Co-Processing of HEFA feedstocks with Petroleum Hydrocarbons for Jet Production

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Introduction

To help mitigate CO_2 emissions/climatic change transport fuels around the world seek to include sustainable, renewable products. These may include:

- Alcohols/ethers for automotive gasoline.
- Fatty acid methyl esters for automotive diesel fuel.

Original Equipment Manufacturers (OEMs) have evaluated the performance of these products and appropriate limits for maximum concentration have been set. For example:

- EN228:2012 Gasoline ≤10% v/v ethanol, ≤ 3.7 m/m oxygen.
- EN590:2013 Diesel ≤7% v/v FAME

Introduction

Various targets for renewable fuel are mandated, for example via:

- US Renewable Identification Numbers (RINS)
- European Renewable Energy Directive

OEM limits, local requirements and production constraints can make it difficult to achieve set targets using standard, oxygen containing renewable components.

To resolve this problem, renewable feed-stocks may be processed by refining technology to yield hydrocarbon components.

Introduction

Provision is made for this in fuel specifications, for example EN590:2013 for automotive diesel fuel:

‘5.4 Other (bio-) components

Limits for adding FAME are set for technical reasons. Limits for FAME do not apply to other (renewable) hydrocarbons such as Hydrotreated Vegetable Oil (HVO), Gas To Liquid (GTL) or Biomass To Liquid (BTL)

derived hydrocarbons, since these paraffinic diesel components are allowed in any proportions provided that the final blend complies with the requirements of EN 590. The use of renewable feedstock at refineries is also allowed provided that the final fuel meets the requirements of EN 590.’

Introduction

To meet renewable targets a refinery may therefore choose to process renewable feed-stocks for diesel manufacture. This may take the form of 'Co-processing' with crude oil derived middle distillates.

But…

What if the middle distillate chain also features jet fuel? At present:

- The jet fuel production would need to be switched off/sent to diesel as such processing of bio-oils is not approved for aviation use.
- The much sought after renewable carbon would be lost from the aviation pool.

Introduction

Chevron, Phillips66 and BP have sought to determine if these renewable hydrocarbons from co-processed bio-oils are suitable for jet fuel to help refinery operation the Aviation Industry mitigate CO_2 *footprint.*

Introduction

NOTE:

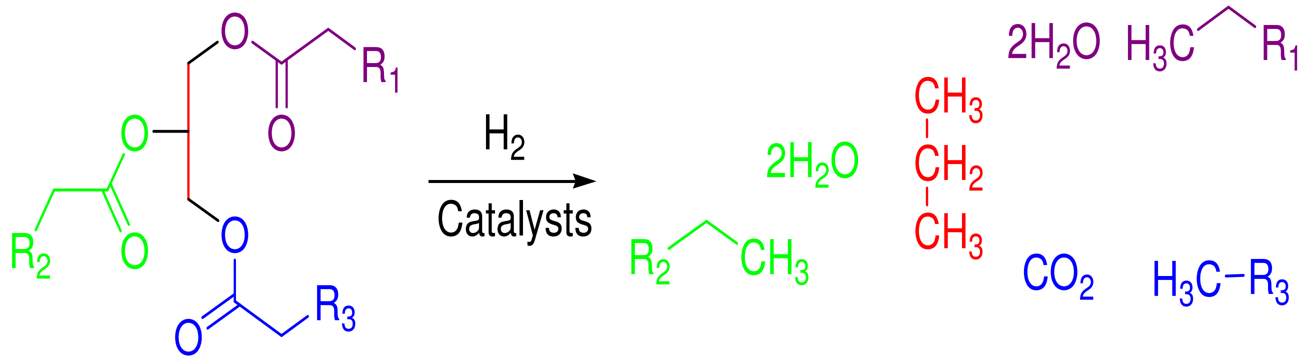
Separate hydroprocessing of middle distillates from crude oil is already approved for jet fuel production under ASTM D1655.

Separate hydroprocessing of bio-oils is already approved for jet fuel production under ASTM D7566 Annex 2 Hydrotreated Esters and Fatty Acids (HEFA).

This study seeks to verify that a combination of the two is reasonable and obtain Aviation Industry approval.

Process Chemistry

When a fatty acid is hydroprocessed, the following reaction occurs:



The final hydrocarbon chain length is largely dependent on the feedstock. For example a C18 bio-oil could be converted into:

- C18 paraffins through hydrodeoxygenation with water as by-product.
- C17 paraffins through hydrodecarboxylation with CO_2 as by-product.

Bio-oil length is therefore a significant influence on amount of bio-derived hydrocarbon which might appear in the diesel or jet boiling range.

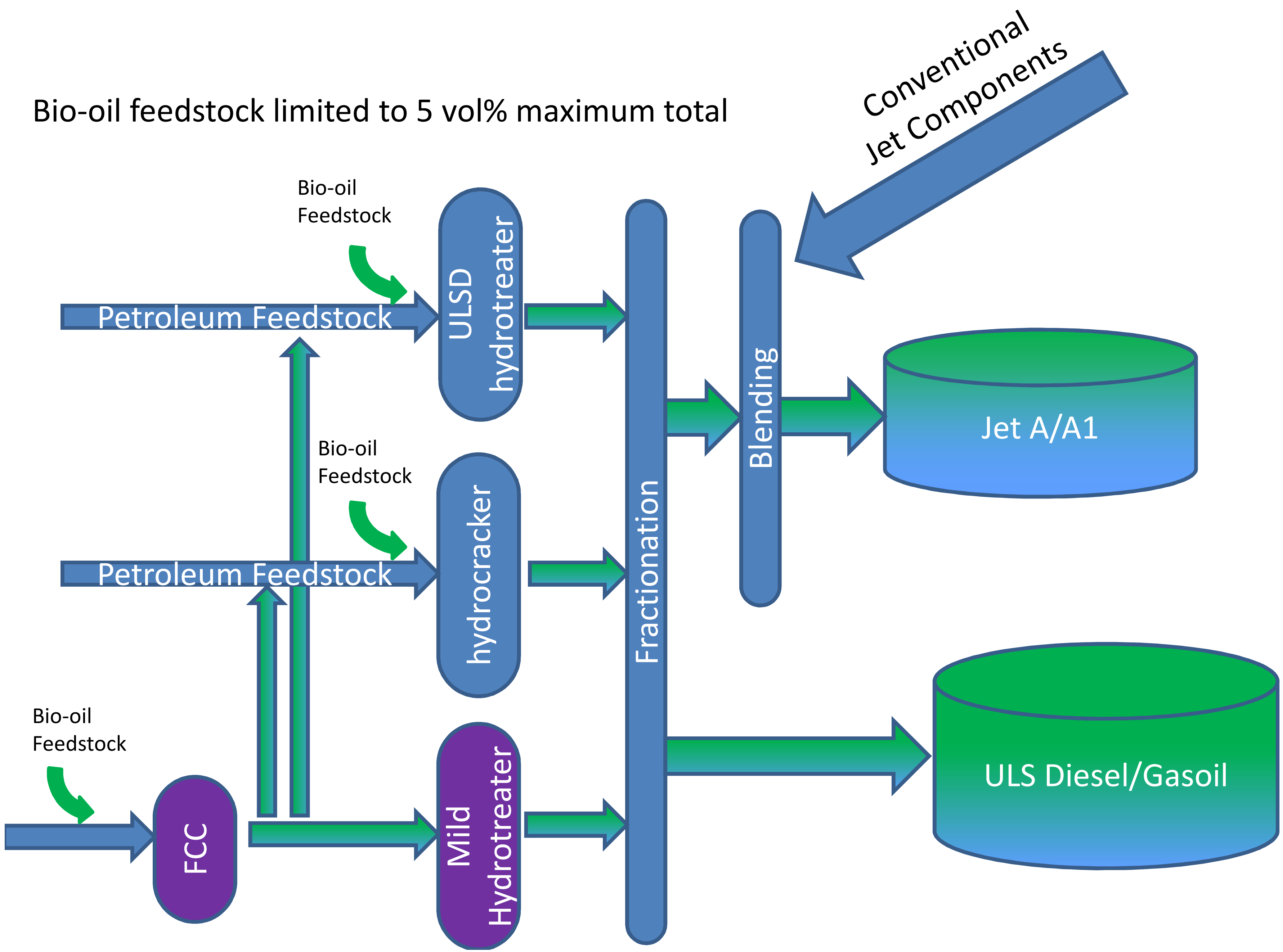
Research

Phillips66, Chevron and BP have undertaken:

- Process simulation studies.
- Pilot plant studies

to determine the impact of co-processing a range of bio-oils (Triglycerides) at up to 5% in combination with middle distillates on jet fuel.

Focus has been on 3 potential routes for including bio-oils into refinery streams:



Bio-oil feedstock limited to 5 vol% maximum total
Conventional
Jet Components
Bio-oil
Feedstock
Petroleum Feedstock
ULSD
hydrotreater
Bio-oil
Feedstock
Petroleum Feedstock
hydrocracker
Bio-oil
Feedstock
FCC
Mild
Hydrotreater
Fractionation
Blending
Jet A/A1
ULS Diesel/Gasoil

Research

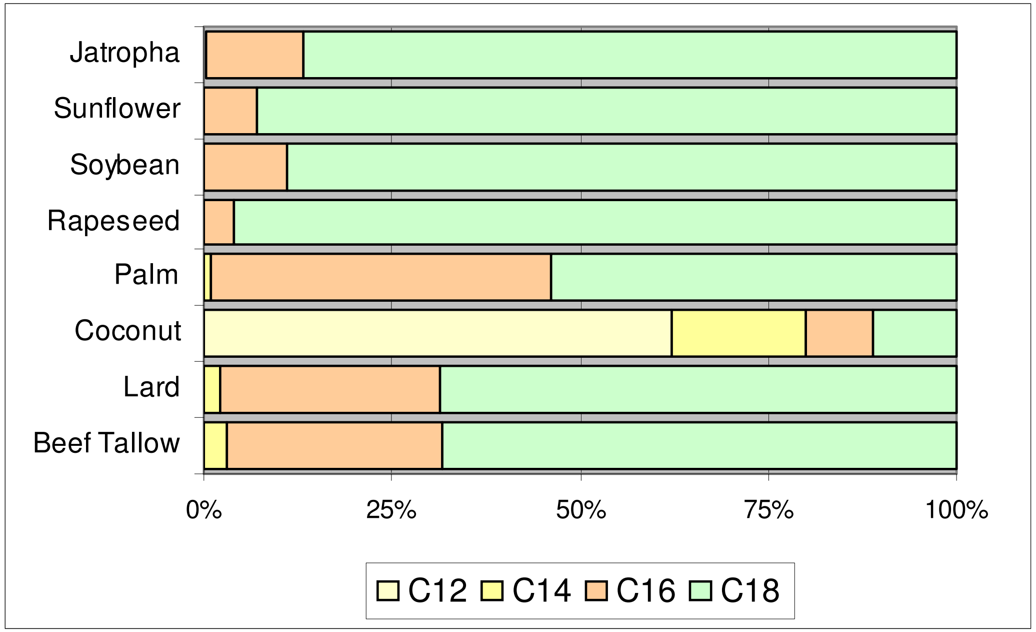
The following aspects have been considered/investigated:

- Process Simulation Study (P66)
- Coprocessing Pilot Plant Studies
  - Co-Hydrotreating Study 1 (Chevron)
  - Co-Hydrotreating Study 2 (BP)
  - Co-Hydrocracking Study (BP)

By way of example, hydrotreatment/hydrocracking data will be presented.

Bio-Oil Selection

- By selecting a range of oils the bio-content in the jet fraction can be varied.
- A theoretical study was undertaken to determine which oils might be of most interest / representative.



Courtesy of Food Fats and Oils, Institute of Shortening and Edible Oils 2006

Theoretical Study

Results indicated 3 oils offer a useful insight into co-processing:

- Coconut
  - low molecular weight bio-carbon formed / rich in jet fraction.
- Rapeseed
  - high molecular weight bio-carbon formed / low in jet fraction.
- Tallow
  - readily available waste oil.

Experimental Study

Two hydro-processing conditions investigated:

- Hydrotreatment, typically used to eliminate sulphur and other trace contaminants in crude oil derived middle distillates.
  - Refinery mixed middle distillate stream prepared from 30% jet / 70% diesel.

- Hydrocracking, used to crack and hydrogenate heavier crude oil fractions to middle distillates and naphtha.
  - Typical refinery hydrocracker crude oil feedstock selected.

Experimental Study

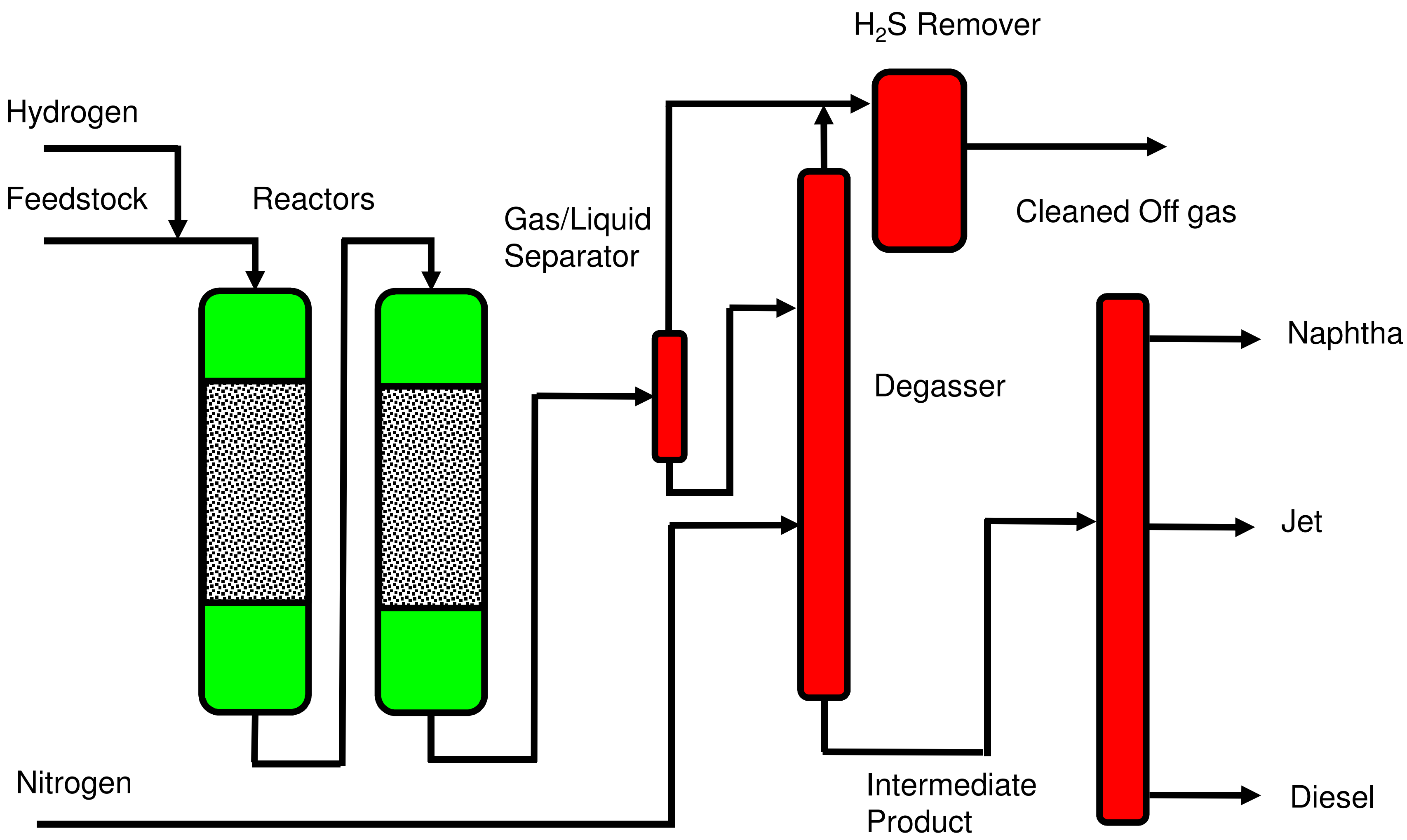
- 4 feedstock samples prepared.
- 5% m/m bio-oil selected for co-hydroprocessing.

Why?

- Bio-oil reaction in unit will form water potentially poisoning catalyst/reducing turn-round time.

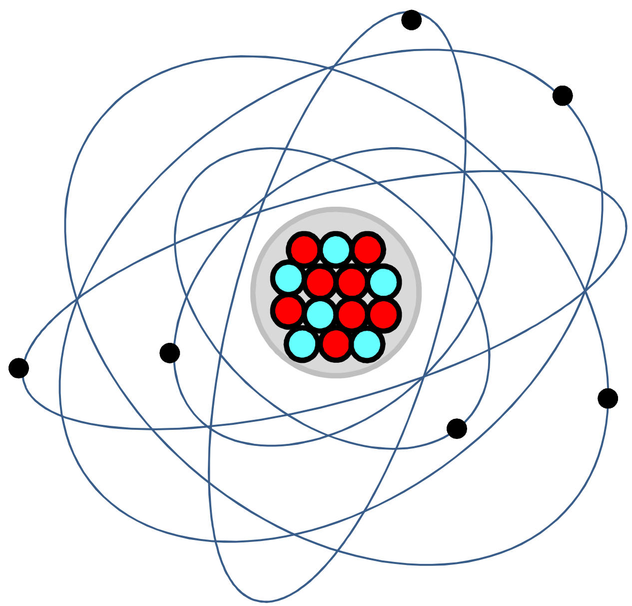
Blends	Sample description
1	Base fuel
2	95 % (m/m) base fuel + 5 % (m/m) Coconut oil
3	95 % (m/m) base fuel + 5 % (m/m) Rapeseed oil
4	95 % (m/m) base fuel + 5 % (m/m) Tallow oil

Experimental Study



Results

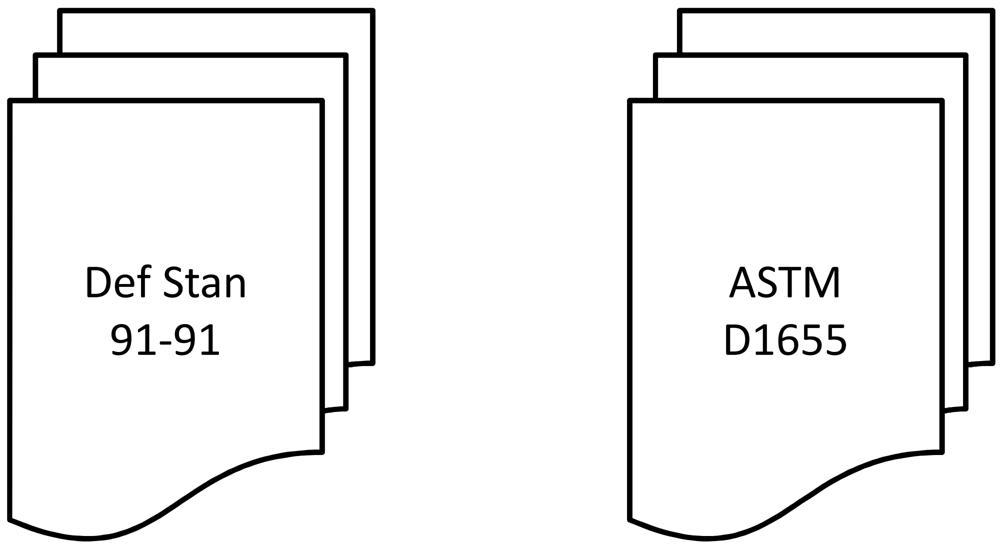
- C14 analysis of hydrotreated samples confirmed bio-carbon reached reaction products:
  - Bio-carbon reached both the kerosene and diesel fractions.
  - The concentration was dependent on carbon number make-up of bio-oil and product boiling range.



Carbon-14
unstable (radioactive)

Results

- Co-processed kerosene fractions analysed versus Def Stan 91-91 / ASTM D1655 specifications.



Results

- Hydrotreated Kerosene:

ANALYSIS	UNITS	Distilled product - Jet (base fuel)	Distilled product - Jet (base fuel + Coconut oil)	Distilled product - Jet (base fuel + Rapeseed oil)	Distilled product - Jet (base fuel + Tallow oil)
Colour	-	30	30	30	30
Density at 15°C	kg/m³	812.9	809.5	813.7	813.6
Sulphur	ppm	<2.9	<3.0	4.3	4.7
IBP	°C	156.0	152.0	149.9	153.8
T10%	°C	183.5	182.7	182.8	182.9
T50%	°C	210.0	209.8	210.1	210.2
T90%	°C	236.3	235.5	235.9	235.9
EP	°C	245.7	245.5	245.5	245.5
Flash Point	°C	48.0	45.5	44.5	45.5
Freezing Point	°C	-49.6	-47.7	-49.7	-49.5
Naphthalene	% v/v	0.3436	0.9765	0.8019	0.7516
JFTOT® (275 °C)	Rating	1	Insufficient sample	1	1
BOCLE (WSD)	mm	0.61	0.62	0.65	0.66

Results

- Hydrocracked Kerosene:

ANALYSIS	UNITS	Distilled product - Jet (base fuel)	Distilled product - Jet (base fuel + Coconut oil)	Distilled product - Jet (base fuel + Rapeseed oil)	Distilled product - Jet (base fuel + Tallow oil)
Colour	-	30	30	30	29
Density at 15°C	kg/m³	815.8	806.9	814.6	811.8
Sulphur	ppm	<0.0003	<0.0003	<0.0003	0.00045
IBP	°C	173.3	172.3	173.5	171.9
T10%	°C	184.9	185.3	184.8	183.3
T50%	°C	206.9	206.2	206.2	205.8
T90%	°C	236.6	235.2	236.0	236.5
EP	°C	248.5	246.3	247.4	248.1
T50 – T10	°C	22.0	20.9	21.4	22.5
T90 – T10	°C	51.7	49.9	51.2	53.2
Flash Point	°C	56.5	56.5	56.5	54.5
Freezing Point	°C	-67.2	-56.9	-67.1	-60.8
Naphthalene	% v/v	0.06	0.04	0.07	0.05
JFTOT® (260 °C)	Rating	1	1	1	1

R&D Challenges

- Differentiating bio-derived hydrocarbons from petroleum derived hydrocarbons is difficult in co-processed products.
- Analysis of lipid contribution to heteroatoms in petroleum process streams is challenging as levels are typically very low when comparing pre/post addition samples.

Metals and Halogens Analysis of Co-Hydrotreated Kerosene Fraction

F	Non-detect
Cl	0.3 ppm
Br	Non-detect

Metal	ppb
Ca	<294
Cr	<5
Cu	<5
K	<267
Mg	<26
Mn	<5
Mo	<5
Na	< 563
P	<267
Ti	<48
Al	<256
Fe	<32
Pb	<8
Ni	<8
Sn	<64
V	<8
Zn	<24

Research Report

A draft ASTM Research Report has been prepared for the Industry covering:

- Co-processing Chemistry
- Process Simulation Study (P66)
- Coprocessing Pilot Plant Studies
  - Co-Hydrotreating Study 1 (Chevron)
    - One Feedstock, D1655, Unreacted Triglycerides, Oxygenates, Metals, Halogens, C14
  - Co-Hydrotreating Study 2 (BP)
    - Multiple Feedstocks, D1655, BOCLE, Ellipsometer, C14
  - Co Hydrocracking Study (BP)
    - Multiple Feedstocks, D1655, BOCLE, Ellipsometer, C14

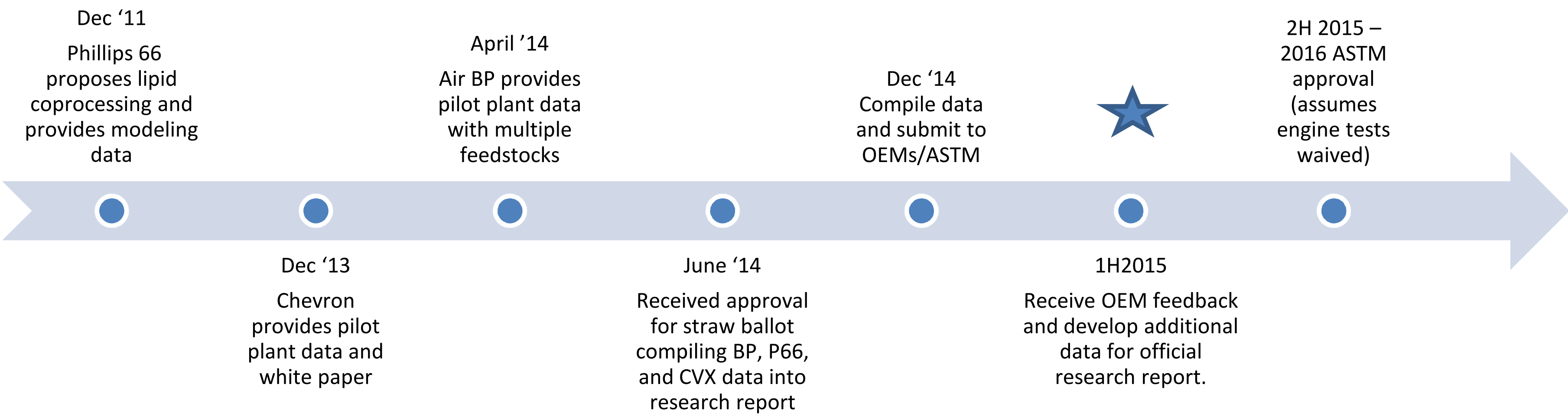
CAAFI members are welcome to join the ASTM Task Force – Please contact Joe, Enrico or Alisdair.

Approval Path

- Propose that ASTM D1655 hydroprocessing of conventional middle distillates and ASTM D7566 hydroprocessing of bio-oils ('HEFA') can be combined in a conventional refinery provided that:
  - The bio-oil component is limited to ≤5% v/v (refinery constraint to protect catalyst from excessive water formation/poisoning).
  - The final product has ≤5 ppm unreacted triglycerides (proof that the bio-oil has been converted to hydrocarbons).
  - Meets ASTM D7566 Table 1 Part 1 (proof that a standard crude oil derived Jet / HEFA blend has been formed).
  - Achieves JFTOT ® ≥ 275 °C Pass (provide additional safety margin over standard ≥ 260 °C limit).
- Include in ASTM D7566 as an additional Annex given Industry approval.

Approval Path

- Time-line:



Approval Path

- Seek OEM/ASTM Feedback
  - Formal Feedback received from
    - FAA, DLA, Metron Aviation
- Draft Annex for ASTM D7566 under development.

Conclusions

- Theoretical and experimental studies have been completed for co-hydroprocessing of bio-oils at 5% m/m in mixture with crude oil middle distillates to determine the impact on jet fuel quality.
- Results suggest D1655 hydroprocessing and D7566 HEFA processing may be combined to give an acceptable 'co-processed' product for Jet as a side-stream to automotive diesel manufacture.
- Given Industry approval, an additional Co-processing Annex to D7566 is proposed featuring:
  - Maximum 5% v/v bio-oil concentration in feed-stock ≤5%.
  - Maximum 5 ppm unreacted triglycerides in product.
  - Minimum JFTOT ® 275 °C
  - Other parameters as ASTM D7566 Table 1 Part 1 for a HEFA/Crude Oil derived jet blend.