Co-processing of virgin oils, wastes oils & fats and advanced feedstocks – Challenges and solutions

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Haldor Topsoe A/S

ETIP 10th Plenary session (November 16-18, 2021)

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Take-home message

Feedstocks

Different renewable feeds demand different catalysts and process considerations

Challenges for 1st and 2nd generation feedstocks

Co-processing challenges can be handled with proper know-how, catalysts and technology

Advanced feedstocks

Co-processing has a high potential to upgrade advanced feedstocks but new challenges need to be addressed (miscibility, stability, product quality e.g.)

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Introduction

A wide range of renewable feedstocks are available to produce biofuels

1st Generation

VIRGIN OILS
Rapeseed oil
Palm oil
Sunflower oil
Soybean oil

2nd Generation

WASTE OILS AND FATS
Used Cooking Oils (UCO)
Animal Fats
Distillers Corn Oil (DCO)
Crude tall oil (CTO)

Palm Oil Mill Effluent (POME)
Palm Fatty Acid Distillate (PFAD)
Spent Bleaching Earth Oil (SBEO)

3rd Generation

SOLID WASTE BIOMASS
Agricultural residue
Sewage sludge
Forestry residue
Organic fraction of MSW

LOW ILUC/ROTATIONAL CROPS
Carinata
Castor
Micro or macro algae

RECYCLED CARBON
Mixed plastic waste
End of life tires

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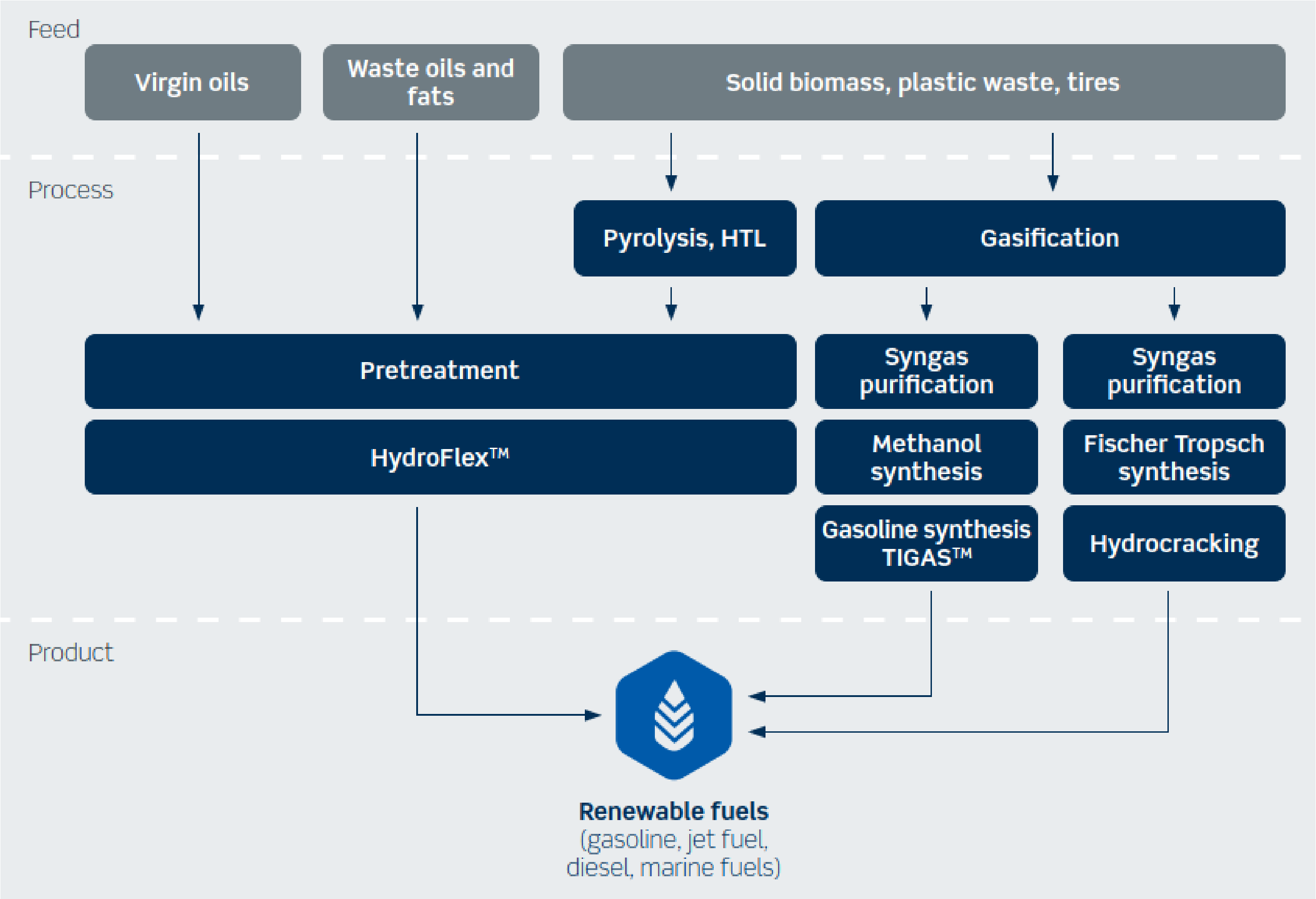
Many pathways exist depending on the feedstock and the desired product



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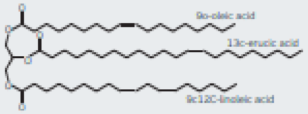
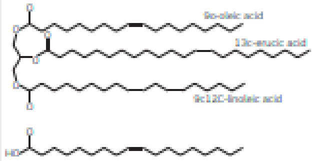
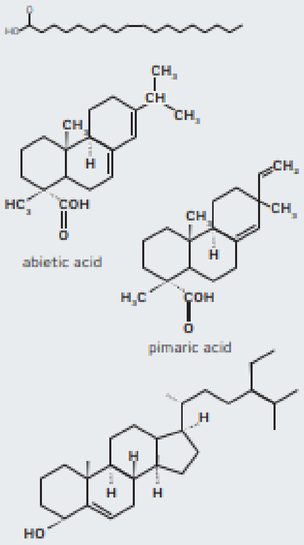
Understanding the feedstock chemistry is key for defining the upgrading strategy

Vegetable oils	UCO, POME Animal fats	Crude tall oil	Fischer Tropsch synthesis product	Pyrolysis oils HTL oils
Fatty acids	Fatty acids Free fatty acids	Free fatty acids Resin acids Neutrals	Alkanes Aromatics Ketones Alcohols	Carboxylic acids Ethers Furans Sugar derivatives Alcohols Hydrocarbons Aldehydes Phenols Ketones...







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There are 5 main options to enter the world of renewables

Processing renewables

Co-processing

Option 1
Catalyst loading

- Co-processing up to 10% renewables with minimal impact on your existing refinery
- Requires loading new catalysts

Option 2
Revamp

- Revamp existing reactor up to 99% co-processing
- Requirements differ depending on capacity for renewable feedstock

Option 3
Grassroot

- New unit to co-process up to 99% renewable feedstocks
- Flexibility to design for optimal performance

Stand-alone

Option 4
Revamp

- Revamp for 100% renewable feedstock
- Requires metallurgical upgrade of both reactor internals and reactor weld overlay

Option 5
Grassroot

- Full feedstock and product flexibility – and a future-proofed business
- Requires a new build with a layout tailored to processing any type of feedstock

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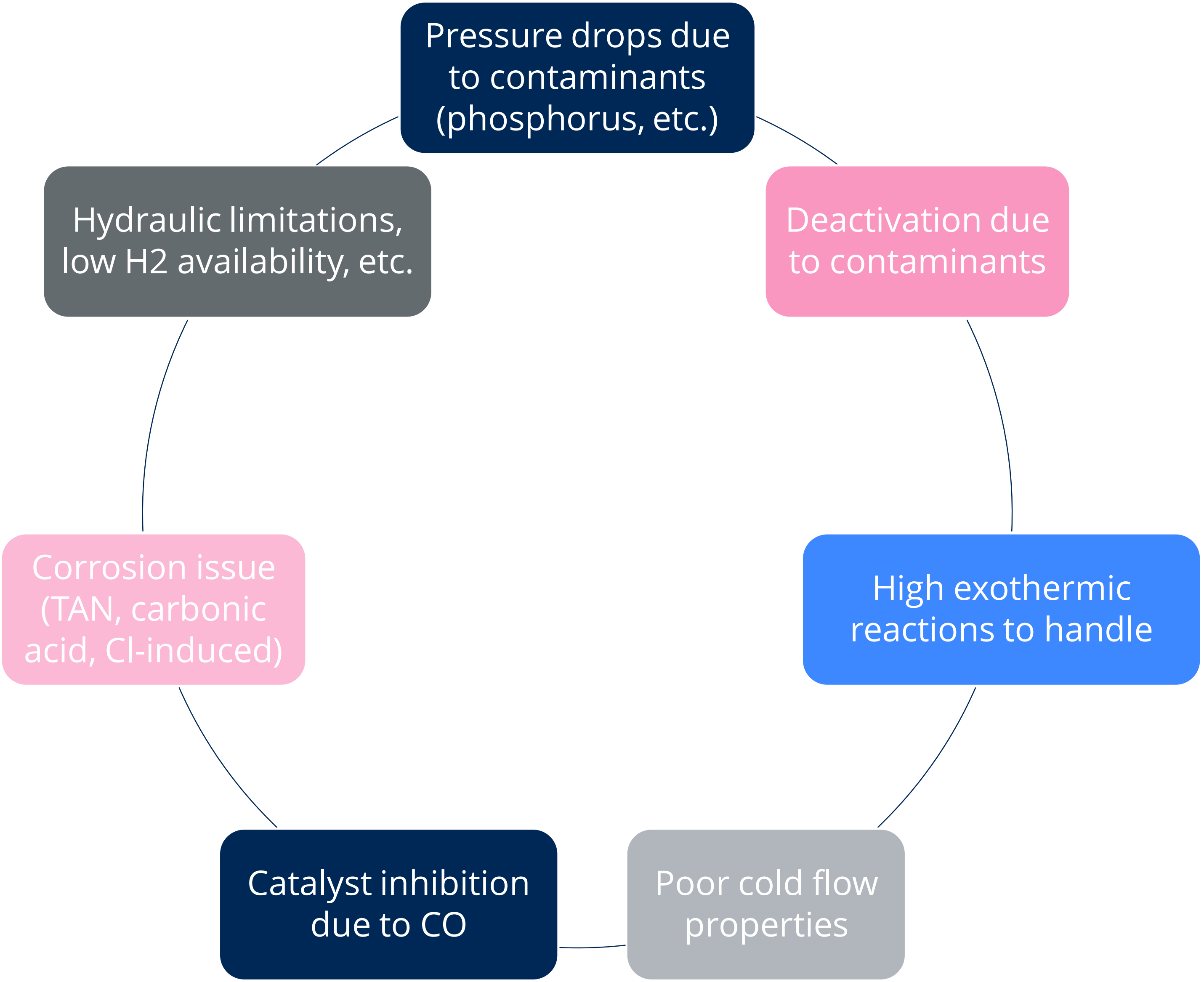
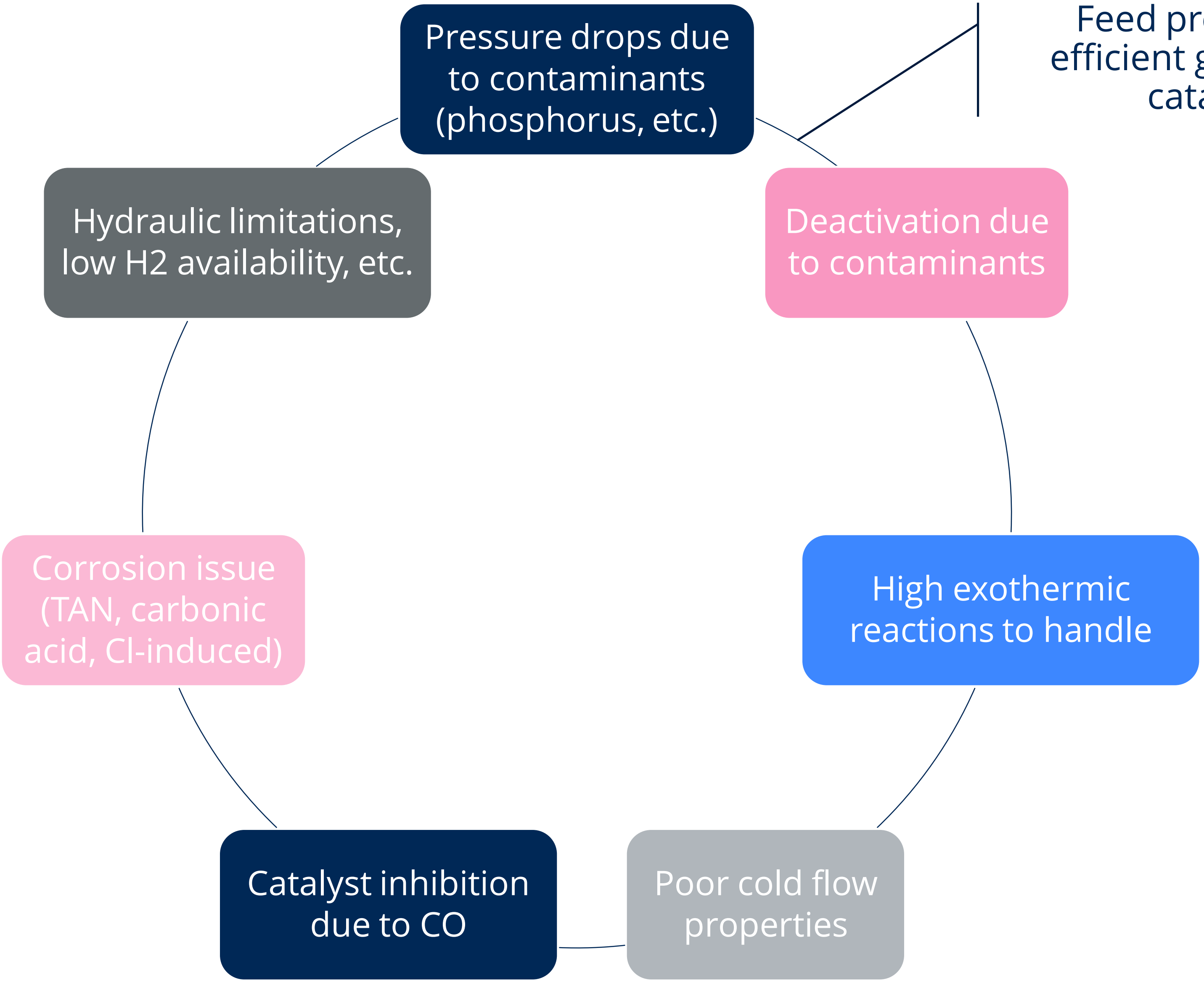
Co-processing of virgins oils and waste oils & fats is a well-established technology

What are the potential issues when co-processing 1st and 2nd generation feedstocks?



What about the solutions?



Feed pre-treatment and efficient guard and grading catalyst system

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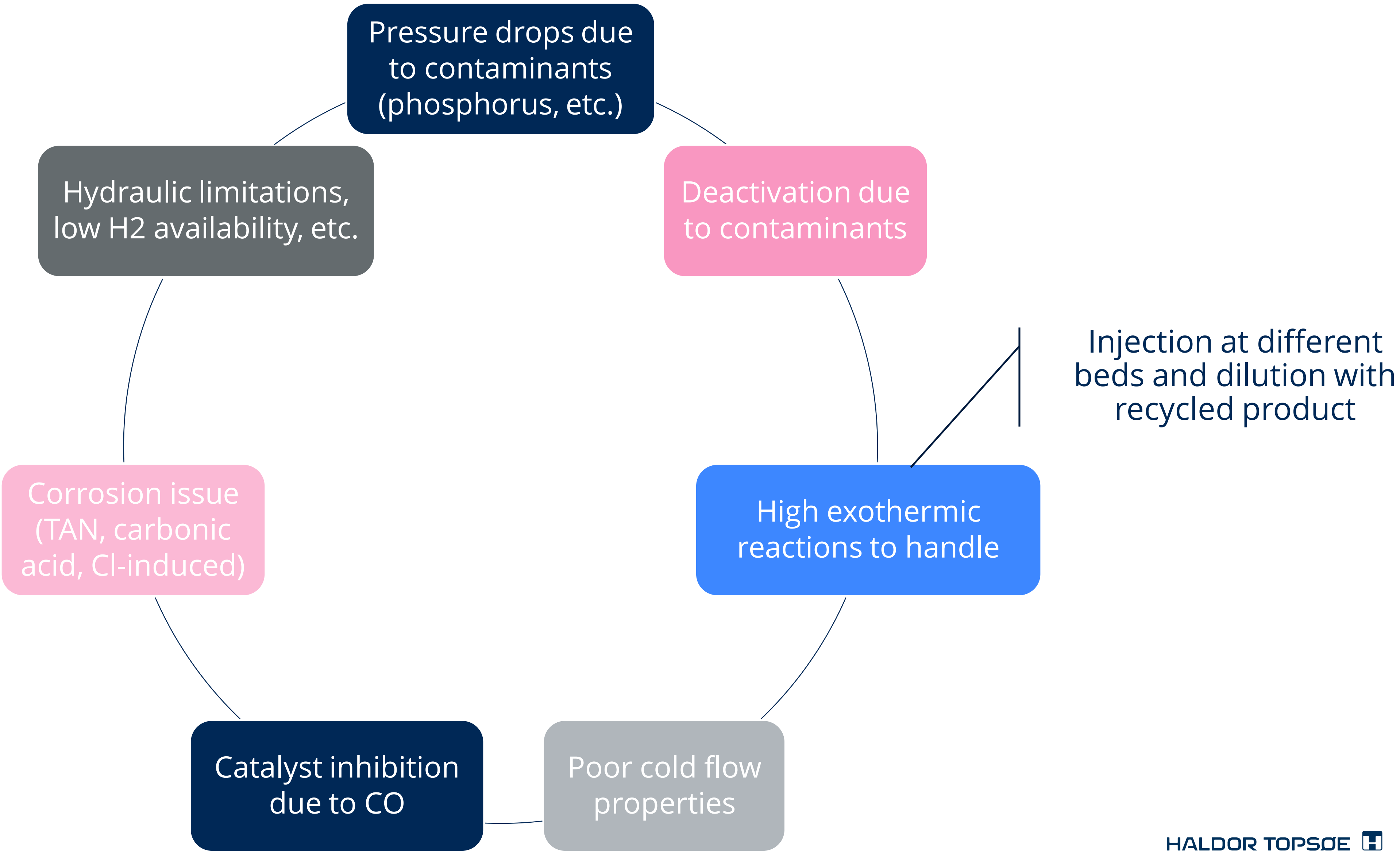
What about the solutions?



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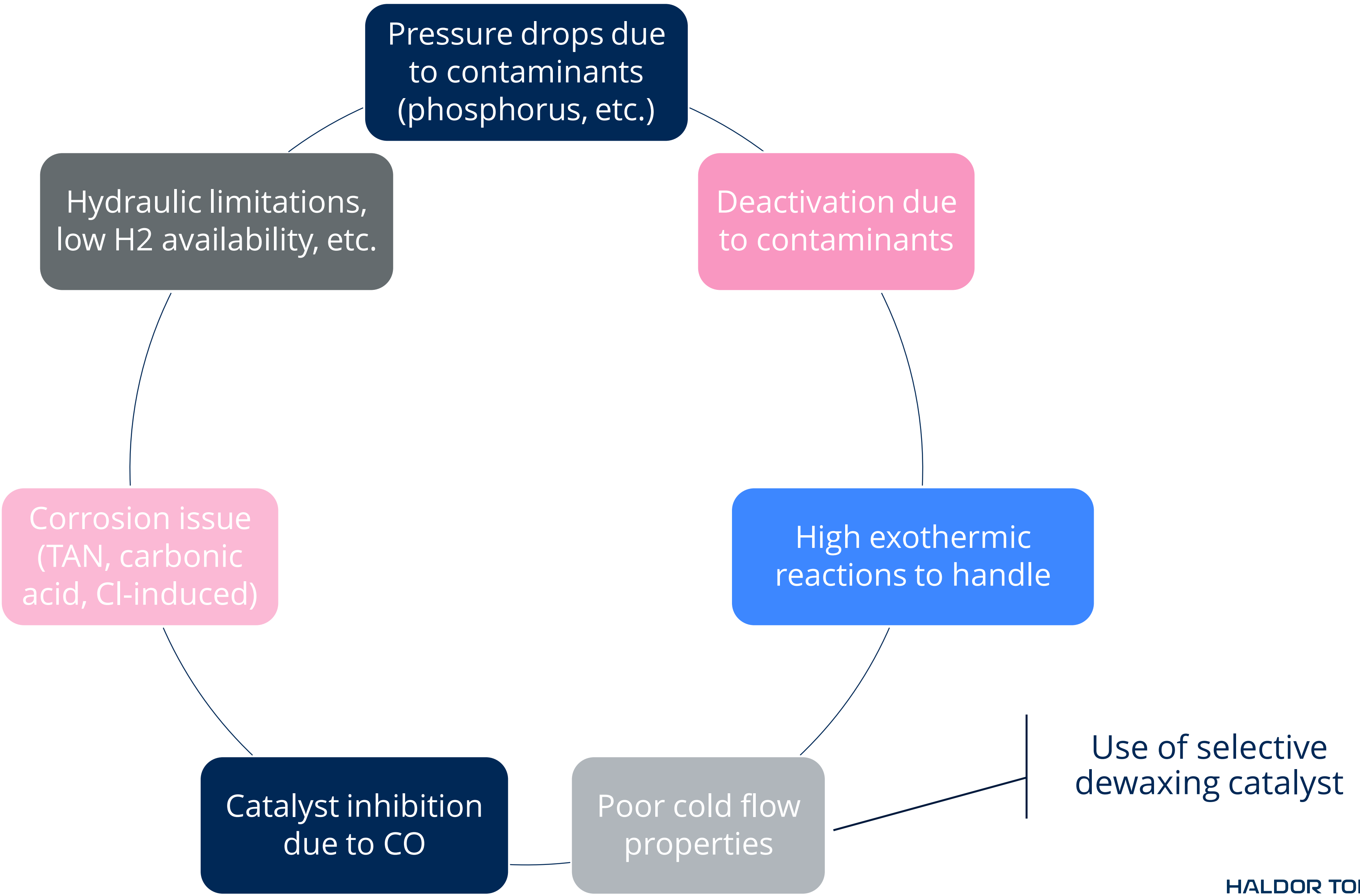

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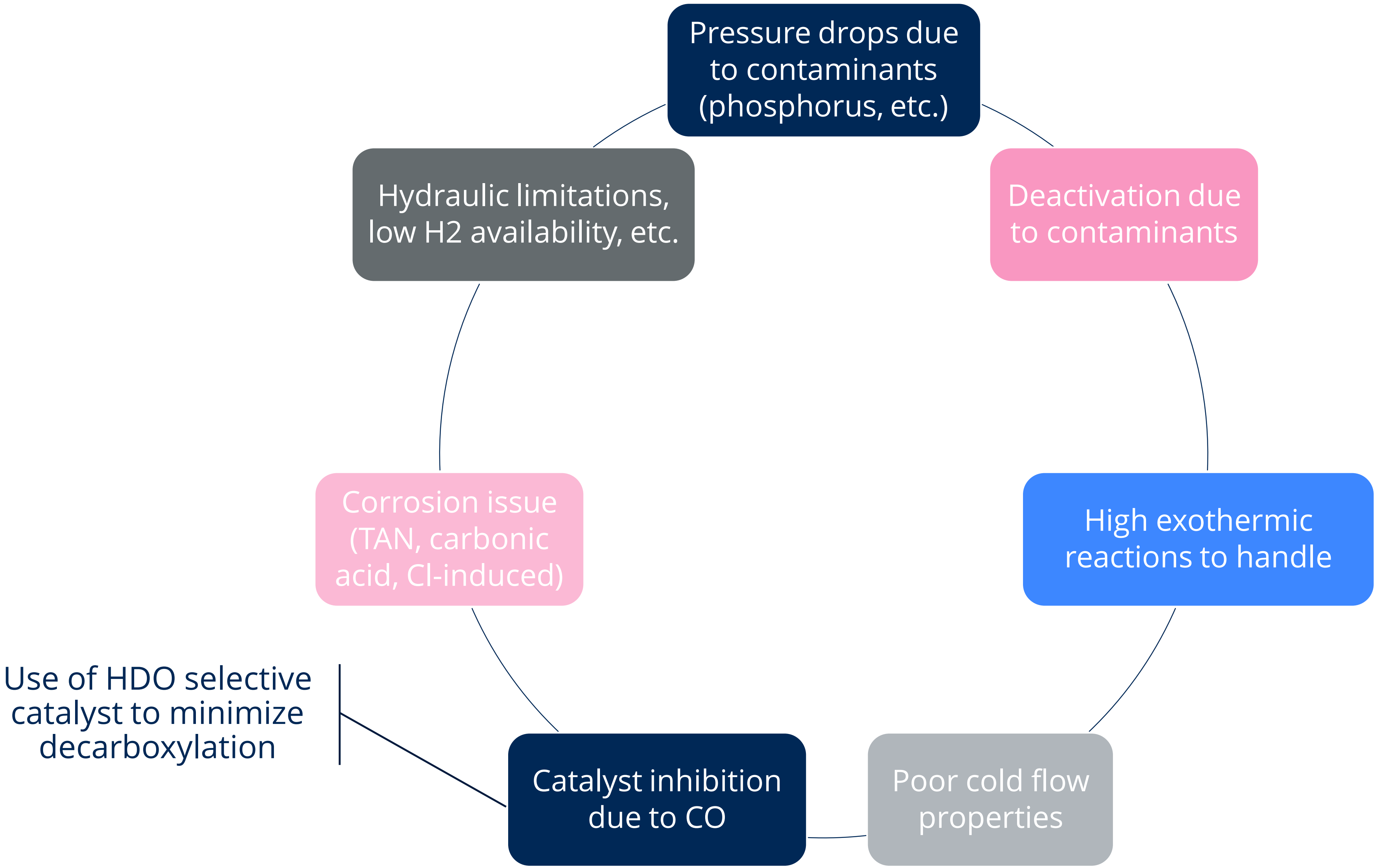

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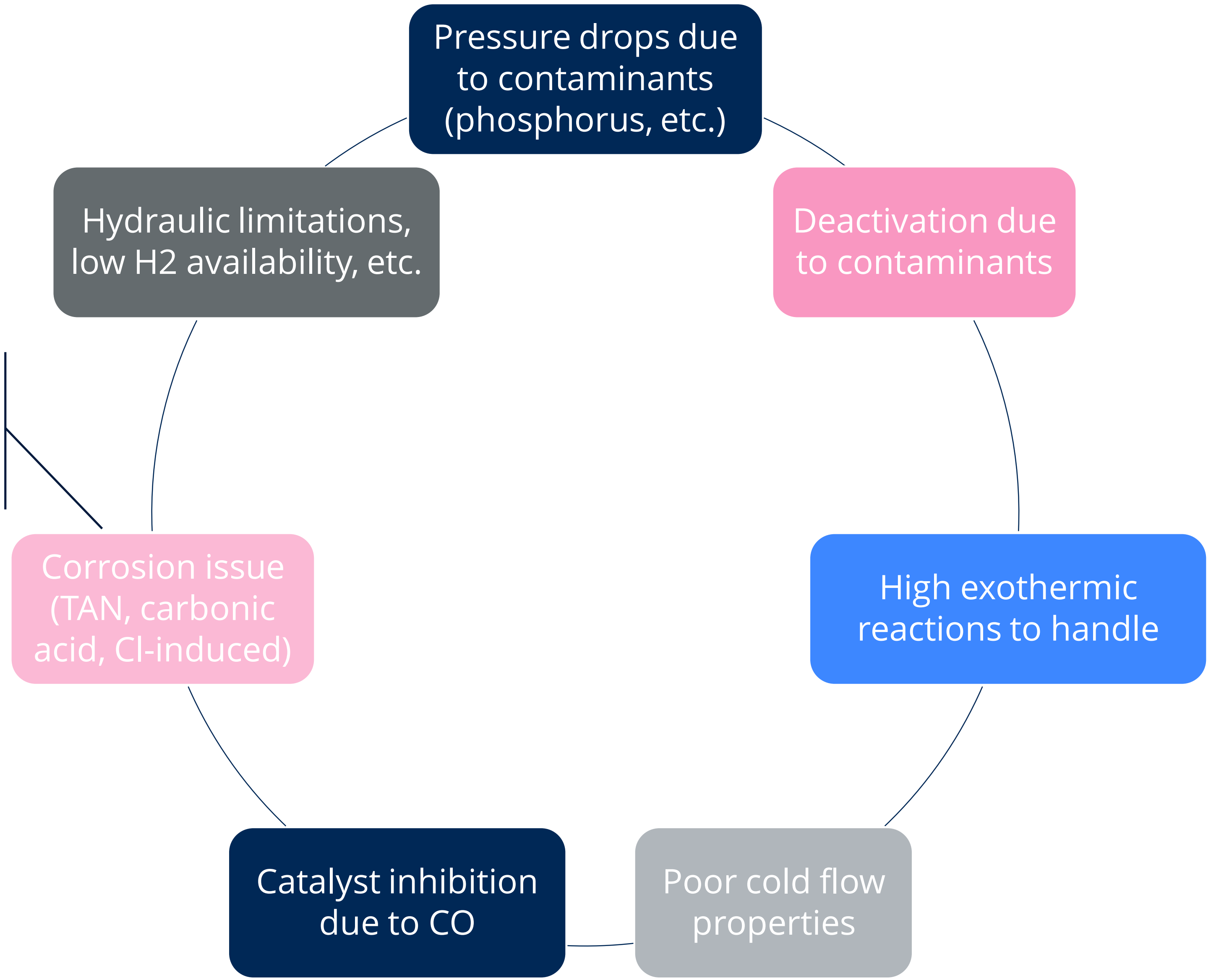
What about the solutions?

Material selection, feed pre-treatment, catalyst choice to minimize CO2 formation



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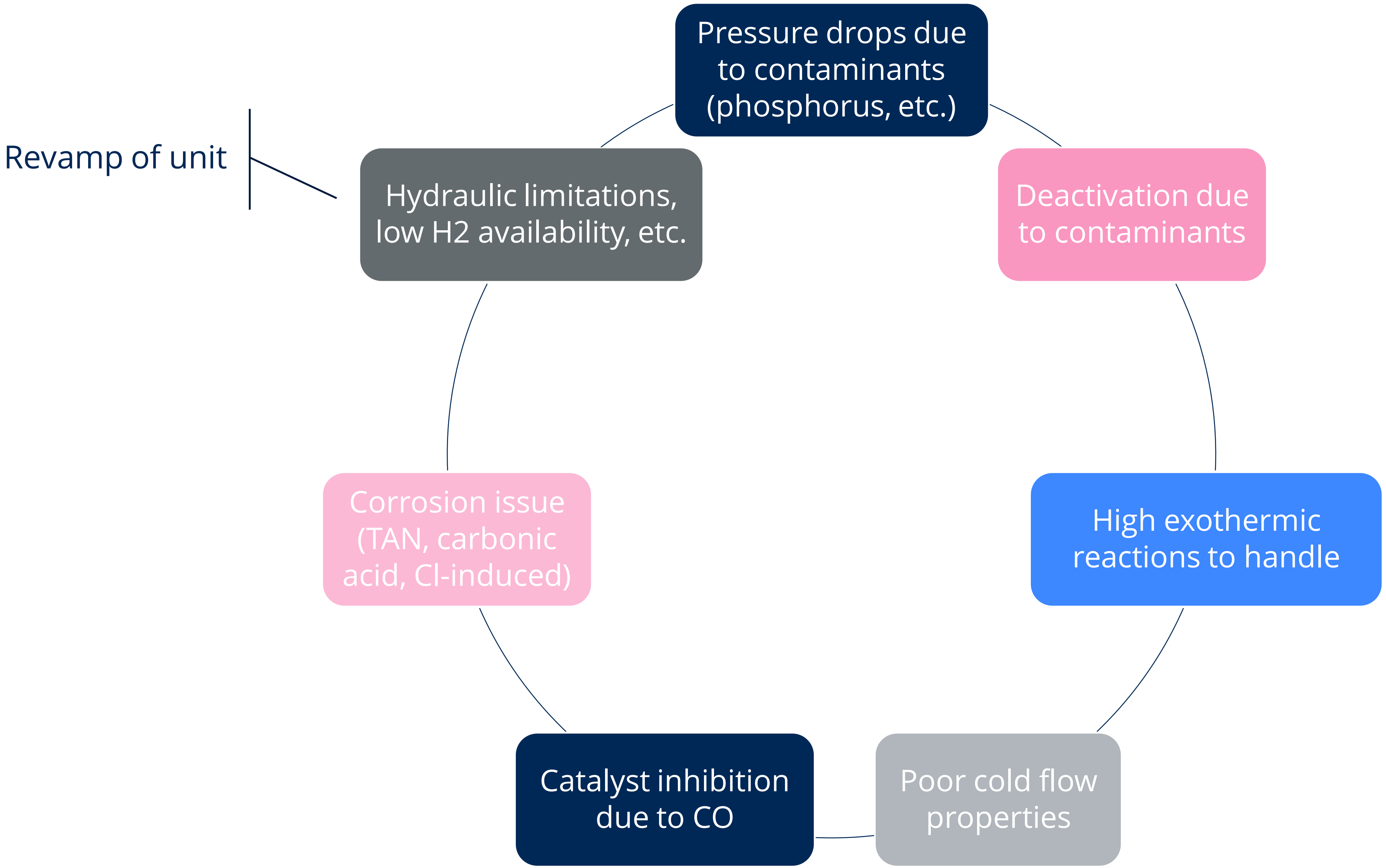

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Topsoe has been providing catalysts and technologies for more than a decade for co-processing of renewable feedstocks

Examples of feedstocks

Virgin oils: Camelina, soybean oil, canola oil, rapeseed oil

Waste oils and fats: Animal fat, tallow, distillers corn oil, crude tall oil, used cooking oils, POME oil,

Co-processing range

Catalyst

2 to 10%

Catalyst and revamp

5 to 85%

Units and products

Low and high pressure, NiMo and CoMo catalysts as bulk catalysts

Note: for jet fuel, co-processing allowed up to 5 vol% (D1655)

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Co-processing of advanced feedstocks is raising new challenges

The biocrude properties depend on the chosen technology and feedstocks

Property	Unit	Pyrolysis	Catalytic pyrolysis	Catalytic Hydro-pyrolysis	HTL	Vegetable oil	Diesel
H	wt%	5.5-7.2	6.5-8	9.6-12	8-11	11-12	13
O	wt%	30-50	10-35	0.5-20	10-20	10-12	0
S	wt%	< 0.1	< 0.1	< 0.03	0.02-1.2	< 0.01	0.001-0.05
N	wt%	< 0.2	< 0.06	< 0.01	0.05-7	< 0.01	< 0.001
H_2 consumption	Nm^3/m^3	800-1000	600-800	200-300	500-800	~350	-

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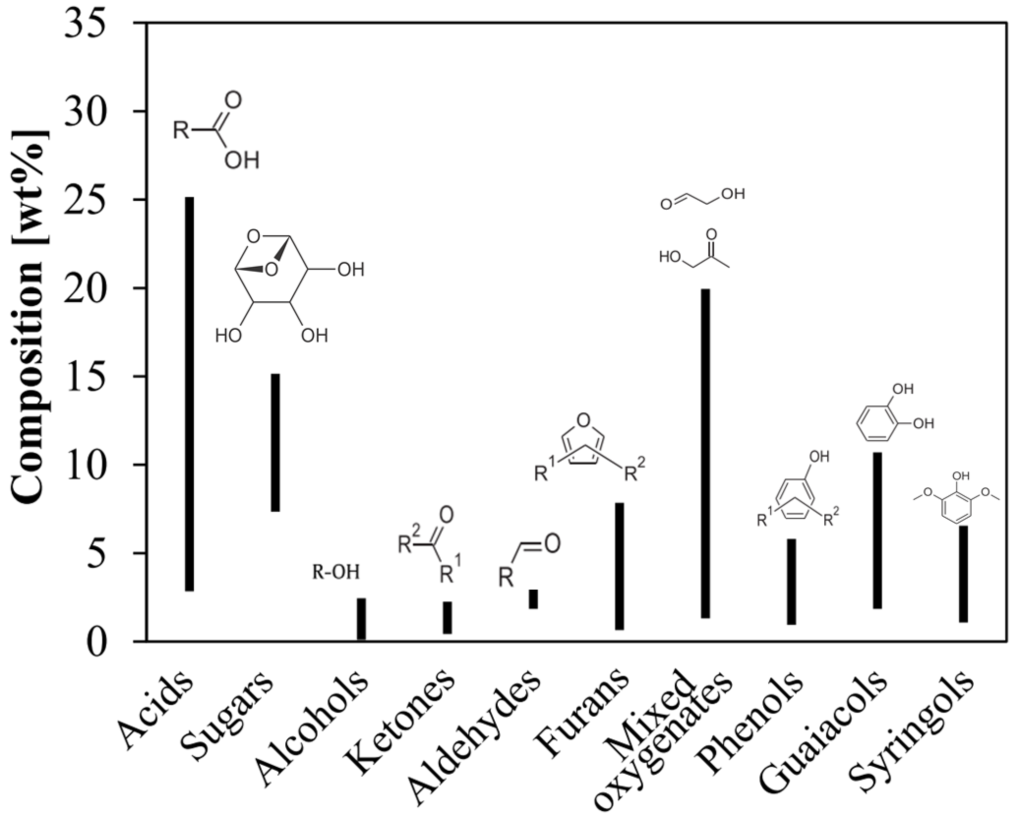
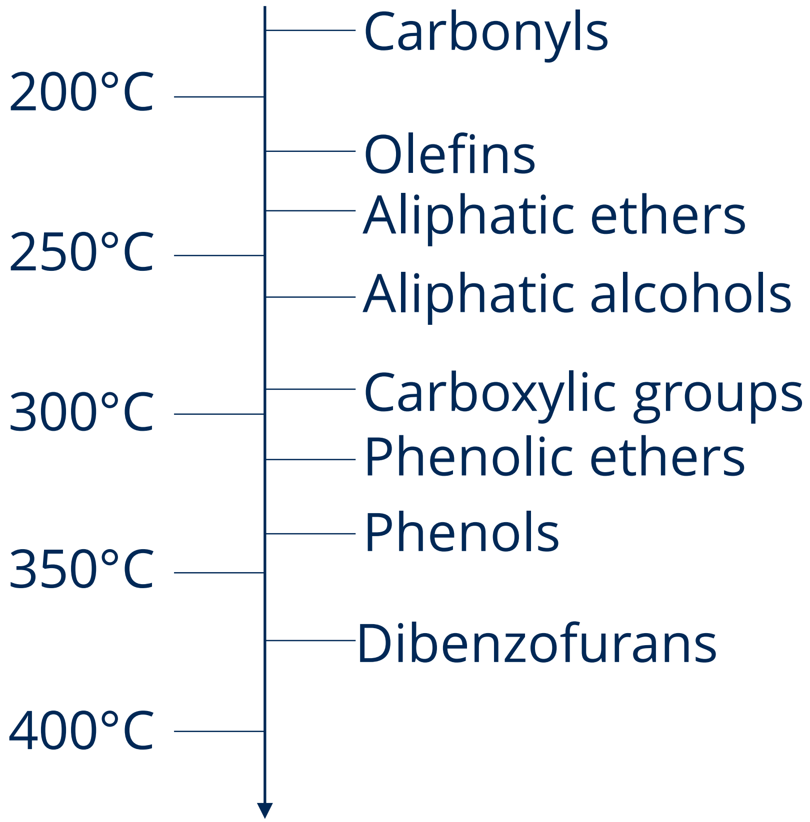
Oxygenates have various reactivities and mastering this is crucial

Fast pyrolysis bio-crude composition



Bio-crude reactivity during hydrotreatment



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What to consider before deciding on the upgrading strategy of advanced feedstocks?

Biocrude properties	Unit consideration	Products
• Miscibility • Stability • Pre-treatment • Batch variations • Logistics	• Hydrogen consumption • Exotherms • Corrosion • CO, CO2, water • Pressure drops	• Yield • Product slate • Product properties • GHG savings

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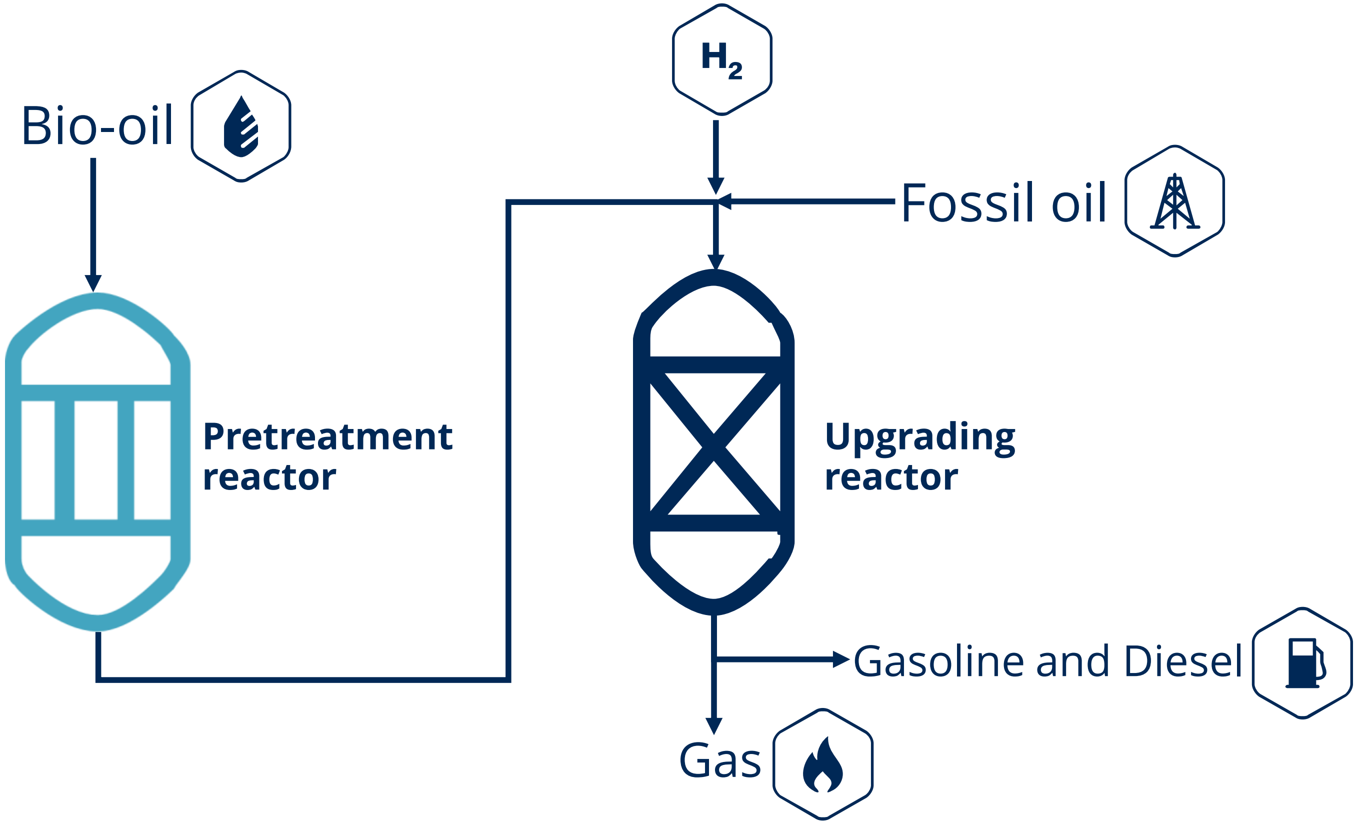
Example: Co-processing of biocrudes with fossil feedstocks



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Example: co-processing of reactive catalytic fast pyrolysis (RCFP) oil with fossil oil

Analysis	Unit	Method	RCFP	LGO
SG at 60/60°F	-	D4052	1.005	0.8541
O	wt %	Perkin Elmer 2400 Series II analyzer	9.65	0
H	wt %	D7171	8.28	13.09
N	wt ppm	D4629	425	147
S	wt ppm	D4294	12	12898
Dist curve IBP	°C	D7213C	36	92
Dist curve 10 wt %	°C		116	216
Dist curve 50 wt %	°C		243	307
Dist curve 90 wt %	°C		406	374
Dist curve FBP	°C		558	433

Test conditions

- NiMo catalyst
- WABT: 340 – 360°C
- $P(H_2)$ = 70 barg
- LHSV = 2 h^{-1}
- H_2/oil = 500 Nm^3/m^3

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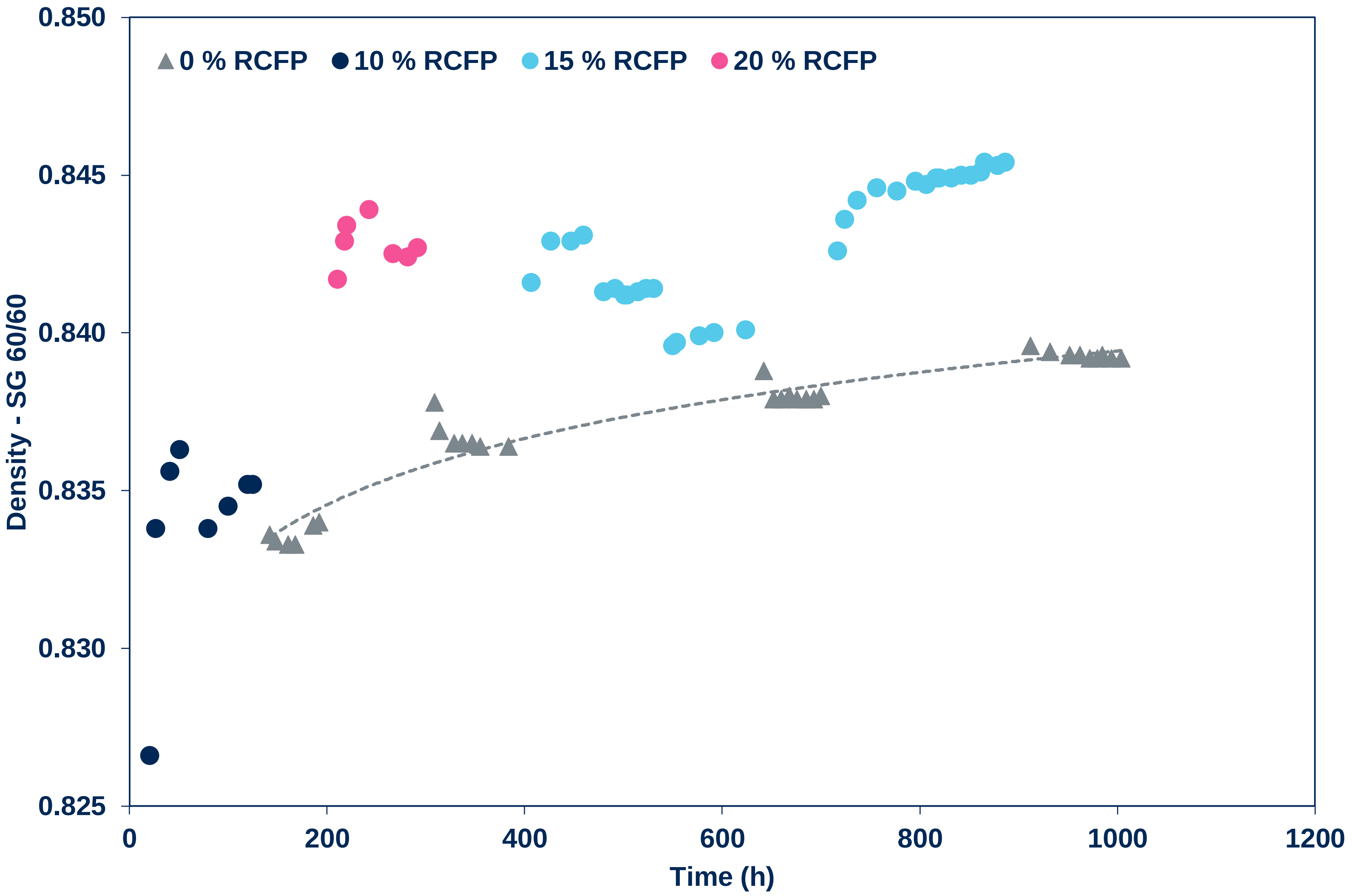
Example: RCFP has a similar effect as LCO and no specific deactivation was observed



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Example: Conclusion of this co-processing study

- Biocrude (with 10% O) was blended with a LGO up to 20%
- No significant deactivation was observed
- Product did not contain O (<5 wt ppm)
- CO and CO2 formation was very low (mostly HDO reaction) so higher product yields
- Co-processing such biocrude is equivalent to co-processing a LCO

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Let us summarize

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Thank you

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