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Refinery Co-processing for Sustainable Aviation Fuel Production

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Agenda



1. Introduction
2. Aviation Fuel Manufacturing Routes
3. Refinery Co-processing
4. Pilot Plant Program
5. Refinery Program
6. Summary



Introduction

- Jet A / A-1 kerosene has been adopted as the primary fuel for global aviation:
 - Liquid with moderate flash point ($\geq +38$ °C) for easy of handling.
 - High energy content per unit weight & volume.
 - Good low temperature flow characteristics.
 - Readily manufactured from crude oil around the world.
- To retain this product and meet the IATA aspiration for carbon neutral operations by 2050 requires technical imagination and innovation:
 - Development of alternative manufacturing routes using sustainable feedstocks to give synthetic blending components (SBCs) for sustainable aviation fuel (SAF) production.
 - Formal review and approval through ASTM and industry groups to maintain operational performance.



Image: NASA

Each day the aviation industry transports up to 12 million passengers – the aim is to achieve this in the future with minimum carbon foot-print.

Aviation Fuel Manufacturing Routes

- In addition to traditional D1655 aviation turbine fuel production 8 Synthetic Blending Component (SBC) manufacturing routes and one re-processing route have been approved by the aviation industry.
- These routes are available to make Sustainable Aviation Fuel (SAF) given appropriate feedstocks.
- For 2 routes the hydroprocessing / fractionation steps can also be undertaken at conventional refineries in mixture with crude oil distillates.
- Significant advantages for CAPEX, production flexibility, supply security, operational expertise and time-to-market.

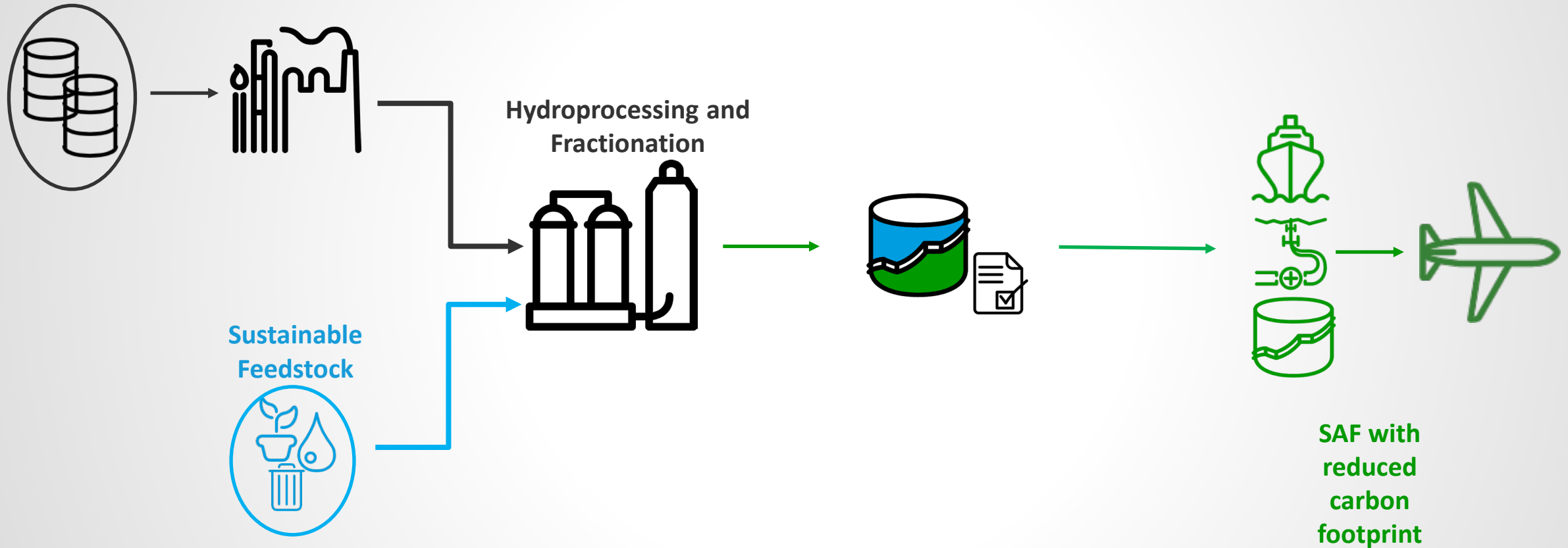


Aviation Fuel Manufacturing Routes



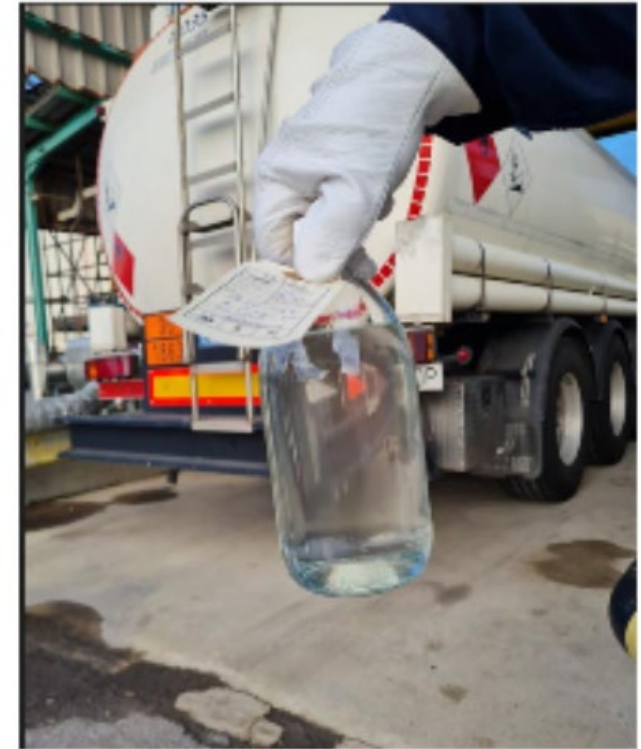
Technology process type	Common name	ASTM annex	Feedstock	Max % blend / feed
Fischer-Tropsch Hydroprocessed synthesized paraffinic kerosene	FT-SPK	A1 (D7566)	Waste CO ₂ and renewable power. Municipal solid waste. Agricultural waste / waste wood	50
Co-processing of Fischer-Tropsch (FT) to yield synthesized paraffinic kerosene in mixture with petroleum distillates	-	A1.2.2.2 (D1655)		5% (feed & product)
Synthesized paraffinic kerosene from hydroprocessed esters and fatty acids	HEFA SPK	A2 (D7566)	Vegetable and waste oils (fats, oils and greases)	50
Co-processing of hydroprocessed esters and fatty acids (HEFA) in mixture with petroleum distillates	-	A1.2.2.1 (D1655)		5% (feed & product)
Synthesized iso-paraffins from hydroprocessed fermented sugars	SIP	A3 (D7566)	Fermentable sugars	10
Synthesized kerosene with aromatics derived by alkylation of light aromatics from non-petroleum sources	FT-SPK/A	A4 (D7566)	Waste CO ₂ and renewable power. Municipal solid waste. Agricultural waste / waste wood	50
Alcohol to jet synthetic paraffinic kerosene (to also include synthetic isobutene)	ATJ - SPK	A5 (D7566)	Ethanol, isobutanol and isobutene from sugars and other sources.	50
Synthesized kerosene from hydrothermal conversion of fatty acid esters and fatty acids	CHJ	A6 (D7566)	Vegetable oils and waste oils (e.g. used cooking oil)	50
Synthesized paraffinic kerosene from hydroprocessed hydrocarbons, esters and fatty acids	HC- HEFA SPK	A7 (D7566)	Botryococcus braunii species of algae	10
Alcohol-to-jet synthetic kerosene with aromatics	ATJ-SKA	A8 (D7566)	C2 – C5 alcohols derived from sugars and other sources.	50
Re-processing of hydrotreated esters and fatty acids in mixture with petroleum distillates	-	A1.2.2.3 (D1655)	Already processed HEFA - Included to manage refinery re-processing of retuned product / pipeline interfaces	24%(feed) 10%(product)

Refinery Co-Processing



Refinery Co-Processing

- Co-processing is popular in Europe to meet SAF demand with refinery production recorded in:
 - UK.
 - Germany.
 - Spain.
 - Italy.
 - Austria.
 - France.
- Increasing the 5% limit offers a good transition route for future SBC / SAF manufacture as the automotive pool diversifies to low carbon alternatives.



Co-processing offers an early transition route to SAF while units adopt 100% operation or stand-alone units are built .

Refinery Co-Processing

- The International Civil Aviation Organization (ICAO) have assessed new synthesis routes for carbon life-cycle emissions.
 - Carbon Off-Setting and Reduction Scheme of International Aviation (CORSIA) Default Life Cycle Emissions Values for CORSIA Eligible Fuels, June 2022.
- SBC carbon reduction is similar for standalone and co-processed molecules:

Region	Feedstock	Pathway	Life Cycle Emissions Factor (gCO ₂ e/MJ)	Life Cycle Emissions Versus Crude Oil Jet
BaseLine	Crude Oil	Conventional	89.0	0%
Global	Tallow	D7566 Annex 2 Unit	22.5	-75%
	Tallow	Refinery Co-Processing	27.2	-69%
Global	Used Cooking Oil	D7566 Annex 2 Unit	13.9	-84%
	Used Cooking Oil	Refinery Co-Processing	16.7	-81%

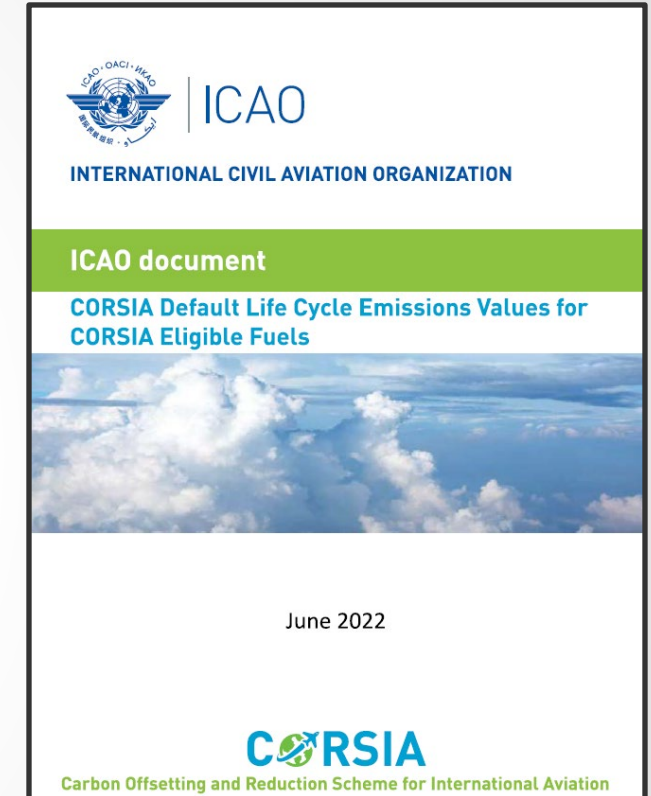


Image: ICAO

Refinery Co-Processing

- An ASTM Task Force is seeking to:
 - Increase refinery co-processing approval from maximum 5 to maximum 30% v/v for HEFA or FT feedstocks.
 - Permit co-processing of mixed HEFA + FT feedstock mixtures.
- Research Report / D4054 technical evidence is required to demonstrate manufacture as fit-for-purpose.
- A major project featuring:
 - 8 pilot plant campaigns.
 - A full-scale refinery demonstration.



Source: www.astm.org

Pilot Plant Program

- Feedstocks featured:
 - Petroleum crude oil hydrocracking feedstock (2 samples, Crude Oil Feedstock 1, Crude Oil Feedstock 2)
 - Coconut oil – short chain HEFA feedstock
 - Mustard seed – long chain HEFA feedstock
 - Used cooking oil – typical commercial HEFA feedstock

Feedstocks were selected to build Aviation Industry technical understanding and demonstrate both short, long and intermediate carbon chain length HEFA feedstocks can be successfully co-hydroprocessed, rather than for sustainability.

Pilot Plant Program

- The two crude oil feedstocks were sourced from the refining network.
- Standard hydrocracking material – heavy, aromatic, high sulfur.

Analysis	Units	Petroleum Feedstock 1	Petroleum Feedstock 2
Appearance	-	Black / Pasty	Black / Pasty
Density at 50°C	kg/m ³	874.9	889.8
Density at 20°C calculated	kg/m ³	895.6	910.2
Mono aromatics	% m/m	20.7	19.3
Di aromatics	% m/m	11.8	10.2
Higher aromatics	% m/m	2.5	4.3
Total aromatics	% m/m	35.0	33.8
Sulfur	% m/m	1.279	0.639

Pilot Plant Program



- HEFA Feedstocks were analysed to confirm density, sulfur, water content and carbon number range.

Coconut Oil



Image: britannica.com

Used Cooking Oil



Image: bioukfuels.co.uk

Mustard Seed Oil



Image: britannica.com

Analysis	Units	Coconut Oil	Mustard Oil	Used Cooking Oil
Density @ 15 °C	kg/m ³	924.1	914.2	896.9
Sulphur	mg/kg	<0.10	<0.10	<0.10
Water content	mg/kg	266	183	598
C06:0	% m/m	0.73	0.00	0.03
C08:0	% m/m	8.22	0.00	0.12
C10:0	% m/m	5.87	0.02	0.08
C12:0	% m/m	42.85	0.28	0.52
C14:0	% m/m	15.95	0.23	0.76
C16:0	% m/m	7.63	2.15	18.43
C16:1	% m/m	0.03	0.15	0.37
C18:0	% m/m	2.35	0.96	4.79
C18:1	% m/m	5.45	23.53	40.50
C18:2	% m/m	1.99	8.70	22.86
C18:3	% m/m	0.10	8.35	0.96
C20:0	% m/m	0.15	0.61	0.34
C20:1	% m/m	0.00	8.86	0.33
C22:0	% m/m	0.05	0.56	0.49
C22:1	% m/m	0.33	34.96	0.06
C24:0	% m/m	0.00	0.35	0.20
C24:1	% m/m	0.10	2.75	0.14

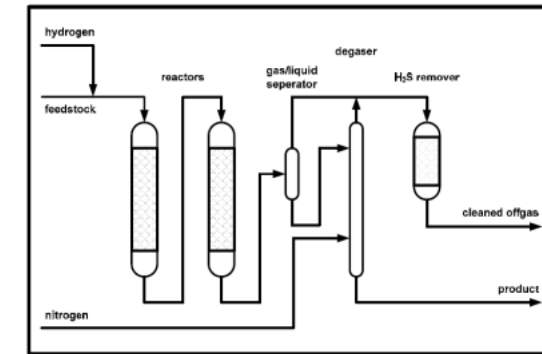
Pilot Plant Program

- Task Force test matrix developed to demonstrate 30% v/v co-processing product quality.
 - 2 additional 5 and 10% v/v runs included.

	Crude Oil Feedstock 1 % v/v	Crude Oil Feedstock 2 % v/v	Used Cooking Oil % v/v	Mustard Seed Oil % v/v	Coconut Oil % v/v
1	100				
2	95		5		
3	70		30		
4		100			
5		70		30	
6		70			30
7		70	10	10	10
8		90			

Pilot Plant Program

- The Test Matrix was hydrocracked on a pilot plant, using standard refinery catalyst / conditions as used for earlier aviation studies:
 - Jet Fuel Desulfurization (IASH 2011).
 - 5% HEFA Feedstock Co-processing (IASH 2013, ASTM 2017).
- Samples were distilled according to ASTM D2892 Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column) to recover a fixed jet fuel fraction (150 to 260 °C) for comparison.



Pilot Plant Program

- C14 and C=O data confirmed the HEFA feedstocks were successfully hydrocracked to yield sustainable carbon in the finished product:

Analysis	C14	Bio-carbon % m/m	Unreacted C=O (IP 583)
Units	dpm/ml	% m/m	mg/kg
100% v/v Crude Oil Feedstock 1	0.140	Background	<10
95% v/v Crude Oil Feedstock 1+ 5% v/v UCO	0.365	2.44	<10
70 % v/v Crude Oil Feedstock 1+ 30% v/v UCO	1.294	12.60	<10
70% v/v Crude Oil Feedstock 2 +30%v/v Mustard Seed Oil	1.296	11.09	<10
70% v/v Crude Oil Feedstock 2 +10% v/v UCO +10% v/v Coconut +10% v/v Mustard	2.321	22.49	<10
70% v/v Crude Oil Feedstock 2 + 30% v/v Coconut Oil	3.738	38.73	<10
90% v/v Crude Oil Feedstock 1 + 10% v/v Coconut Oil	2.222	21.27	<10
100% v/v Crude Oil Feedstock 2	0.249	Background	<10

Pilot Plant Program

- All co-processed product met ASTM D1655 A1.2.2.1 developed for 5% v/v co-processed HEFA:
 - Aromatic content was low, 2.5 to 12.9% v/v, a reflection of the HEFA formed and hydrocracking saturating C=C bonds in a large proportion of the feedstock aromatics.
 - Naphthalene concentration low, $\leq 0.13\%$ v/v.
 - Sulfur content was very low, 0.0064% w/w maximum, $< 0.0003\%$ w/w typical.
 - Viscosity @ $-40\text{ }^{\circ}\text{C}$ ranged from 8.06 to 10.07 cSt.
 - Freeze point ranged from -41.7 to $-69.3\text{ }^{\circ}\text{C}$ and could further be improved with slack on flash point, $+44.5$ to $+59.5\text{ }^{\circ}\text{C}$.
 - $280\text{ }^{\circ}\text{C}$ Thermal Stability visual ratings of 1, $\leq 39.58\text{ nm}$ deposit and minimal ΔP , $\leq 2\text{ mmHg}$.
 - Unconverted C=O was below the detection limit of 10 mg/kg.

Pilot Plant Program

Analysis	Units	Limits	100% v/v Petroleum Feedstock 1	95% v/v Petroleum Feedstock 1+ 5% v/v UCO	70 % v/v Petroleum Feedstock 1+ 30% v/v UCO	70% v/v Petroleum Feedstock 2 +30% v/v Mustard Seed Oil	70% v/v Petroleum Feedstock 2 +10% v/v UCO +10% v/v Coconut +10% v/v Mustard	70% v/v Petroleum Feedstock 2 + 30% v/v Coconut Oil	90% v/v Petroleum Feedstock 2 + 10% v/v Coconut Oil	100% v/v Petroleum Feedstock 2
COMPOSITION										
Acidity	mgKOH/g	0.10 max	0.003	0.003	0.001	<0.001	0.003	0.003	0.004	0.004
Aromatics (D6379)	% v/v	26.5 max	4.3	3.5	2.5	8.6	7.8	5.9	7.6	12.9
Mercaptan Sulfur	% m/m	0.003 max	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Total Sulfur	% m/m	0.30 max	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.00064	<0.0003
VOLATILITY										
Distillation										
IBP	°C		168.9	169.0	169.1	169.5	174.1	175.3	174.9	170.6
T10%	°C	205 max	181.4	178.8	178.4	182.3	186.6	186.4	187.3	184.2
T50%	°C	Report	200.7	196.3	195.0	202.9	205.8	200.2	207.5	205.9
T90%	°C	Report	231.6	227.4	226.2	228.7	233.3	215.9	234.5	235.1
FBP	°C	300 max	245.0	249.9	242.9	246.8	246.4	226.7	248.1	249.4
Residue	% v/v	1.5 max	1.5	1.5	1.4	1.2	1.2	1.1	1.2	1.2
Loss	% v/v	1.5 max	0.4	0.4	0.4	0.7	0.8	0.7	0.6	0.6
Flash Point	°C	+38 min	54.5	53.0	44.5	53.5	57.0	57.0	59.5	55.5
Density @ 15 °C	kg/m3	775 - 840	803.8	797.9	790.2	802.1	798.6	782.5	804.1*	819.1
FLUIDITY										
Freeze Point	°C	-40 max (Jet A)	-67.5	-65.2	-65.4	-63.6	-47.3	-41.7	-49.9‡	-69.3
Viscosity @-20 °C	mm2/s	8.0 max	More severe specification of viscosity @-40°C applies – See below							
COMBUSTION										
Net Heat of Combustion	MJ/kg	42.8 min	43.5	43.5	43.6	43.39	43.48	43.67	43.42	43.17
Naphthalenes	% v/v	3.0 max	0.01	0.01	0.01	0.05	0.05	0.04	0.07	0.13
Smoke Point	mm	18.0 min	29.7	31.3	35.2	28.3	30.1	36.4	28.7	22.8
CORROSION										
Copper Corrosion	Rating	1 max	1	1	1	1	1	1	1	1

* Average of 2 results (802.7, 805.4 kg/m³)

‡ Average of 2 results (-48.7, -51.1 °C)



Pilot Plant Program



Analysis	Units	Limits	100% v/v Petroleum Feedstock 1	95% v/v Petroleum Feedstock 1+ 5% v/v UCO	70 % v/v Petroleum Feedstock 1+ 30% v/v UCO	70% v/v Petroleum Feedstock 2 +30% v/v Mustard Seed Oil	70% v/v Petroleum Feedstock 2 +10% v/v UCO +10% v/v Coconut +10% v/v Mustard	70% v/v Petroleum Feedstock 2 + 30% v/v Coconut Oil	90% v/v Petroleum Feedstock 2 + 10% v/v Coconut Oil	100% v/v Petroleum Feedstock 2
THERMAL STABILITY @ 260°C			More severe specification of thermal stability @ 280°C applies – See below.							
Visual Rating	Rating	<3 max/no P or A								
dP	mmHg	25 max								
Thickness	ETR nm	85 max								
CONTAMINANTS										
Existent Gum†	mg/100ml	7 max	<1	1	<1	<1	0	1	1	4
MSEP	Rating	85 min (no SDA)	95	99	97	99	99	100	90	86
ADDITIVES										
Conductivity + 0.5 mg/L SDA	pS/m	50 – 600 (For information)	168	167	160	235	170	160	160	190
Conductivity temperature	°C	Report (For information)	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5

† Without any anti-oxidant added to samples.



Pilot Plant Program

Analysis	Units	Limits	100% v/v Petroleum Feedstock 1	95% v/v Petroleum Feedstock 1+ 5% v/v UCO	70 % v/v Petroleum Feedstock 1+ 30% v/v UCO	70% v/v Petroleum Feedstock 2 +30% v/v Mustard Seed Oil	70% v/v Petroleum Feedstock 2 +10% v/v UCO +10% v/v Coconut +10% v/v Mustard	70% v/v Petroleum Feedstock 2 + 30% v/v Coconut Oil	90% v/v Petroleum Feedstock 2 + 10% v/v Coconut Oil	100% v/v Petroleum Feedstock 2
THERMAL STABILITY @ 280°C										
Visual Rating	Rating	<3 max/no P or A	1	1	1	1	1	1	1	1
dP	mmHg	25 max	0	0.0	2.0	0.0	0.1	0.0	0.0	0.0
Deposit Thickness	ETR nm	85 max	13.95	22.71	14.47*	12.20‡	9.44	9.66	39.58	21.47
	ITR nm	85 max	14.7	24.0	22.9	13.4	15.2	14.9	25.3	32.4
Viscosity @-40 °C	mm ² /s	12.0 max	9.24	8.39	8.06	9.37	9.68	8.18	9.97	10.07
Unconverted esters and fatty acids (IP 583)	mg/kg	Δ15 max	<10	<10	<10	<10	<10	<10	<10	<10

* Average of 2 results (12.00, 16.94 nm)

‡ Average of 2 results (7.00, 17.39 nm)



Pilot Plant Program

To ensure finished product will be 'typical' additional criteria have been proposed for Jet containing 5 – 30% co-processed HEFA:

- 7000 kPa hydrogen partial pressure to help define hydrocracking.
- Aromatic concentration limits based on CRC Project AV-2-04a:
 - 8 (D1319) / 8.4 (D6379) % v/v minimum
 - supported by 50% v/v maximum co-hydrocracked Jet blending limit
- Additional distillation parameters:
 - T50% - T10% \geq 15 °C
 - T90% - T10% \geq 40 °C
- Lubricity, BOCLE 0.85 mm maximum.
- Anti-oxidant 17 – 24 mg/l (similar to MIL-DTL-83133 JP-8).

Pilot Plant Program: Peroxides

Sample (17 mg/l RDE/A/609 Aviation Anti-Oxidant)	Peroxides ASTM D3703	
	Initial mg/kg	After ASTM D5304 Aging (16 Hours / 100 °C / 100 psi Oxygen) mg/kg
Jet A-1	0.911	2.041
50:50 Blend Jet A-1 + Co-processed HEFA (19% HEFA to demonstrate ruggedness).	0.812	2.015

Refinery Program

- A full-scale refinery trial has been completed in support of the Task Force:
 - Carinata feedstock (sustainable cover-crop).
 - Standard refinery petroleum feedstock.
 - 10% v/v campaign.
- All product sent to diesel (no limitation on HEFA co-processing):
 - Kerosene sample taken and blended 50:50 with Jet A-1 run-down streams to demonstrate aviation fuel quality which would have been present in finished product tank.

Refinery Program

- Petroleum and Carinata feedstock analysis:

Analysis	Units	Petroleum Feedstock 3
Density at 15°C	kg/m³	914.8
Initial Boiling Point	°C	269.0
Final Boiling Point	°C	595.1
Sulfur	% m/m	0.62

Analysis	Units	Carinata Oil
Density @ 15 °C	kg/m³	916.6
Sulfur	mg/kg	-
Water content	mg/kg	400
C06:0	% m/m	<0.1
C08:0	% m/m	<0.1
C10:0	% m/m	<0.1
C12:0	% m/m	<0.1
C14:0	% m/m	<0.1
C15:0	% m/m	0.1
C15:1	% m/m	<0.1
C16:0	% m/m	4.0
C16:1	% m/m	<0.1
C17:0	% m/m	<0.1
C17:1	% m/m	<0.1
C18:0	% m/m	1.2
C18:1	% m/m	15.0
C18:2	% m/m	20.6
C18:3	% m/m	13.1
C19:0	% m/m	0.1
C20:0	% m/m	0.9
C20:1	% m/m	1.0
C22:0	% m/m	<0.1
C22:1	% m/m	40.3
C22:2	% m/m	1.2
C24:0	% m/m	<0.1
C24:1	% m/m	1.8

Refinery Program

- Jet A-1 Quality

Analysis	Units	Limits	Refinery Co-processed HEFA Jet A-1
COMPOSITION			
Acidity	mgKOH/g	0.10 max	0.002
Aromatics (D6379)	% v/v	26.5 max	18.0
Mercaptan Sulfur	% m/m	0.003 max	0.0002
Total Sulfur	% m/m	0.30 max	0.0009
VOLATILITY			
Distillation			
IBP	°C		167.5
T10%	°C	205 max	179.5
T50%	°C	Report	196.8
T90%	°C	Report	226.6
FBP	°C	300 max	256.3
Residue	% v/v	1.5 max	1.2
Loss	% v/v	1.5 max	0.6
Flash Point	°C	+38 min	52.0
Density @ 15 °C	kg/m3	775 - 840	810.5
FLUIDITY			
Freeze Point	°C	-47 max (Jet A-1)	-51.3
Viscosity @ -20 °C	mm2/s	8.0 max	4.262
COMBUSTION			
Net Heat of Combustion	MJ/kg	42.8 min	43.15
Naphthalenes	% v/v	3.0 max	0.17
Smoke Point	mm	18.0 min	22
CORROSION			
Copper Corrosion	Rating	1 max	1a



Refinery Program

- Jet A-1 Quality

Analysis	Units	Limits	Refinery Co-processed HEFA Jet A-1
THERMAL STABILITY @ 260°C			More severe specification of thermal stability @ 280°C minimum applies – See below.
Visual Rating	Rating	<3 max/no P or A	
dP	mmHg	25 max	
Thickness	ETR nm	85 max	
CONTAMINANTS			
Existent Gum	mg/100ml	7 max	<0.5
MSEP	Rating	85 min (no SDA)	92
ADDITIVES			
Anti-oxidant RDE/A/609	mg/L	17 - 24	20



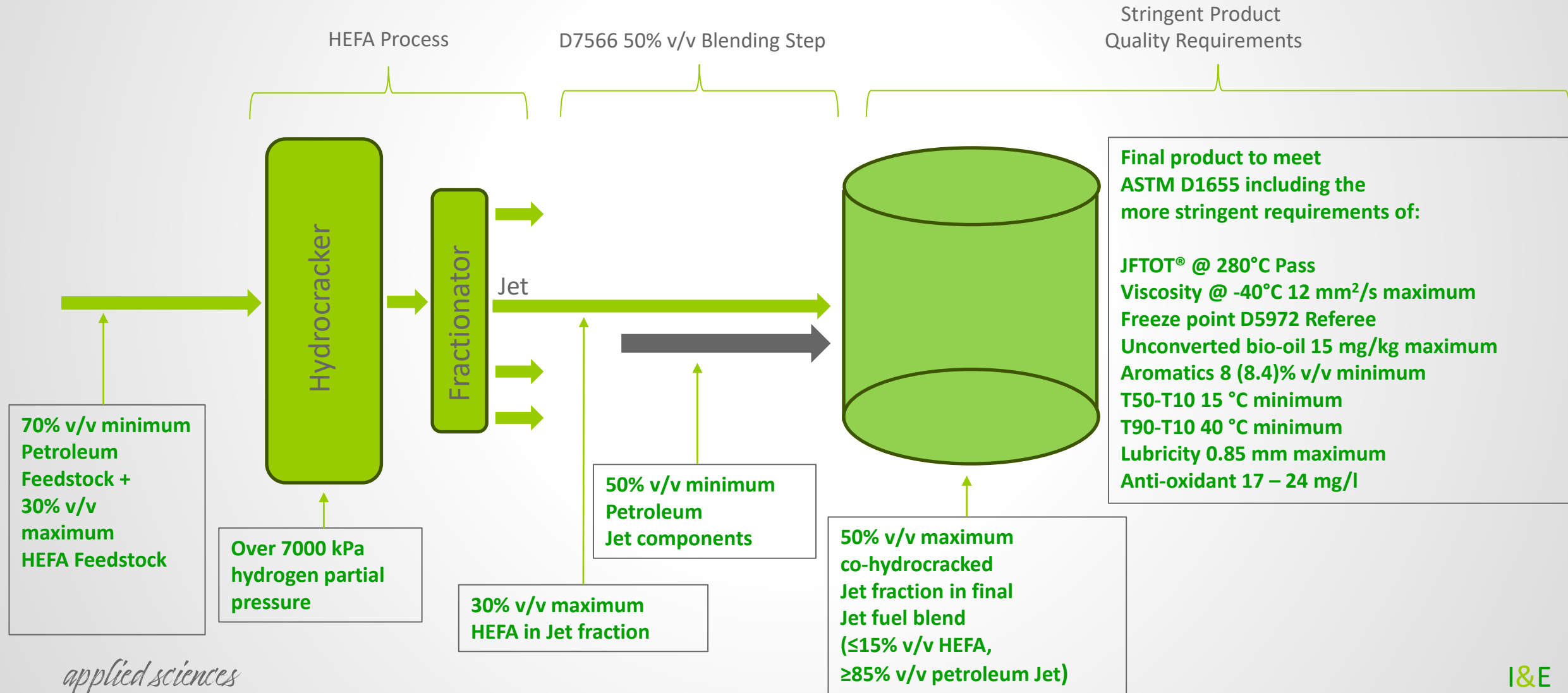
Refinery Program

- Jet A-1 Quality

Analysis	Units	Limits	Refinery Co-processed HEFA Jet A-1
THERMAL STABILITY @ 285°C			
Visual Rating	Rating	<3 max/no P or A	0
dP	mmHg	25 max	0.0
Deposit Thickness	ETR nm	85 max	63.34
Viscosity @-40 °C	mm ² /s	12.0 max	8.559
Freeze Point D7153	°C	-47 max (Jet A-1)	-51.3
Unconverted esters and fatty acids (IP 583)	mg/kg	Δ15 max	<10
Aromatics (D6379)	% v/v	8.4 min	18.0
T50 - T10	°C	15 min	17.3
T90 - T10	°C	40 min	47.1
Lubricity	mm	0.85 max	0.64



Summary



Summary

- To meet the IATA aspiration of carbon neutral operations by 2050 requires production of new synthetic kerosene blend components from sustainable feedstocks.
- To meet this goal utilization of refinery hydrotreatment and fractionation facilities offers advantages - CAPEX, production flexibility, supply security, operational expertise and time-to-market.
- An ASTM Task Force has demonstrated the current 5% HEFA feedstock co-processing limit can be increased up to 30% v/v:
 - 8 pilot plant campaigns.
 - A full-scale refinery demonstration at 10% v/v.
- All product met current D1655 $\leq 5\%$ v/v HEFA co-processing requirements.
- Additional requirements have been included to promote industry approval.

Co-processing: A flexible Jet manufacturing route to assure product availability and reduce environmental foot-print.

Thank You

