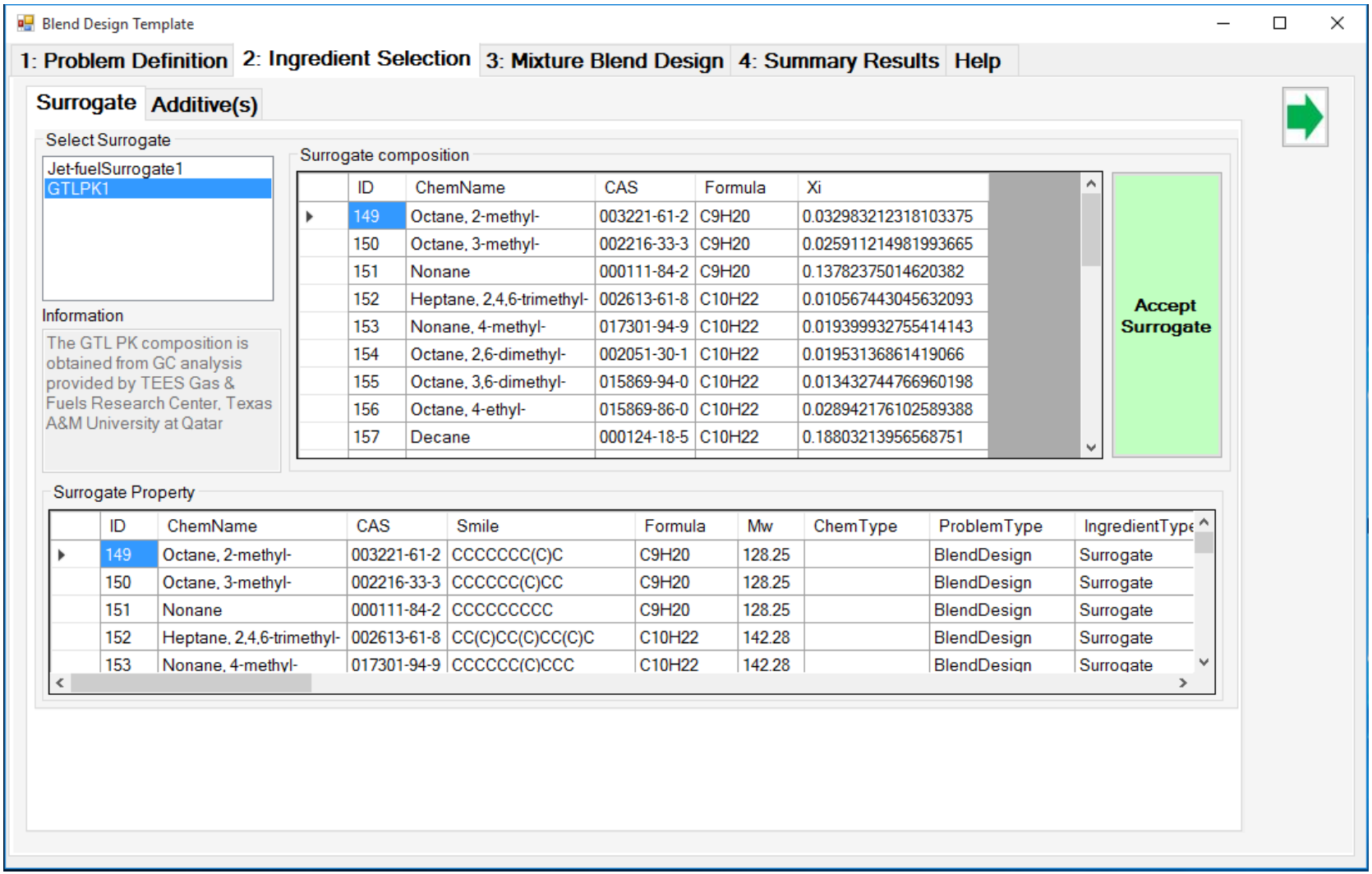
Design of a tailor-made jet-fuel blends

Screenshot of step-1 using Blend Design Template in ProCAPD



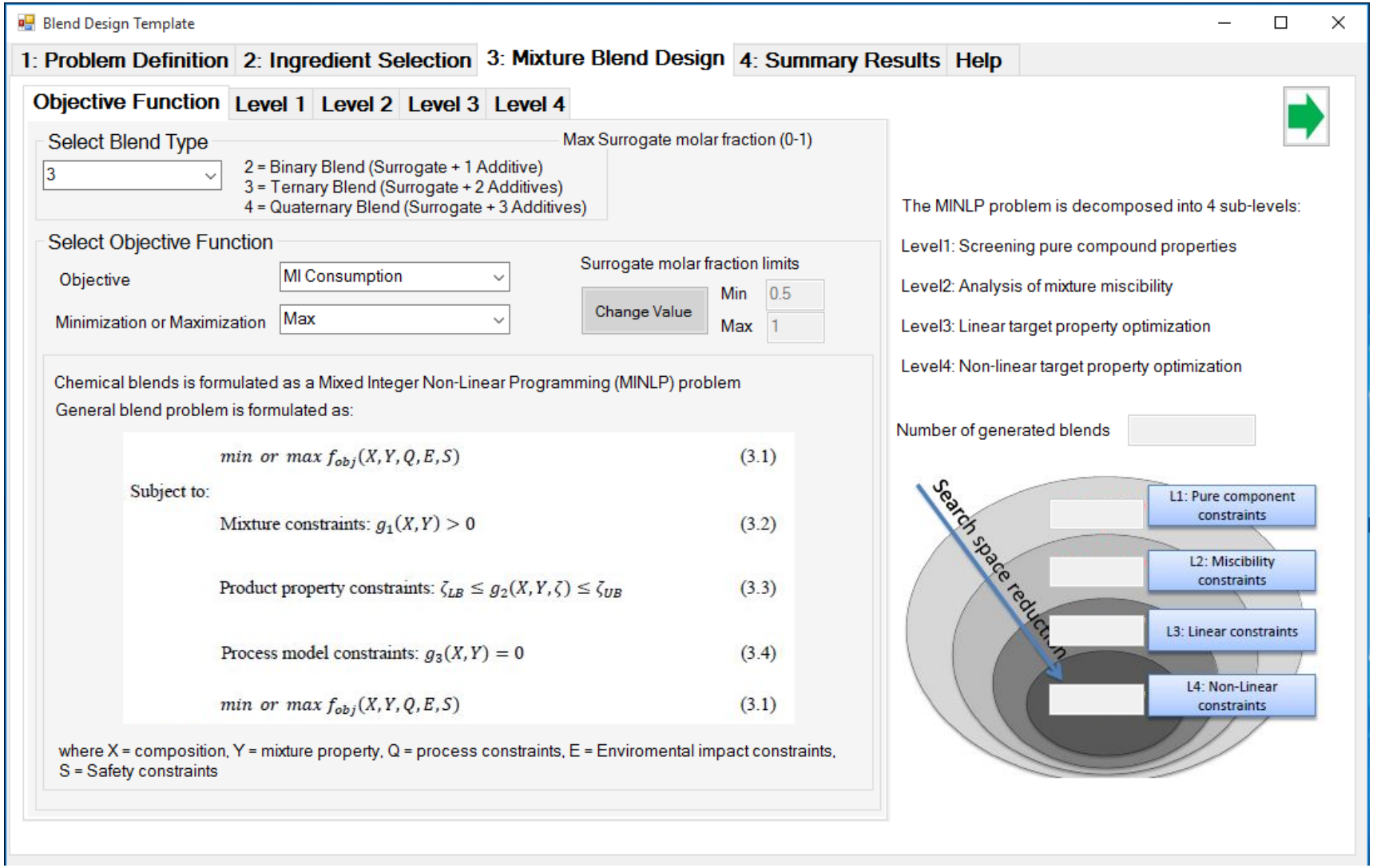
Design of a tailor-made jet-fuel blends

Screenshot of step-2 using Blend Design Template in ProCAPD



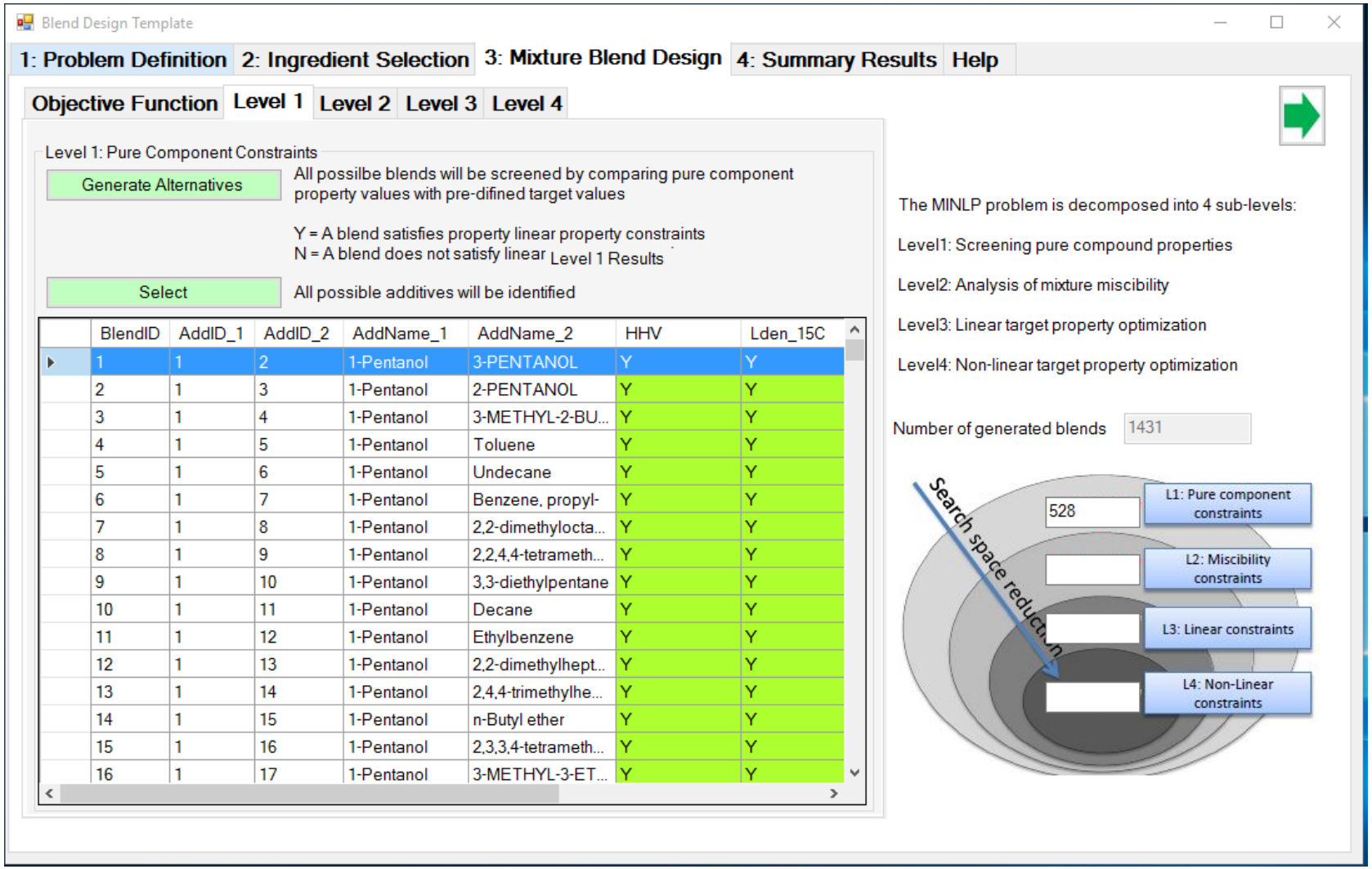
Design of a tailor-made jet-fuel blends

Screenshot of step-3 Objective function identification



Design of a tailor-made jet-fuel blends

Screenshot of step-3 Level1: Pure component



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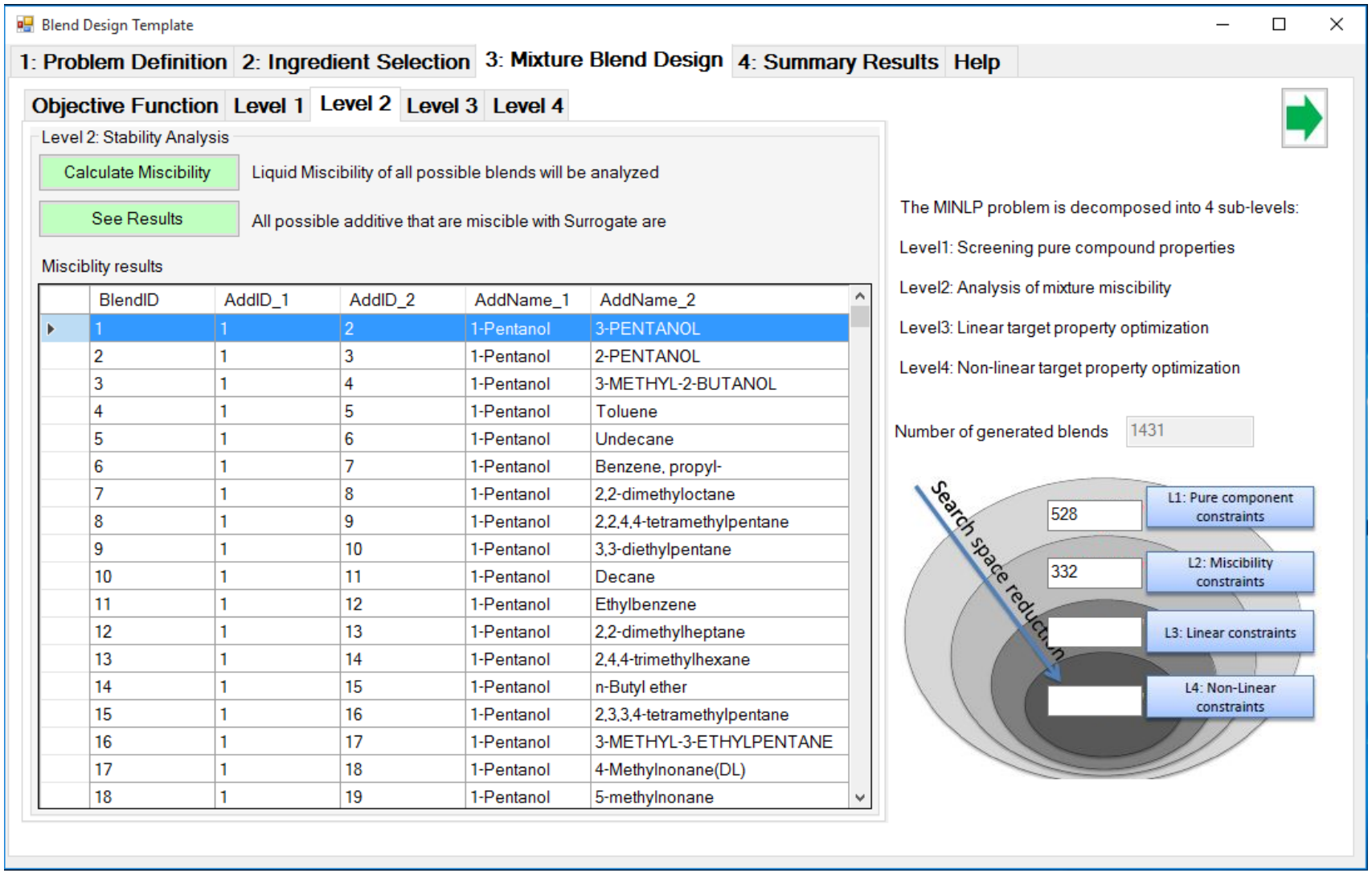
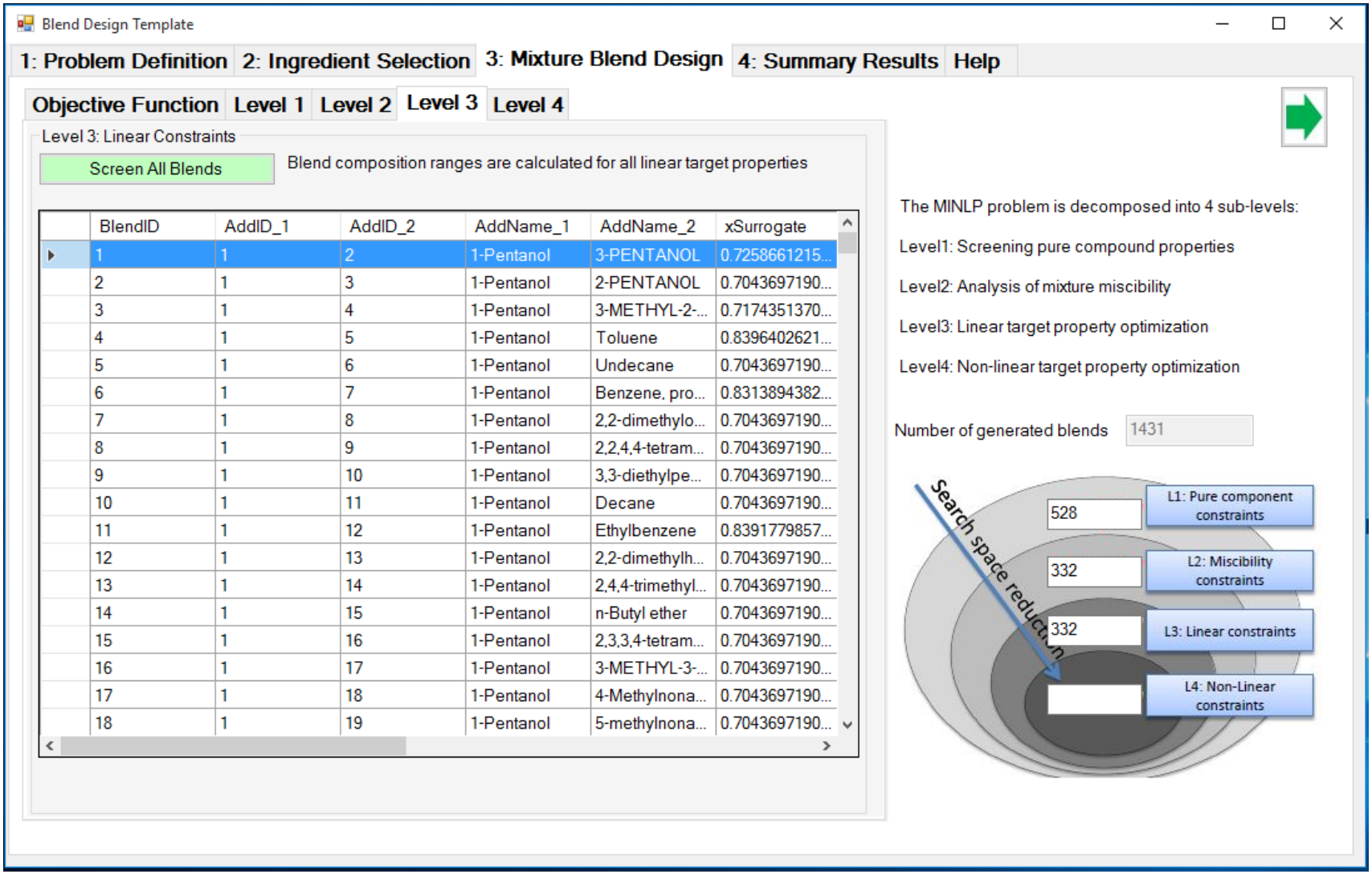
Screenshot of step-3 Level2: Miscibility constraints



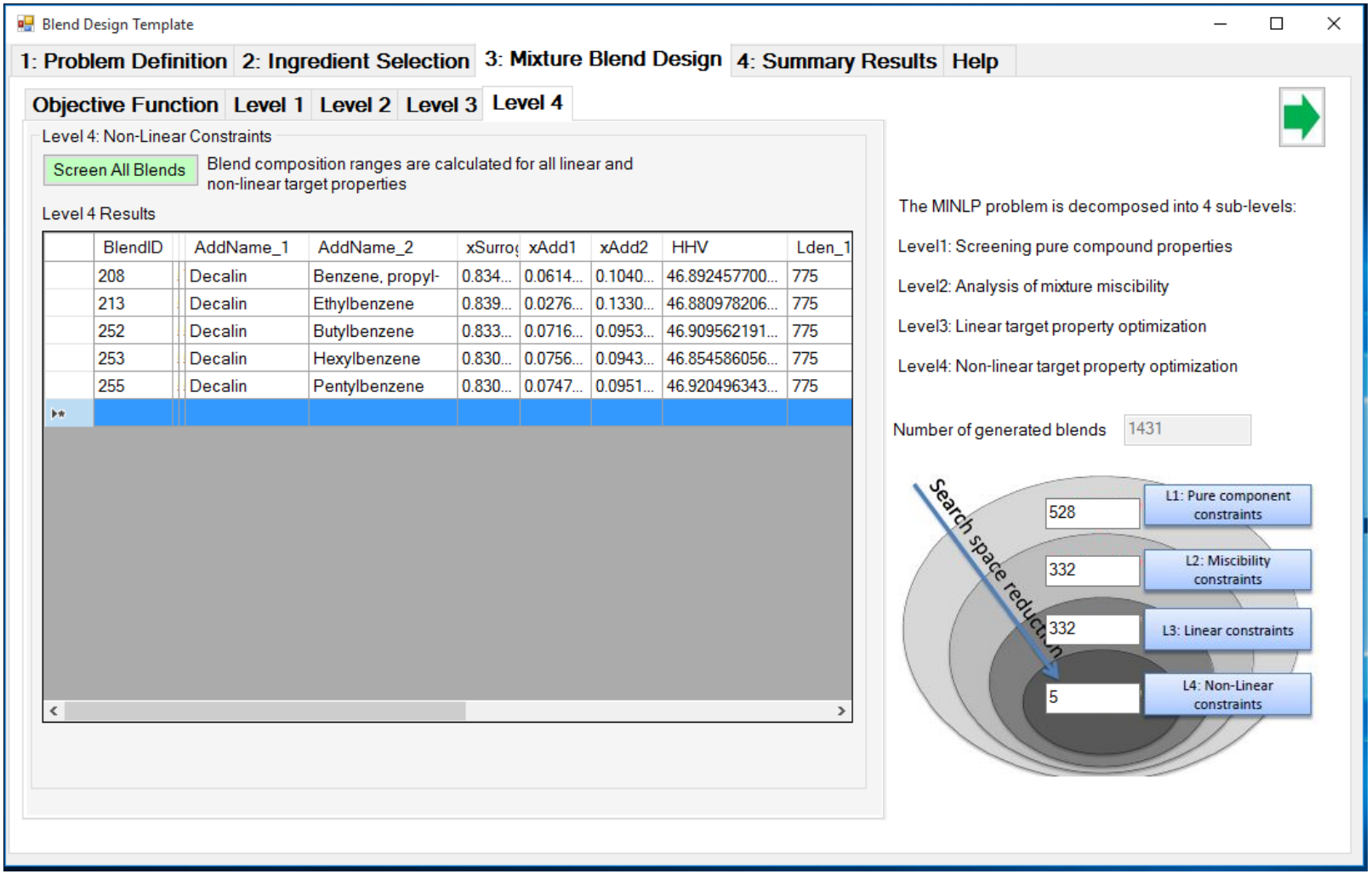
Design of a tailor-made jet-fuel blends

Screenshot of step-3 Level3: Linear optimization



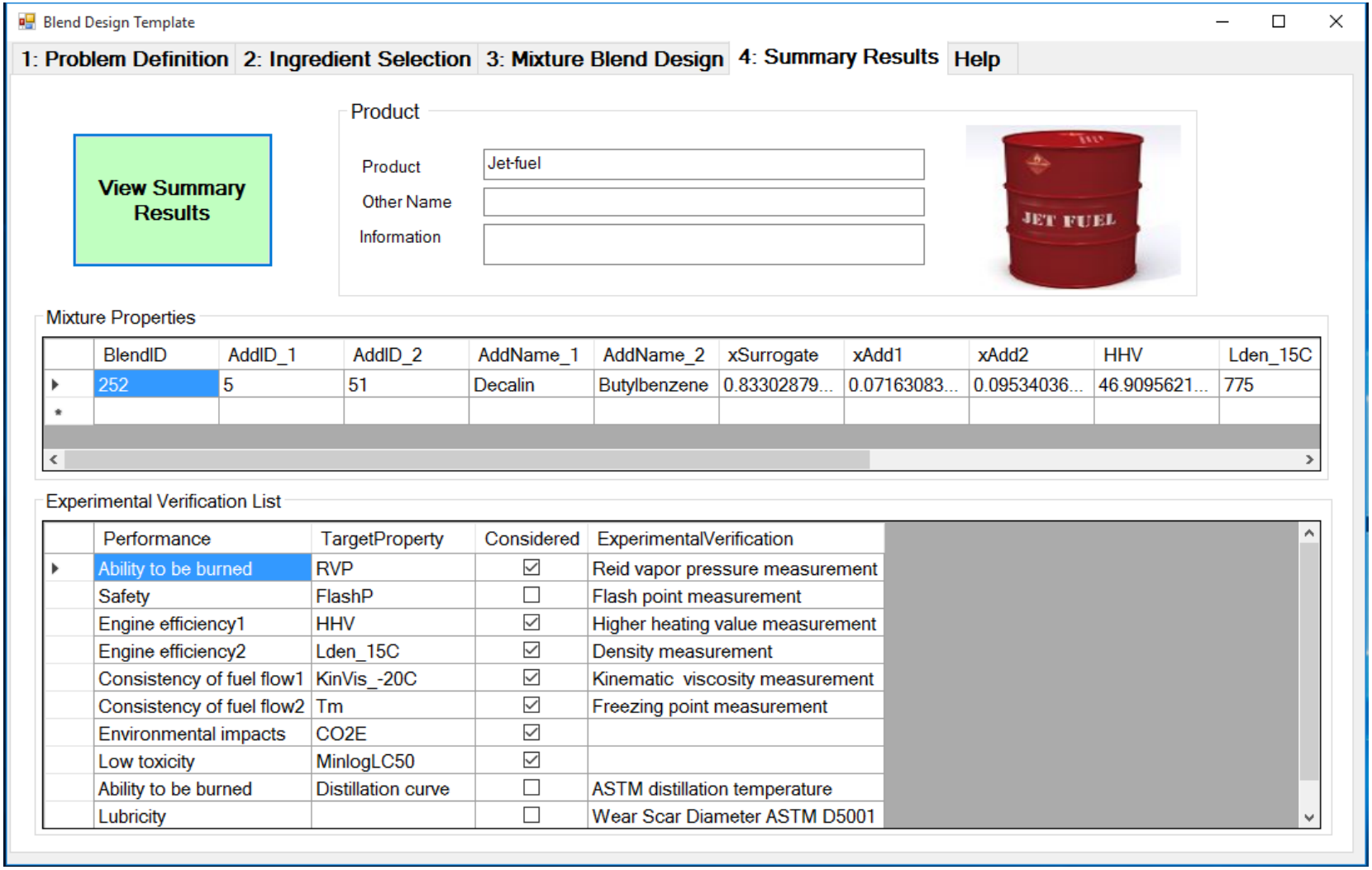
Design of a tailor-made jet-fuel blends

Screenshot of step-3 Level4: Non-linear optimization



Design of a tailor-made jet-fuel blends

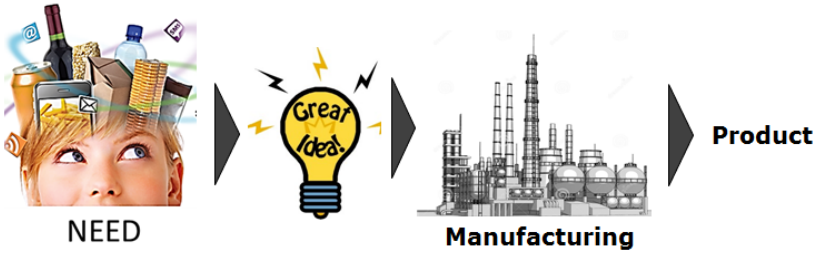
Screenshot of summary results



CHEMICAL PRODUCT DESIGN (CPD)

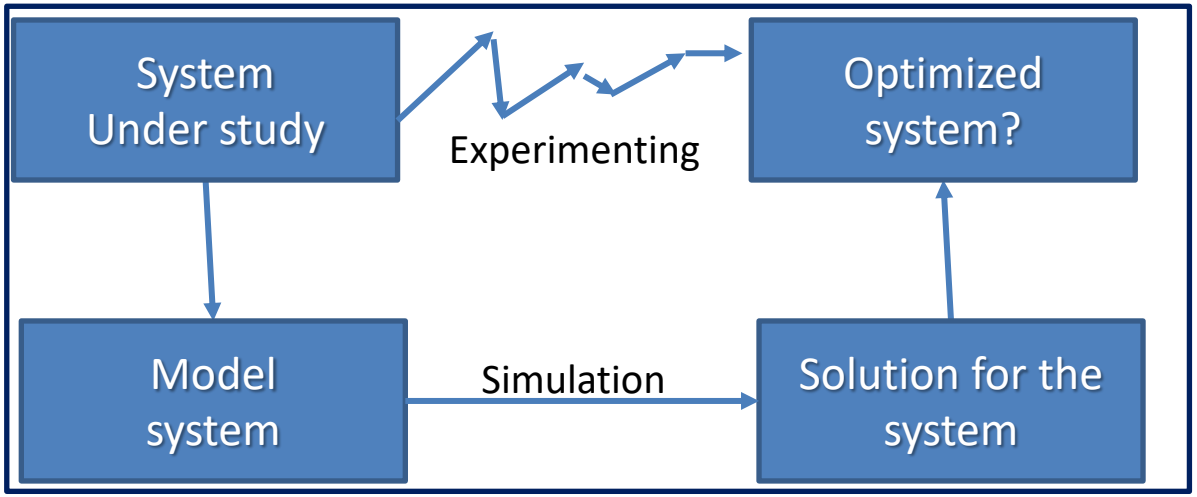
Why CPD

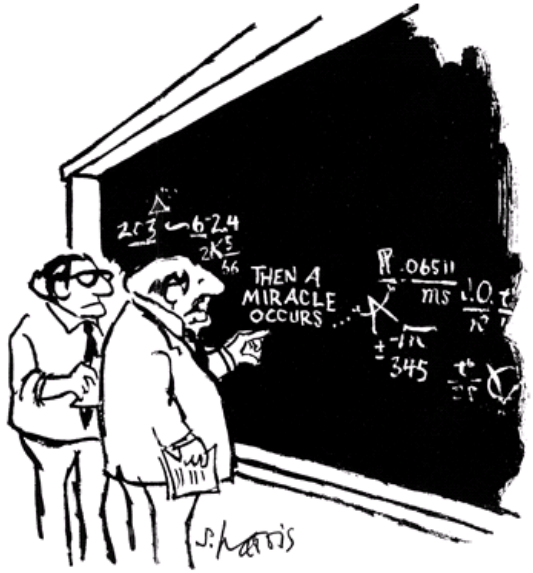
Synthesize and design chemical products that exhibit desirable target behaviour and test for their performance



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."