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Tire pyrolysis oil processing in a refinery

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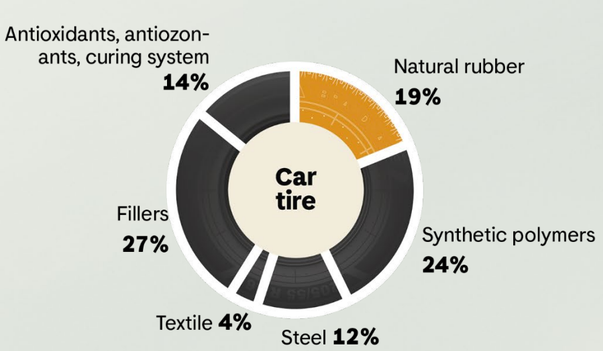
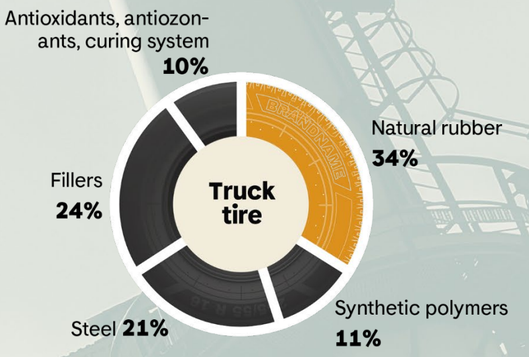
What is Tire Pyrolysis Oil (TPO)?

- Recycling of end-of-life tires by pyrolysis gives carbon black, metal and a tire pyrolysis oil.
- Commercial tire recycling plants under construction.
- Tire pyrolysis oil volume potential about 600 kton per year in Europe.
- Circular/renewable oil.
- The renewable content around 40-50% (depending on type of tires).
- Typical elemental composition of TPO: C: 87%, H: 11%, S: 0.9% and N: 0.5%.
- TPO is olefinic and aromatic in character.
- Relatively miscible with refinery hydrocarbons.





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Example of literature sources for upgrading of TPO

FCC upgrading

French patent (ERAP) 1976 FR2357630 (B1)

- Improved yields of gasoline and liquefied gas.

University of Basque Country in collaboration with KAUST

- Scrap tire pyrolysis oil prepared in house.
- 20% co-feed with VGO resulted in synergistic effect.
- Increase of naphtha (C5-C12) and LCO (C13-C20).
- Over cracking is decreased resulting in lower yield of dry gas and LPG. Tire pyrolysis oil promotes cracking of HCO.
- Reduction in aromatic coke, increase of olefinic and aliphatic coke
- Aromatics and olefins increase in the naphtha lump.

Rodriguez et al. Waste Management 105 (2020) 18–26.

Rodriguez et al. Energy Conversion and Management 224 (2020) 113327.

Hydrotreating

- Stand alone hydroprocessing studied by e.g. Debek et al. in Fuel 159 (2015) 659-665) and Straka et al. in Chem. Eng. Journal 460 (2023) 141764.
- Their studies point to that hydrotreatment above 330 °C seems necessary to obtain clear liquid product with low S, N and olefinic content.
- Poly aromatics are reduced while cycloalkanes are increasing around 300 °C.

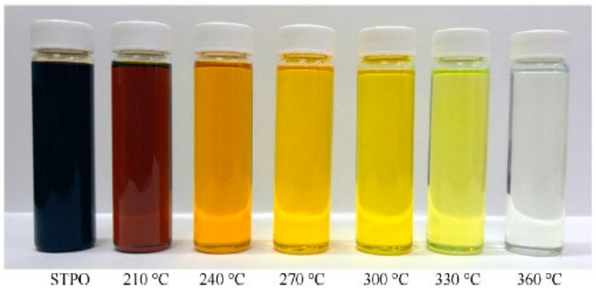


Fig. 2. Appearance of the STPO (on the left) and the hydrotreated liquid products obtained at various temperatures and 10 MPa pressure.

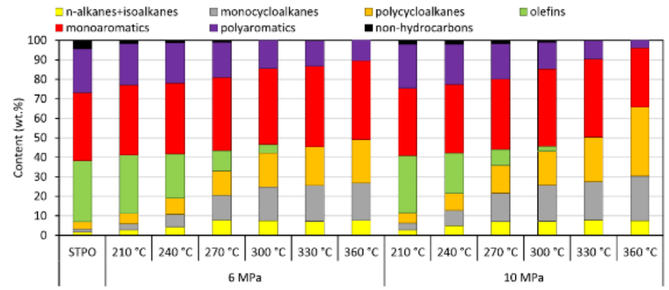


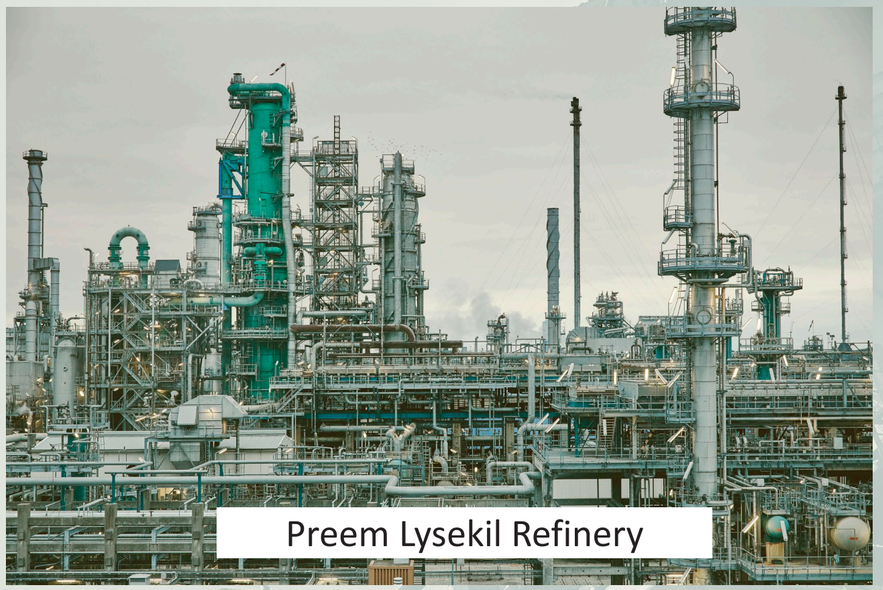
Fig. 11. Group type composition of diesel fraction (150–360 °C) from the STPO and hydrotreated products at various temperatures and pressures.

Outcome from Preem lab and full-scale co-processing FCC trials

1. Small scale testing (grams) in FCC-MAT units.
2. Successful full-scale trial: 200-ton TPO co-processed in Preem Lysekil FCC unit.

- Basic nitrogen is increasing strongly upon blending with TPO, and this can cause deactivation of acid sites of the catalyst.
- Aromatics do not crack easily in FCC.
- Incremental yield are showing a high gasoline and LCO yield. FCC-MAT show that C4, gasoline and LCO make up 77% of reaction products.
- Gasoline and LCO are likely to be more aromatic.
- Sulfur in the gasoline product increase strongly in both tests.

FCC-MAT testing


Preem Lysekil Refinery

FCC-MAT	0 % TPO	10 % TPO	15 % TPO
	S (mg/kg)	S (mg/kg)	S (mg/kg)
Gasoline product	14	144	219

Lysekil FCC full-scale trial	0 m3/h TPO	1 m3/h TPO	2 m3/h TPO
	S (mg/kg)	S (mg/kg)	S (mg/kg)
Heavy cracker naphtha (HCN)	5	17	31
Light cracker naphtha (LCN)	3	7	15

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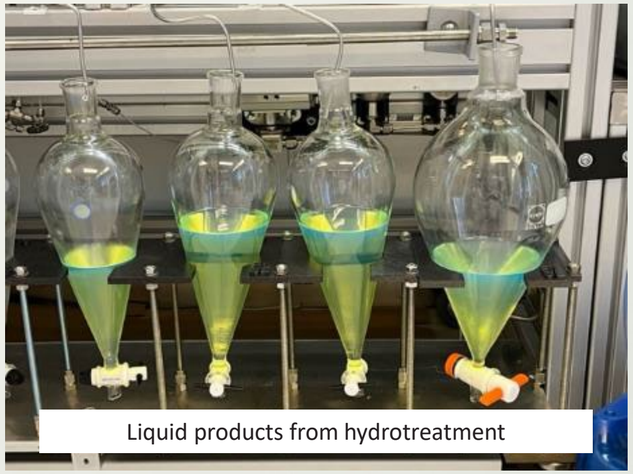
Outcome from initial co-processing hydrotreating trial

Initial continuous hydrotreating trial

- Continuous co-processing in a fixed bed pilot hydrotreater.
- 20% co-processing of TPO with light gas oil (LLGO).
- 70 bar, 360-380 °C, LHSV 1.0 h-1, GTO 500, Ni-Mo/Al2O3 catalyst.
- Run time 54 h (27 h at 360 °C, 27 h at 380 °C).

Tire pyrolysis oil


Liquid products from hydrotreatment

Observations from initial continuous hydrotreating trial

- Olefins were saturated and aromatics to some extent.
- Successful HDN and HDS.
- Water wash of liquid product reduced S and N even further.
- Some cracking effect noted on the heavy end (>350 °C) at 380 °C compared to 360 °C.
- No pressure drop during the initial trials.

	TPO	LLGO	Feed 20% TPO, 80% LLGO	HT LLGO 70 bar, 360 °C	HT Product 70 bar, 360 °C	HT Product 70 bar, 380 °C
C (%)	86.0	86.9	86.4	85.3	86.2	86.1
H (%)	10.9	13.7	13.1	14.3	13.9	13.7
N (mg/kg)	5 000	100	1 003		6	11
S (mg/kg)	8 700	480	2 308		166	222
Density (kg/m3)			847		833.5	831.5
TAN (g KOH/kg)			4.0		0.13	0.36
1H-NMR Olefinic H	2.2-2.8	0	0.32	0	0	0
1H-NMR Aromatic H	7.5-13.8	3.95	4.6	1.5	3.2	3.4
1H-NMR Aliphatic H	83.3-90.2	96.05	95.0	98.5	96.8	96.6

NMR data: Normalized Integrals

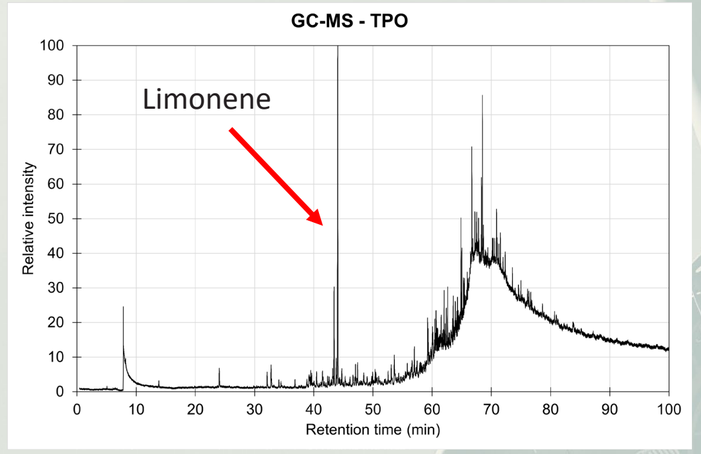
Other potential risks except known impurities?

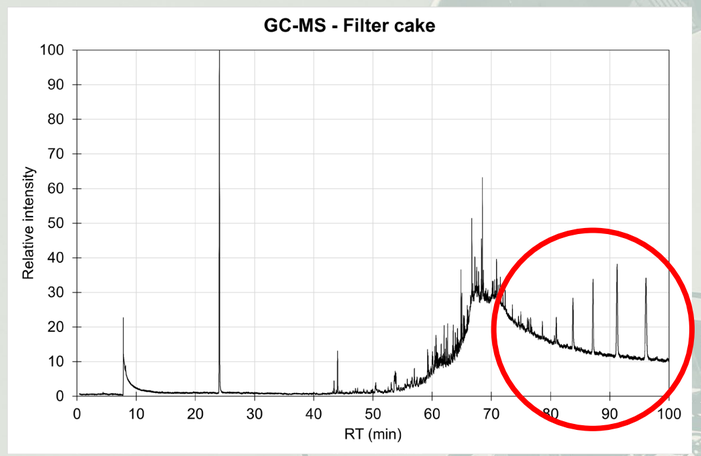
- Tire pyrolysis oil has a small fraction of “waxy” material.
- “Wax” in turn contain smaller fraction of solid matter (~0.04%) with atomic H/C=1.88.

Filtration of Tire Pyrolysis Oil

- GC-MS analysis of filter cake (wax) show some clear chromatogram peaks absent in tire pyrolysis oil (or very small peaks) identified such as Octosane (C28H58), Tricontane (C30H62) and Hentricontane (C31H64).
- The large peak of Limonene in TPO is reduced in the wax after filtration.

	C %	H %	N %	S %	O %	Atomic H/C
Tire pyrolysis oil	86.0	10.9	0.5	0.87	1.7	1.52
Solids (part of the wax)	79.0	12.4	1.86	0.27	6.5	1.88
Hexadecannitrile (C16H31N)	80.9	13.1	5.9			1.94
Tricontane (C30H62)	85.2	14.7				2.07
Toluene (C7H8)	91.1	8.7				1.14
Naphthalene (C10H8)	93.6	6.2				0.80





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Analysis of filter cake and solid matter

Thermogravimetric (TG-DSC) analysis of filter cake

- Endothermic process 40-90 °C, associated with 28 % weight loss. 135-430 °C a 67 % weight loss, no specific exotherm or endotherm associated.
- Large exotherm from combustion at end at 600 °C, but low weight loss (1%). No ash remaining after test.

IR spectroscopy of solid matter isolated from filter cake

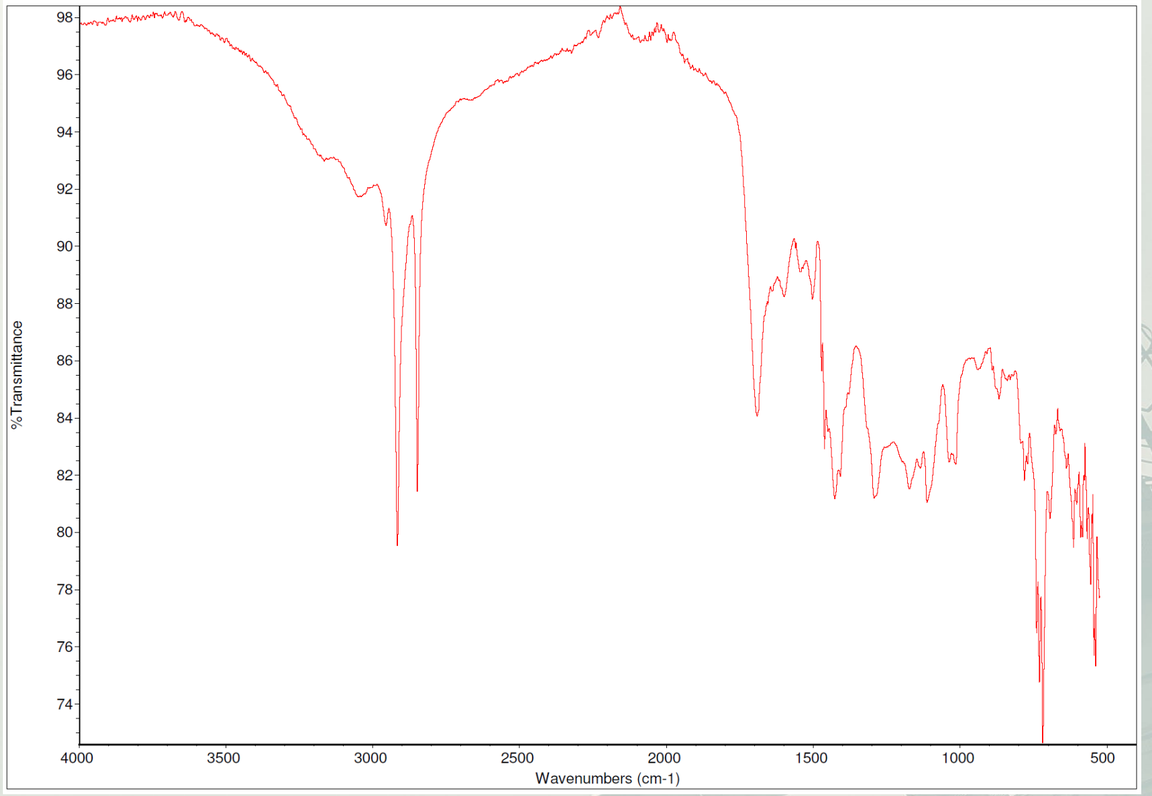
- IR spectra of particles show presence of hydrocarbons and does not look like carbon black or char in concert with the elemental analysis of solid matter.

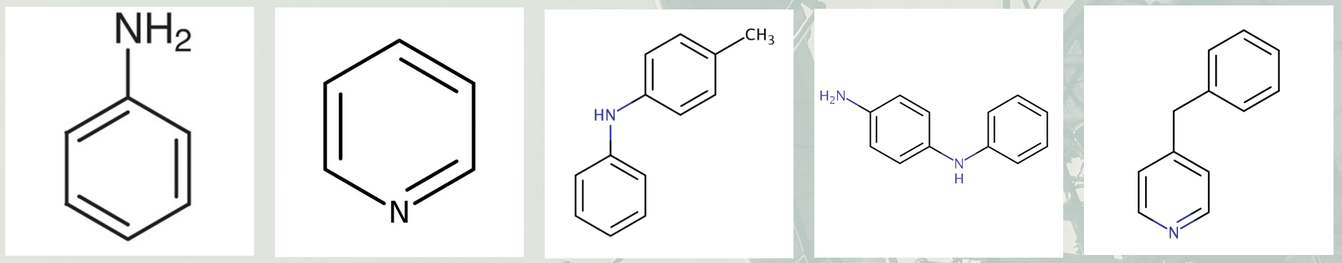
Pyro-GCMS of solid matter isolated from filter cake

- Toluene
- Aromatic nitrogen compounds (Aniline, Pyridine, N-phenyl-1,4-Benzenediamine, 4-methyl-N-phenyl benzene amine)
- Thiol and thiazole

Conclusion: It was not carryover of carbon black to the TPO. Instead, likely asphaltene like material within the tire pyrolysis oil.

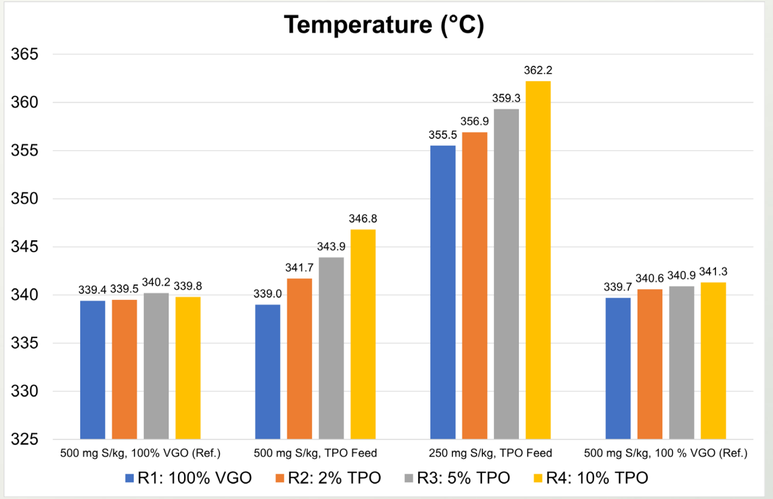
IR spectra below of particles show presence of hydrocarbons and does not look like carbon black or char in concert with the elemental analysis of solid matter.

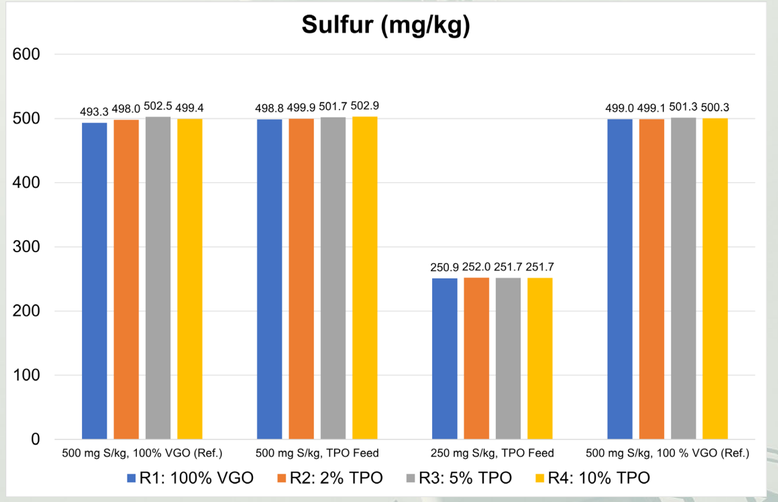


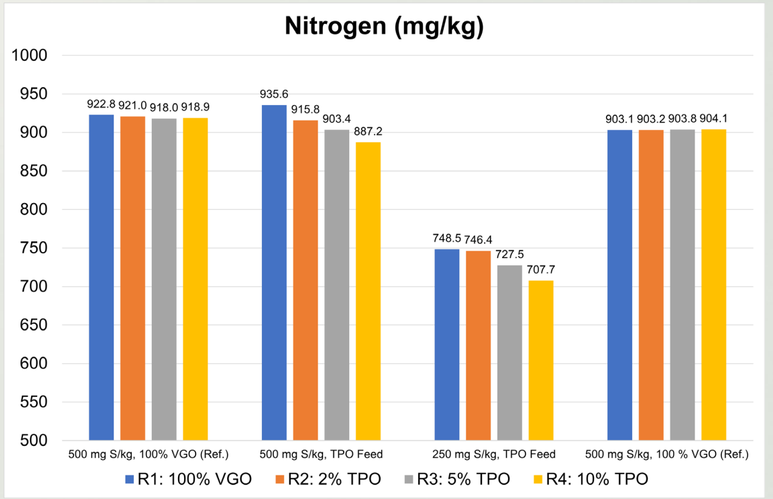


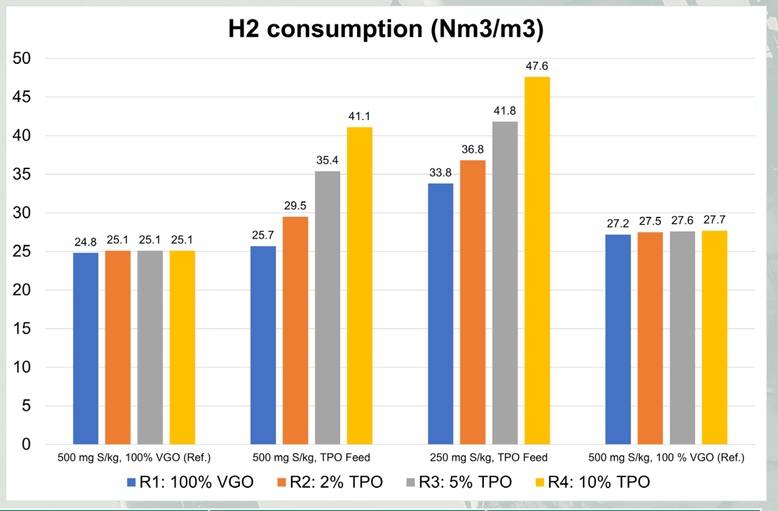
Long duration continuous hydrotreating trial (34 days)

- 4 reactors (R1-R4) and 4 test conditions:
  - R1: 100 % VGO
  - R2: 2% TPO
  - R3: 5% TPO
  - R4: 10% TPO
- S target: 500 and 250 mg/kg. VGO reference before and after feeding TPO.
- 60 bar, 330-365 °C, LHSV 1.22 h^{-1}, GTO 270, Co-Mo based catalyst.
- Test performed without any plugging tendency.
- Increasing the TPO content in feed requires higher temperature to reach a target S level.
- The higher T also results in lower N content.
- Hydrotreatment decreased di/poly-aromatics significantly and slightly increased mono-aromatics.









Gross Mass Yield (%)	R4: 100% VGO 500 mg S/kg	R4: 10% TPO 500 mg S/kg	R4: 10% TPO 250 mg S/kg	R4: 100% VGO 500 mg S/kg
C5 + Cut: 30 - 160 °C	0.13	0.45	0.57	0.18
Cut: 160 - 265 °C	12.75	16.68	18.04	13.85
Cut: 265 °C - FBP	86.89	82.61	81.06	85.76

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Compatibility test with Crude oil using the Oil Compatibility Model

- TPO is miscible with typical refinery streams such as light gas oil and VGO.
- Preferentially handled between 10 – 60 °C to avoid high viscosity and potential precipitation of wax/asphaltene phases at low temperatures and volatilization at higher temperatures.
- Oil compatibility tests using method in Wiehe et al. Energy Fuels 2000, 14, 1, 56–59.
- Asphaltenes tends to foul refinery equipment or adsorb on metal surfaces to cause fouling and at water interfaces to form stable emulsions.
- The criterion for compatibility according to the Oil Compatibility Model is that the volume average solubility blending number (S_{BN}) must be greater than the insolubility number (I_N) of every component in the blend ($S_{BN} > I_N$).
- Thus, the two samples are expected to compatible in all proportions on blending.

Sample	Density (kg/dm3)	API	TE	HD	SOE	S_{BN}	I_N
Crude oil (Oseberg)	0.8272	39.4	<6	11.75	56.5	42	12
Tire pyrolysis oil	0.9288	20.7	29	1.75		42	31

Method

- Mixing 5 ml of each sample with 10 ml n-heptane precipitated asphaltenes in each case.
- Heptane (non-solvent) dilution test used to measure the insolubility number (I_N) for both samples. This is done by determining the maximum volume of n-heptane that can be added to a given volume of oil without precipitating asphaltenes.
- The toluene equivalence test (TE) is the minimum % toluene in mixture with n-heptane to dissolve asphaltenes at a concentration of one gram of oil and 5 ml of toluene-n-heptane mixture (test liquid).
- Crude oil was too soluble (<6) to accurately determine the insolubility number (I_N).
- Solvent oil equivalence (SOE) test used to measure the solubility blending number (S_{BN}) for the crude oil.

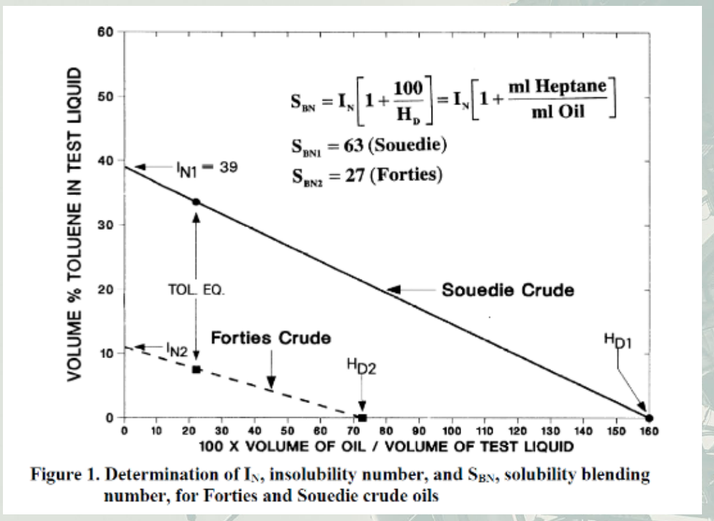

Figure 1. Determination of I_N, insolubility number, and S_{BN}, solubility blending number, for Forties and Souedie crude oils

Wiehe et al. Fouling of nearly incompatible oils. Second International Conference on Petroleum and Gas Phase Behavior and Fouling in Copenhagen, Denmark on August 27 – 31, 2000.

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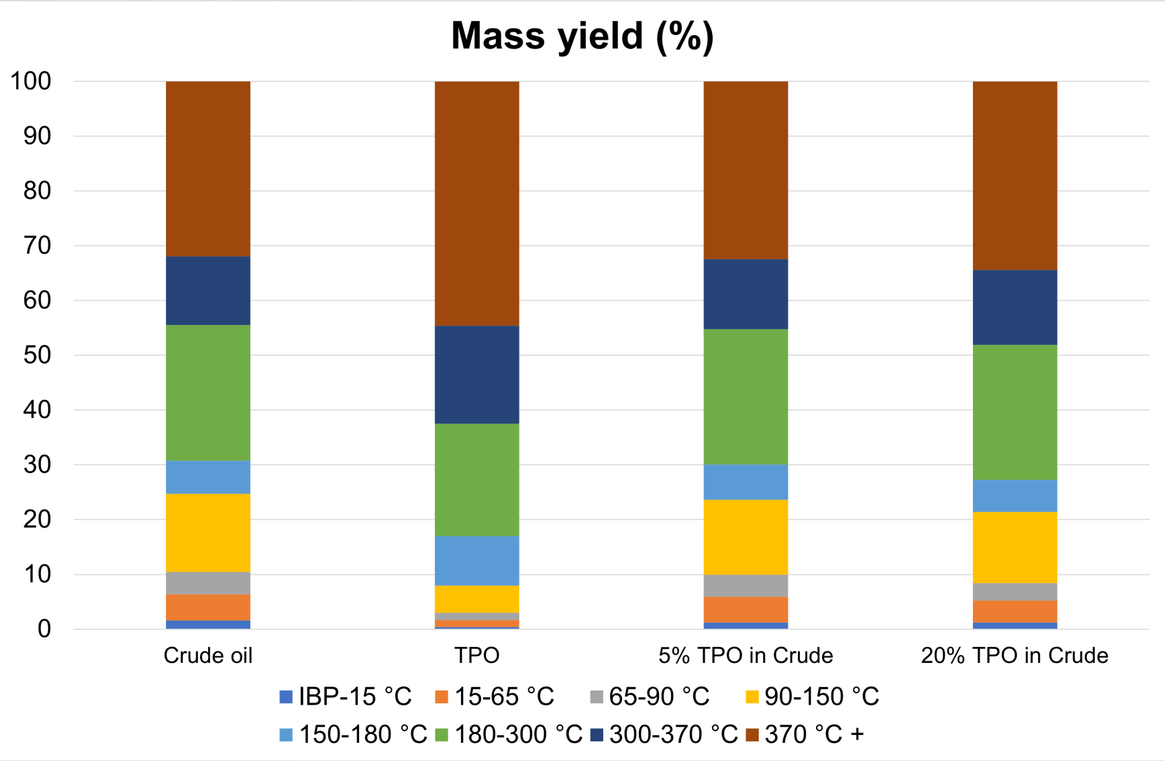
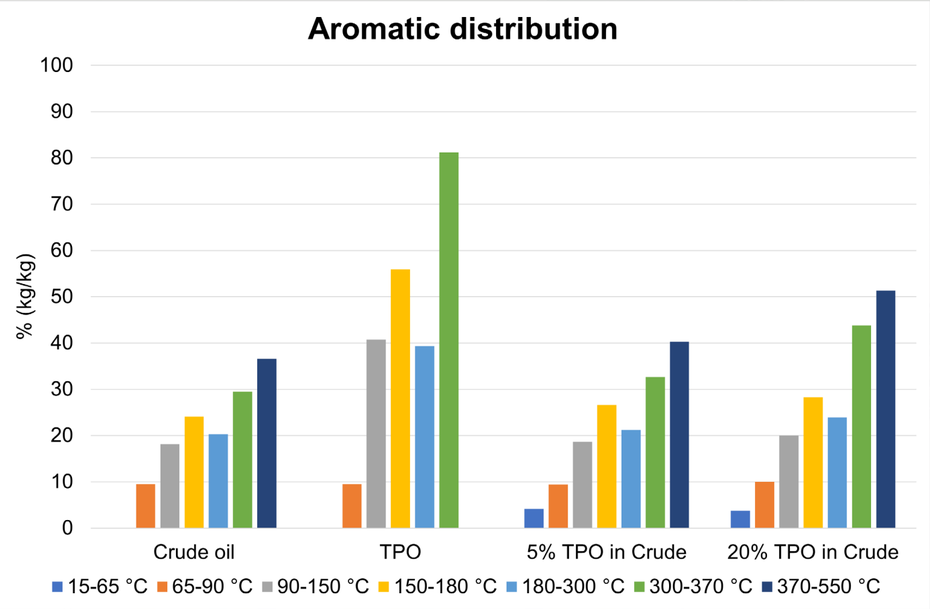
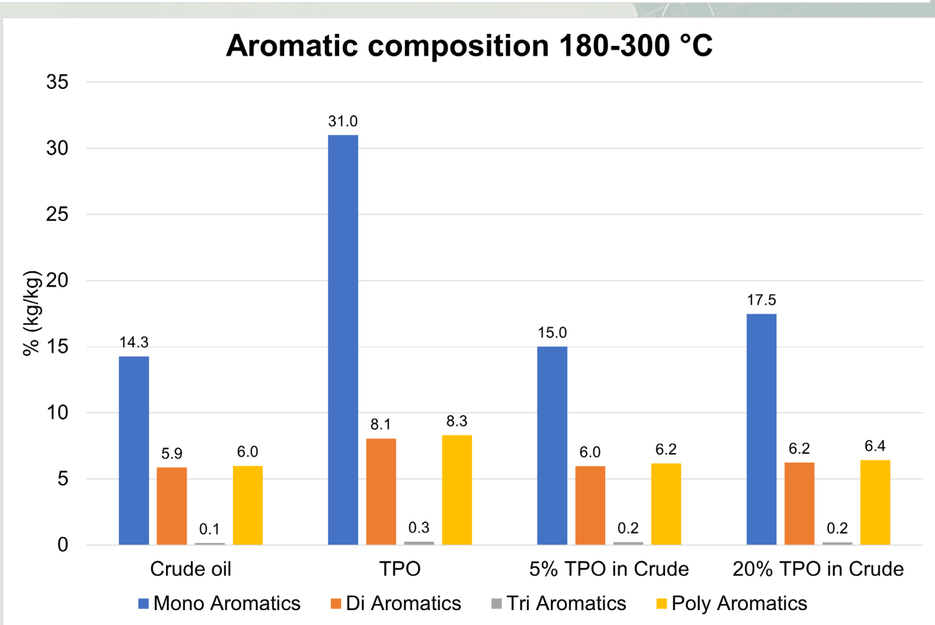
Co-distillation of Crude oil and TPO (pilot unit)







- Co-distillation tests in 50 dm3 scale.
- TPO blends may need manual determination of cloud point (automatic can give false detection).
- Foaming > 370 ° for pure TPO.
- TPO higher in aromatics > 90 °C compared to crude oil (Oseberg).
- TPO rich in mono-aromatics (180-300 °C).
- Co-distilled 180-300 °C fraction has higher concentration of mono-aromatics compared to crude oil.

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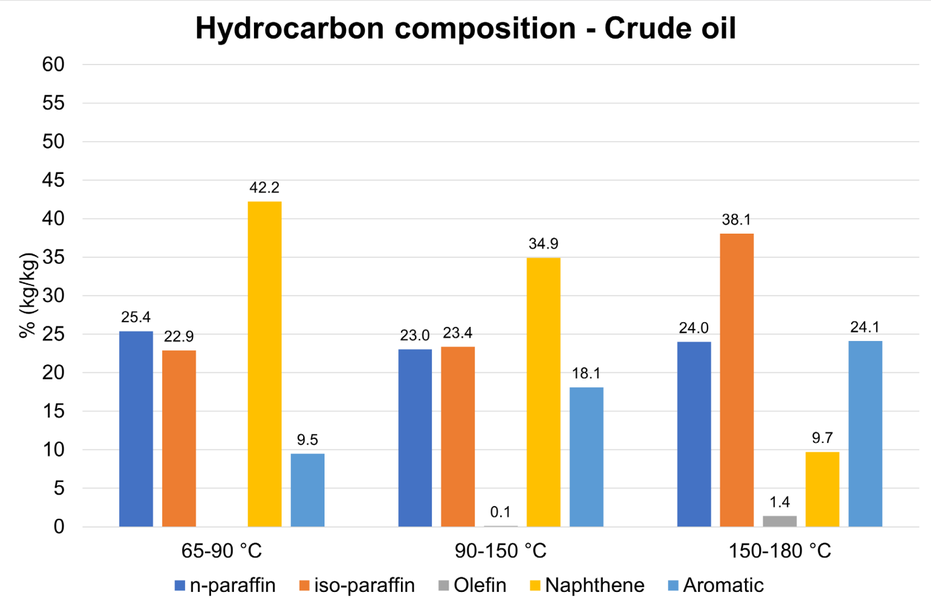
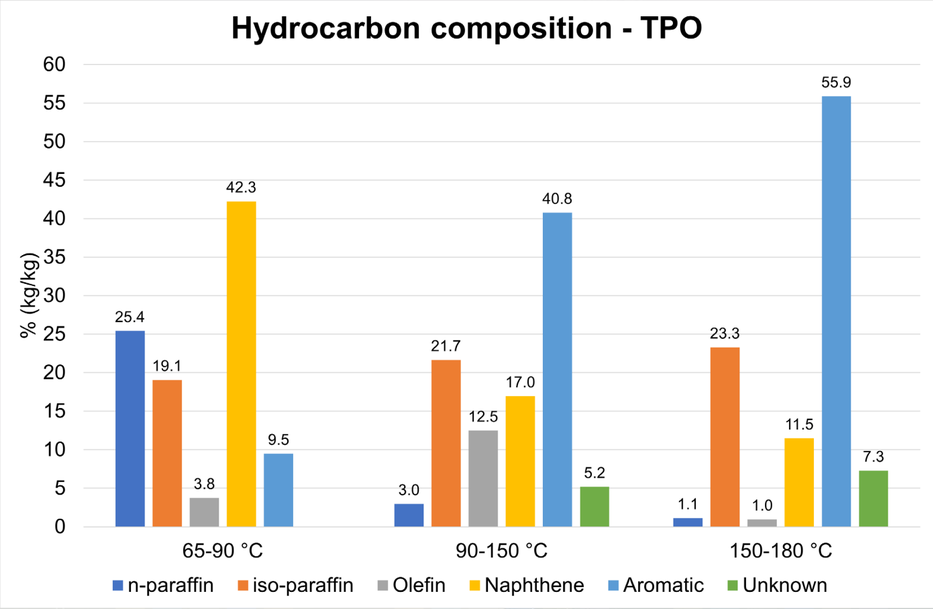
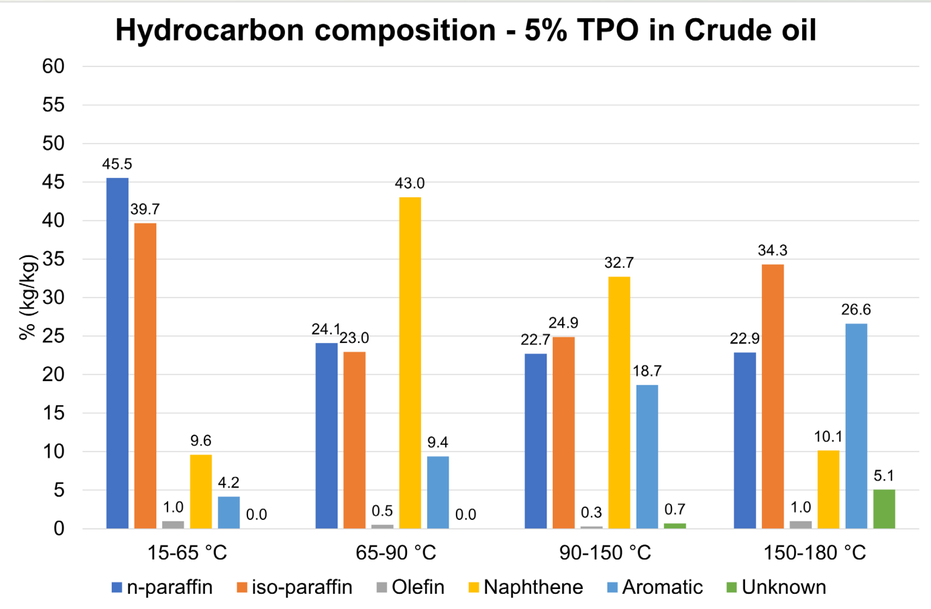
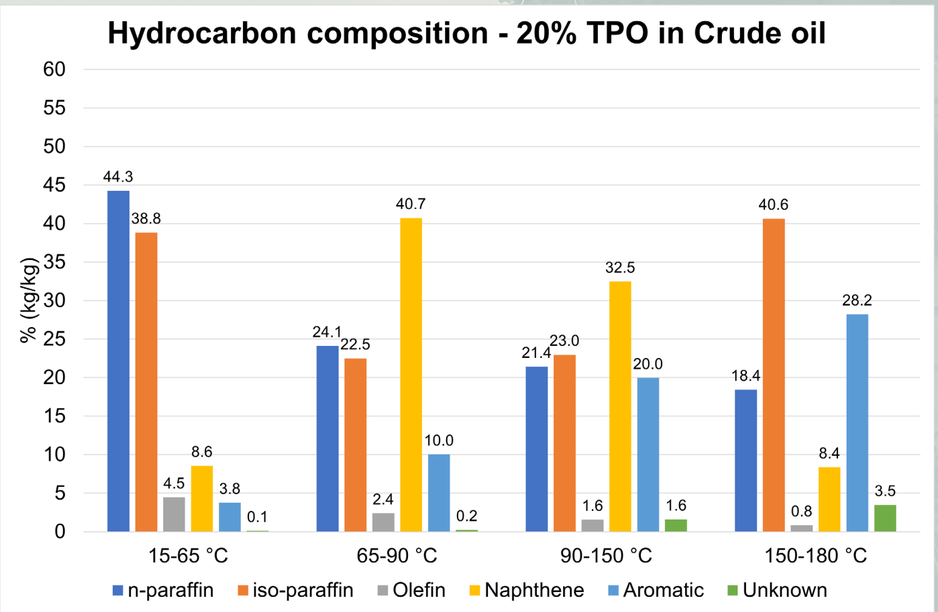
Hydrocarbon composition in co-distilled fractions

- More olefins in TPO fractions compared to Crude oil (Oseberg), especially in fraction 90-150 °C.
- n-paraffin in TPO found predominantly in lighter fraction 65-90 °C.
- Aromatics concentrate in heavier TPO fractions.
- Aromatic content in co-distilled samples increase (compared to crude oil), especially in fraction 150-180 °C.









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Conclusions

- TPO is miscible with refinery streams such as light gas oil, VGO and crude oil but separate compatibility testing and temperatures (10-60 °C) could be important.
- TPO contains olefins, aromatics and small amount of waxy and solid asphaltene like material.
- A successful refinery full-scale co-processing FCC trial was executed on 200 tons of TPO.
- TPO is suitable for gasoline production in FCC, but sulfur and nitrogen removal might be necessary.
- Successful co-processing (for HDS and HDN) with other refinery streams at conventional hydrotreating conditions were verified in different pilot reactor trials.
- Co-distillation with a crude oil resulted in increased aromatic content, especially in fractions > 150 °C, and increased olefin content in lighter fractions.
- Long duration processing (weeks/months) will give further information of long-term effects on the refinery.

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