

Production of Hydroprocessed Esters and Fatty Acids (HEFA) – Optimisation of Process Yield

Laurie Starck^{1*}, Ludivine Pidot¹, Nicolas Jeuland¹, Thierry Chapus²,
Paul Bogers³ and Joanna Bauldreay³

¹ IFP Energies nouvelles, 1-4 avenue de Bois-Préau, 92852 Rueil-Malmaison - France

² IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize - France

³ Shell Global Solutions Downstream, Shell Technology Centre Thornton, P.O. Box 1, Chester CH1 3SH - United Kingdom
e-mail: laurie.starck@ifpen.fr - ludivine.pidot@ifpen.fr - nicolas.jeuland@ifpen.fr - thierry.chapus@ifpen.fr
paul.bogers@shell.com - joanna.bauldreay@shell.com

* Corresponding author

Abstract — Both Fischer-Tropsch (FT) and Hydroprocessed Esters and Fatty Acids (HEFA) Synthetic Paraffinic Kerosine (SPK) fuels are considered as leading alternative replacements for conventional jet fuel. To satisfy the requirements of Civil Aviation Authorities (CAA), their drop-in incorporations have been subjected to a rigorous certification process. To reach the ambitious incorporation targets, new routes for biofuels incorporation may need to emerge, involving optimizing the production processes and the blending strategies. This paper focuses on a new strategy for incorporating HEFA, allowing the process yield to be optimised.

One of the major steps limiting the process yield for HEFA remains the isomerisation that allows production of a biofuel with very good cold flow properties. But this step introduces a substantial decrease of the overall yield (fuel component per kg of starting material) due to the production of light compounds, unsuitable for conventional jet fuel. In this work relaxing the freezing point requirement for the neat HEFA component (by decreasing the severity of the isomerisation step) is proposed in order to minimize the production of less valuable light compounds. This strategy could lead to a significant additional biofuel yield with respect to the oil compared to a process making a better freezing point component. This allows the land surface area necessary for HEFA feedstock cultivation to be reduced for a given amount of bio-jet fuel produced.

Résumé — **Production d'huiles végétales hydrotraitées (Hydroprocessed Esters and Fatty Acids, HEFA) – Optimisation du rendement** — Le développement des carburants alternatifs est en plein essor, notamment dans le domaine aéronautique. Cela se concrétise par la possibilité, d'incorporer jusqu'à 50 % de carburants de synthèse de type Fischer-Tropsch (FT) ou *Hydroprocessed Esters and Fatty Acids* (HEFA) dans du carburéacteur. Ces cibles d'incorporation sont ambitieuses. C'est pourquoi, l'objectif de cet article est d'étudier une stratégie innovante pour l'incorporation des carburants alternatifs, et plus précisément des carburants de type HEFA, dans le domaine aéronautique en optimisant les stratégies de mélanges c'est-à-dire en cherchant à optimiser les rendements des procédés.

En effet, l'un des moyens d'action permettant d'améliorer les rendements des procédés HEFA est d'agir sur l'étape d'hydrotraitement. Cette étape permet d'améliorer les propriétés à froid. Cependant la contre partie est l'impact que cela peut avoir sur le rendement : améliorer les

propriétés à froid est synonyme de perte en rendement (carburant produit par kg par rapport à la masse de matière première) à cause de la production de produits légers qui ne sont pas utilisables dans la coupe jet. Ce travail propose donc de relâcher la contrainte sur le point de disparition des cristaux, exigée pour les carburants de type HEFA, en jouant sur la sévérité de l'étape d'hydrotraitement et donc en minimisant la production de produits légers afin de maximiser les rendements. Cette stratégie pourrait amener à avoir un meilleur rendement en biojet par rapport à l'huile de départ comparée à une stratégie dans laquelle on recherche un meilleur point de disparition des cristaux. Ainsi, il serait envisageable de réduire les surfaces agricoles utilisées pour la culture des plantes pour un même volume de biojet produit.

DEFINITIONS / ABBREVIATIONS

ASTM	American Society for Testing and Materials International
CAA	Civil Aviation Authorities
DCO	Decarboxylation
EU-ETS	European Union Greenhouse Gas Emission Trading Scheme
FT	Fischer-Tropsch
HDO	Hydrodeoxygenation
HEFA	Hydroprocessed Esters and Fatty Acids
HIS	Hydroisomerization
HRJ	Hydroprocessed Renewable Jet
HVO	Hydrotreated Vegetable Oil
<i>n</i> P	Normal (Linear) Paraffins
<i>i</i> P	Iso Paraffins
SPK	Synthetic Paraffinic Kerosene
SWAFEA	Sustainable Way for Alternative Fuel and Energy in Aviation

INTRODUCTION

World wide air traffic has been steadily increasing for many years and is predicted to grow at a rate of close to 4-5% per year, with even higher growth rates in the Middle East and Asia [1, 2].

Moreover, the increased focus on climate change over the last decade has created pressure to reduce greenhouse gases emissions. It has been estimated that the aeronautics sector represents 2 to 3% of the global CO₂ emissions [3]. Such a contribution may seem to be minor but the air traffic is expected to strongly increase in the next years while other industries move to lower carbon options. This is one reason it has been decided to include the aeronautics sector in the EU-ETS (European Union Greenhouse Gas Emission Trading Scheme) from 2012.

International Air Transport Association (IATA) has adopted a voluntary ambitious fuel efficiency goal:

reducing CO₂ emissions by 50% by 2050, compared to the 2005 level, as illustrated in Figure 1. Consequently, the search for new alternative fuels for aircraft seems to be a promising and necessary solution from an energy security and environmental perspective. If aviation wants to reduce its greenhouse gas emissions, it has to turn to biofuels, which are the only fuels having the potential to achieve significant greenhouse emissions savings. Some of the steps towards a reduced CO₂ goal can be achieved with the efficiency increases anticipated through aircraft improvement, operational measures or infrastructure changes. But these measures are not enough and additional reductions are required. It is why biofuel appears to be the main candidate to achieve these reductions. Significant emissions reduction can be achieved with biofuel, provided that low emissions are achieved in the cultivation step of the biomass and if there is a rigorous control of land use change. Without these controls, some biofuels can have very poor CO₂ footprints.

The effort to develop alternative aviation fuels has already begun, focused on Fischer-Tropsch (FT) fuels.

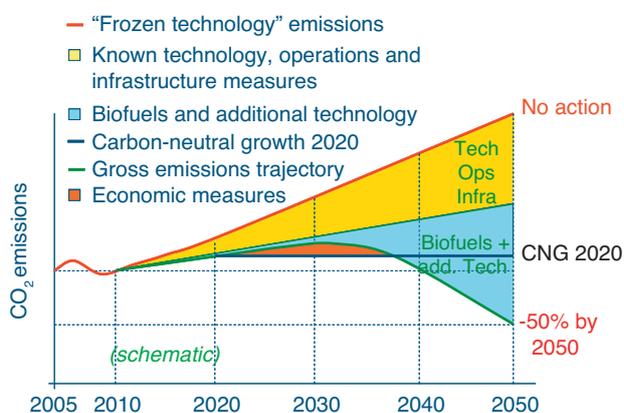


Figure 1

CO₂ emissions reduction targeted by IATA (Source IATA).

Generic FT Synthetic Paraffinic Kerosene (SPK) was approved for use in blends, at up to 50% volume, with Jet A-1 in ASTM D7566 in August 2009 [4, 5]. The second class of alternative fuels approved for certification is Hydroprocessed Esters and Fatty Acids (HEFA), also called Hydrogenated Vegetable Oil (HVO) or Hydroprocessed Renewable Jet (HRJ); it covers hydrocarbon aviation fuel produced from animal oils or vegetable oils (triglycerides) by hydroprocessing. This fuel has also been called BioSPK, although one should remember that the FT SPK include biomass to liquid fuels that can equally be called BioSPK. The ASTM D7566 specification is structured to support various classes of alternative fuels in its appendices and HEFA was approved for use at up to 50% volume in blends with conventional kerosene in ASTM D7566 in July 2011 [6]. It can now be used in ASTM D1655 fuels and, following an update to DEF STAN 91-91, HEFA has also been approved under “Check List”. The results of a study by the EU-funded Sustainable Way for Alternative Fuels and Energy in Aviation (SWAFEA) [7] have shown that the incorporation of biofuels in aviation fuel is necessary to reach the ambitious IATA targets in terms of CO₂ reduction. These conclusions also show that a massive incorporation ratio will be needed, so that huge investments need to be made. Moreover, the question of biofuels deployment has been raised, linked with a need for an optimised production yield to meet those targets.

There is competition for biofuel components which affects the design and economics of facilities that convert bio-oils into fuel. Specifically, there is competition between gasoil (*e.g.* automotive Diesel, heating and industrial Diesel) and kerosene users. Most bio-oils naturally yield product in the gasoil range so further processing steps are needed to make a product that is technically better suited to kerosene (jet fuel) production, in particular having better low temperature features than required for Diesel applications. The objective of this work is to study product quality trade-offs that could affect the economics of biojet production in the initial periods when biofuel availability will be limited. Specifically, it considers incorporating low levels (considerably less than the 50% volume now approved) of SPK with freezing points higher than those currently approved (−40°C maximum) into Jet A-1, while keeping the blend freezing point specification unchanged. Increasing (worsening) the freezing point decreases the level of processing of the SPK, which should produce higher biofuel component yields [8] and a potentially better overall profitability than a route that produces a higher proportion of better freezing point products that can be incorporated at higher percentages into the final Jet A-1. The recommendation for low or medium HVO (HEFA) concentrations is also studied for Diesel engines [9].

This paper does not deal with the economics themselves but provides technical data that could assist in understanding the relationship between process costs (usually related to process complexity), process yield, HEFA quality, and blending rate. IFPEN and Shell Global Solutions have joined their expertise to produce two different qualities of HEFA from the same original oil for the purposes of the SWAFEA project. The level of hydroisomerisation applied to a hydroprocessed oil to improve the low temperature properties was varied between the two HEFA:

- if, as expected, important constraints are put on oil availability and HEFA production capacity, in the short term the incorporation process will have to be optimised to incorporate this product into conventional Jet A-1. In this case, the global optimisation of the production yield will be of major importance. A major factor limiting the process yield remains the isomerisation step, which allows production of a bio-fuel with very good cold flow properties. It also leads to a substantial decrease in the overall yield because of the co-production of light compounds that cannot be incorporated in conventional jet fuel. To evaluate the impact of this production step, an extreme view has been chosen: a specific HEFA has been produced to have limited cold flow properties (target: freezing point around −20°C) and the resulting product has been blended into conventional jet fuel at different blending ratios. The overall yield has been calculated, to evaluate if a substantial gain can be obtained with such a strategy, while keeping the final blend in the limits of the Jet A-1 specification (freezing point $\leq -47^\circ\text{C}$);
- the current specification limits the incorporation rate of HEFA to a maximum of 50% volume. To meet the IATA targets, higher blending rates may eventually be needed. Indeed, during the ramp-up period, this product may not be available everywhere. The capacity to blend higher ratios in some locations can therefore help to meet the incorporation targets, taking into account the local availability of the product. A specific HEFA meeting the ASTM D7566 specifications has been made to evaluate the potential of such a product being blended at a high ratio (75%) in Jet A-1. To summarize the different strategies:
- Case 1: aim for a reduced HEFA incorporation ratio for HEFA with poor cold flow properties (target: freezing point around −20°C). Blends of this HEFA production (called HEFA1) with a conventional Jet A-1 have been prepared with 10%, 20% and 30% volume of HEFA1;
- Case 2: aim for a larger HEFA incorporation ratio than permitted by ASTM D7566: one blend of HEFA

production (called HEFA2) with the same conventional Jet A-1, has been prepared with an incorporation ratio of 75% volume of HEFA2.

1 GENERAL INFORMATION ON THE HYDROTREATMENT PROCESS OF VEGETABLE OILS

1.1 Vegetable Oil Composition

Renewable sources such as vegetable oils are mainly composed of triglycerides, which are tri-esters comprising 3 fatty acid hydrocarbon chains and a glycerol backbone, as shown in Figure 2. The degree of unsaturation of the fatty acid chains (*i.e.* the number of double bonds), as well as the carbon distribution, varies according to the nature of the oil.

Vegetable oils contain 6 oxygen atoms per mole, which leads to oxygen contents of about 10 to 12 wt%. According to the nature of the starting vegetable oils, fatty acid hydrocarbon chains can exhibit various carbon atom distributions, which are generally in the range C8 to C24. The nature of the feedstock also impacts the degree of unsaturation of the hydrocarbon chain; there can be between 3 and 6 unsaturated bonds. Table 1 gives some characteristics typically seen for rapeseed oils [10].

1.2 Main Process Steps

The present work has been achieved using a rapeseed oil sent to hydrotreatment, followed by a hydroisomerization step; rapeseed oil was chosen for reasons of feedstock availability. It is important to note that it would have been possible to use any other type of oil to demonstrate the two strategies for HEFA incorporation, though the absolute results obtained could vary according to the fatty acid distribution of the source oil.

The hydrogenation process generally comprises two steps [11, 12]:

- hydrotreatment, which is a treatment involving hydrogen, using an hydrotreatment catalyst in appropriate operating conditions;

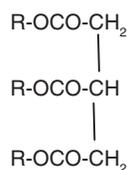


Figure 2

Typical structure of triglycerides, major components of vegetable oils.

TABLE 1
Composition of a typical rapeseed oil

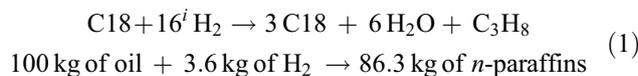
Origin	Method	Unit	Rapeseed oil
Density 15/4	NF EN ISO 12185	kg/m ³	920.0
Sulphur	ASTM D5453	wt ppm	4.2
Nitrogen	ASTM D4629	wt ppm	23.3
Carbon	ASTM D5291	wt%	77.7
Hydrogen	ASTM D5291	wt%	11.75
Oxygen	ASTM D5622	wt%	11.17
Acid value	EN14104	mg KOH/g	0.03
Water	EN ISO 12937	wt ppm	485

- hydroisomerization.

The hydrotreatment step consists of oxygen removal, which leads to the production of a paraffinic middle distillate (boiling at 150°C+). Oxygen removal can be achieved *via* 2 pathways:

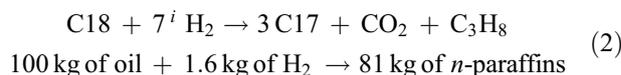
- hydrogenation of the fatty acid chain, to produce water and a paraffinic product, maintaining the hydrocarbon chain length (HDO pathway for hydrodeoxygenation, *Eq. 1*):

Fatty acid chain in



- hydrogenation of the fatty acid chain with production of carbon oxides (such as CO₂ and CO), and a paraffinic product with a loss of one carbon atom in the chain length (DCO pathway for decarboxylation, *Eq. 2*):

Fatty acid chain in



This is all a rather theoretical depiction; CO and CH are also made. It is also important to note that, despite the increased carbon yield in Equation (1), more H is required. In practice the mechanisms of Equation (1) and Equation (2) both occur but their relative contributions can vary

ⁱ This number depends on the number of unsaturation of triglycerides. This equation has been established for triglycerides with 4 unsaturated bonds.

TABLE 2
Boiling and melting points of *n*C16, *n*C17 and *n*C18

	<i>n</i> C16	<i>n</i> C17	<i>n</i> C18
Boiling point (°C)	286.9	302.2	316.7
Melting point (°C)	18	22	28.6

depending on conditions, catalyst, etc. However, the objective is to favour the HDO pathway, to maximize the yield of valuable fuel products.

After this first hydrotreatment section, oxygen is completely removed, and a pure paraffinic product is obtained, with typically the same carbon atom distribution as in the starting feedstock. For instance, starting from rapeseed oil, the paraffinic product after hydrotreatment is mainly composed of linear (normal) paraffins (*n*P) such as *n*C16, *n*C17 and *n*C18. This product exhibits a very high cetane, but very poor cold flow properties. This product is located in the Diesel boiling range, and the yield typically obtained is in the range 80-85 wt% relative to the feed.

Table 2 below gives the boiling and melting points of some linear paraffins, which are the major hydrocarbon components of the paraffinic product after hydrotreatment. Note: for pure products, there is a discrete melting point; for fuels, the melting of wax crystals occurs over a temperature range and the freezing point for jet fuels is the temperature at which, on warming up a cold fuel, the last wax crystals disappear. Therefore for “melting point”, think freezing point.

After hydrotreatment, the liquid hydrocarbon product is a 100% paraffinic Diesel product, composed mainly of *n*C16 – *n*C18 linear paraffins. The boiling range of the product is consequently 280°C+, well above the range seen for typical jet fuels.

To improve the cold flow properties of this paraffinic Diesel, it is necessary to subject the product to a hydroisomerization (HIS) treatment, which will convert linear paraffins into iso-paraffins. This improves low temperature performance for kerosene applications but has a detrimental effect on cetane quality in Diesel engine applications as shown in Figure 3 [13].

The HIS step is generally achieved using an appropriate catalyst in hydrogenation conditions. The catalyst is a bifunctional one, comprising both a hydrogenation function and an acid function. The objective, ideally, is to convert linear paraffins (*n*P) into iso-paraffins (*i*P), while avoiding cracking reactions which lead to yield loss by formation of gases and naphtha or gasoline cuts (that boil below 150°C). To be as close as possible to this ideal situation, an appropriate choice of the catalyst and operating conditions has to be made.

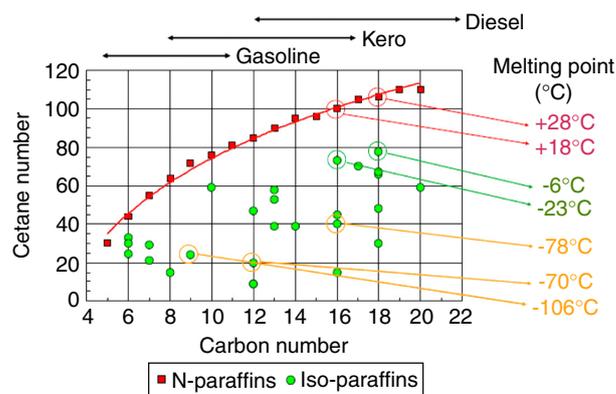


Figure 3

Melting point and cetane number of some normal and iso-paraffins present in the jet fuel and Diesel range [13].

Here is a general description of the reactions which take place in the HIS section:

- after hydrotreatment, the hydrocarbon product is a 100% paraffinic Diesel product, with a boiling range 280°C+. It is therefore necessary to convert *n*P into *i*P, to improve cold flow properties, and convert the Diesel boiling range product into a jet fuel boiling range product (150-300°C);
- when the severity of the HIS section is increased, it leads to a higher conversion of *n*P into *i*P, which leads to lower boiling and melting points (improved cold flow) of the hydrocarbons. Consequently Diesel is progressively converted into jet fuel (kerosene), and then into gasoline and gases at higher HIS severities. These lighter cuts (gasoline and gases) may be of lower value, for example in the EU where there is already a surplus of gasoline. From biofuel producers' perspectives, the discussion would need to be: a) Diesel *versus*; b) Diesel + low amounts high freeze jet component *versus*; c) not much Diesel + larger amounts of low freeze jet component.

At the end of the HIS step, there is a final distillation step to remove gasoline range material.

To summarize, the challenge of HIS operation for HEFA production is to convert a paraffinic Diesel into a paraffinic jet fuel. As jet fuel is an intermediate product between Diesel and gasoline, there is an optimum degree of conversion in terms of jet fuel yield. This optimum can be attained by selecting the more appropriate catalyst as well as carefully tuning the operating conditions. This is the condition to reach the maximum jet fuel yield, together with jet fuel quality meeting the specifications (distillation range and cold flow properties, *i.e.* freezing point when referring to jet fuel).

Figure 4 below shows the typical evolution of yields during HIS operation. There is a maximum jet fuel yield, which can be reached by carefully tuning the severity of HIS operation. The severity has to be sufficient to convert the hydrocarbons from the Diesel range (280°C+) into the jet fuel range (150-300°C), but not too high, to

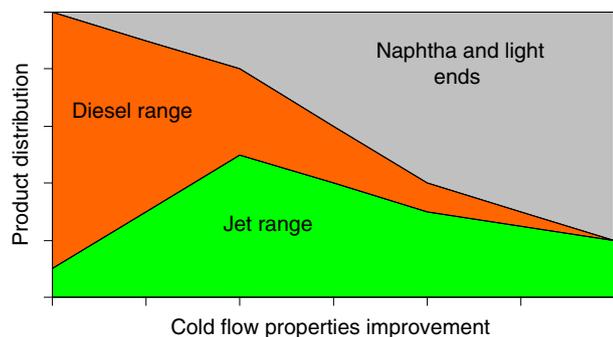


Figure 4

Impact of cold flow properties on kerosene yield of HEFA (source: IFP Energies nouvelles).

avoid excessive production of less economically attractive gases and gasoline (150°C) components.

1.3 Final Product Properties

The specifications requirements included in Table 3 have to be met in the final jet fuel after blending. It should be noted that it is necessary to blend the paraffinic jet fuel with a conventional jet fuel from petroleum, since an 8% volume minimum aromatics content is specified, to comply with material compatibility requirements. The current certification for HEFA allows no more than 50% volume HEFA in the final jet fuel, in part to help achieve this minimum aromatics level.

2 PRODUCTION OF HEFA JET FUELS WITH VARIOUS QUALITY REQUIREMENTS

2.1 Neat Materials (HEFA and Jet Fuels)

The previous section showed that there is an optimum conversion in terms of jet fuel yield and quality.

TABLE 3
Characteristics of the Jet A-1 fuels used in this work

Analysis	Unit	Jet A-1 specifications	Jet fuel A	Jet fuel B
Density 15°C	kg/m ³	775-840	803.3	821.0
Sulfur	wt ppm	3 000 maximum	697	< 5
Total aromatics	vol%	25.0 max (FIA)	16.1	20.2
		26.5 max (hplc)	18.9	20.4
Distillation Initial point	°C		147.6	152.1
T10 D86	°C	205 max	167.0	170.2
T20 D86	°C		175.5	176.6
T50 D86	°C		199.0	201.5
T90 D86	°C		245.3	240.2
Final point D86	°C	300 max	270.6	258.9
T90-T10 D86	°C	22 min	78.3	70.0
Freezing point	°C	-47 max	-49.6	-64.9
Smoke point	mm	25 min or 19 min (*)	21	19
Viscosity at -20°C	mm ² /s	8.0 max	4.04	4.19
Flash point	°C	38 min	40.5	42.5

(*) and Naphthalenes < 3.0 wt% (D1840).

TABLE 4
Cold flow properties of HEFA1 and HEFA2

Analysis	Unit	HEFA1	HEFA2
Freezing point	°C	−27°C	−57.5°C
Viscosity at −20°C	mm ² /s	11.72	7.52

The target which is set for HEFA jet fuel quality (freezing point in particular) consequently has an impact on the overall jet fuel yield.

The objective of this work was to examine the possibility of relaxing the quality requirement for the freezing point of the HEFA jet fuel component, and to estimate the corresponding gain of yield. It was decided to set two distinct freezing point targets for the jet fuel candidate HEFA:

- one HEFA to have a freezing point close to −20°C;
- one HEFA to have a freezing point below −47°C.

Table 4 presents the cold flow properties, freezing point and viscosity at −20°C, for the HEFA that were produced from rapeseed oil for this study.

Two different jet fuels were used to prepare further blends with HEFA1 and HEFA2. A first Jet A-1 (Jet fuel A) with conventional characteristics and a second Jet A-1 (Jet fuel B), with some more extreme but still “on spec” properties (in particular, exceptionally good freezing point). The main characteristics of the conventional Jet A-1 used for this work are gathered in Table 3.

2.2 Strategy of Blending and Characterization

Two blending strategies were adopted to optimise the amount of each HEFA which could be incorporated into Jet fuel A and Jet fuel B based on freezing point and viscosity at −20°C.

Jet fuel A: this fuel offered a typical freezing point of −49.6°C and a low blending ratio strategy of 10%, 20% and 30% volume was adopted for HEFA1 due to the −27°C freezing point of this product. HEFA2 however, offered an excellent −57.5°C freezing point was therefore blended at one high concentration, 75% volume.

Jet fuel B: this fuel offered an excellent freezing point of −64.9°C allowing greater scope for blending HEFA1 and a concentration range of 20%, 30%, 40%, 50%, 60%, 70% volume was selected. While no freezing point issues were expected for blending HEFA2, a broad range of concentrations was also chosen 25%, 40%, 50%, 60% and 75% volume to investigate if any other specification constraints might limit incorporation.

Tables 5 and 6 present the characteristics of blends of Jet fuel A with HEFA1 and HEFA2, respectively.

The main conclusions from the analysis are as follows:

- all blends have densities that match predicted densities, within method precision – the blending is reliably linear by volume and the mixing steps have produced homogeneous blends;
- all the blends met the current ASTM specifications except for freezing point (for some blends with HEFA1) and aromatic content (blend with HEFA2);
- blending HEFA in conventional fuels produces substantial increases (improvements) in smoke point;
- all the HEFA blend fuels have Lower Heating Values (LHV) higher than the minimum limit imposed by the specification and the blending of HEFA in conventional jet fuel resulted in an increase of mass LHV as expected from the component data.

If we focus on cold flow properties, the main results obtained for freezing points are presented in Figure 5.

The main conclusions are:

- HEFA1 blending ratio is limited by the freezing point. Nevertheless, significant blending ratios can be obtained before reaching this limit. With Jet fuel A this maximum blending ratio has been estimated to be 16% volume. Nevertheless, this point has to be further checked and does not represent a fixed value; there can be measurement uncertainties with freezing points of highly hydroprocessed fuels and the maximum ratio will also be very dependent on the freezing point of the crude oil based component;
- HEFA2 can be blended at any concentration without any limitation on the freezing point, due to the very good freezing point of the pure product;
- with Jet fuel A, the blend freezing point behaviour for both HEFA seems to be close to linearity, which could mean that the maximum blending ratio could be easily calculated according to pure product properties. The blending ratio of these HEFA could consequently be adjusted, taking into account the initial freezing point of the conventional Jet A-1. Nevertheless, this point still has to be confirmed using other Jet A-1, to check that this linearity is not dependent on Jet A-1 composition.

As far as viscosity is concerned, the best fit to the results is not always linear, particularly for HEFA1, a fuel whose freezing point is only slightly lower than the −20°C test condition. Nevertheless, starting from a viscosity of 4 mm²/s for the pure Jet A-1 (which is representative of typical Jet A-1 available on the market), a blend of 75% HEFA2 still stays below the specification viscosity limit. Moreover, all the blends made with HEFA2 are expected to pass the ASTM D7566 viscosity limit (8 mm²/s at −20°C). These results are presented in Figure 6.

TABLE 5
Characteristics of blends of Jet fuel A with HEFA1

Analysis	Unit	Jet A-1 specifications	Jet fuel	HEFA1	Jet + 10% HEFA1	Jet + 20% HEFA1	Jet + 30% HEFA1
Density 15°C	kg/m ³	775-840	803.3	773.5	800.0	797.0	794.0
Total aromatics (hplc)	vol%	26.5 max	18.9	0.0	16.9	15.0	13.3
Distillation Initial	°C		147.6	174.2	148.7	153.6	152.4
T10	°C	205 max	167.0	201.2	170.2	174.5	174.5
T20	°C		175.5	218.4	179.6	183.3	184.0
T50	°C		199.0	267.5	204.7	210.7	214.5
T90	°C		245.3	288.9	260.8	271.1	277.4
Final	°C	300 max	270.6	293.2	282.8	288.5	289.5
T90-T10	°C	22 min	78.3	87.7	90.6	96.6	102.9
Freezing point	°C	-47 max	-49.6	-27	-49.0	-46.5	-44.5
Smoke point	mm	25 min or 19 min (*)	21	> 50	25.0	26.0	28.0
Viscosity at -20°C	mm ² /s	8.000 max	4.04	11.72	4.426	4.859	5.363
Flash point	°C	38 min	40.5	67	43	43.5	45
Specific energy, net	MJ/kg	42.8 min	43.25	44.07	43.31	43.41	43.49

(*) and Naphthalenes < 3.0 wt% (D1840).

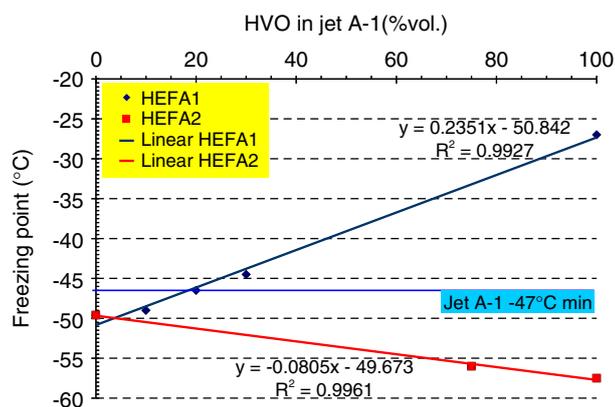


Figure 5
Impact of HEFA content on final blend freezing point for blends in Jet fuel A.

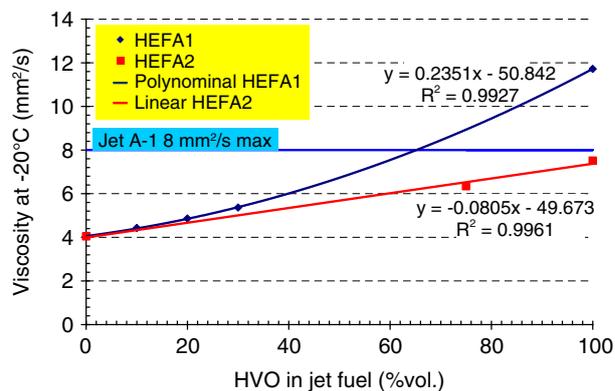


Figure 6
Impact of HEFA in Jet fuel A blending rate on final blend viscosity at -20°C.

Following the blend production and test results discussed above, blends were made with another Jet A-1, Jet fuel B, that has excellent low temperature results;

as shown in Table 3, it has a significantly better freeze point than average and represents a close to “best case” blend partner for a poorer freezing point HEFA

TABLE 6
Characteristics of blends of Jet fuel A with HEFA2

Analysis	Unit	Jet A-1 specifications	Jet fuel	HEFA2	Jet + 75% HEFA2
Density 15°C	kg/m ³	775-840	803.3	765.9	775.0
Total aromatics (hplc)	vol%	26.5 max	18.9	0.0	4.8
Distillation Initial	°C		147.6	188.0	171.8
T10	°C	205 max	167.0	201.6	192.2
T20	°C		175.5	206.7	199.2
T50	°C		199.0	224.7	218.9
T90	°C		245.3	279.9	276.0
Final	°C	300 max	270.6	287.3	287.2
T90-T10	°C	22 min	78.3	78.3	83.8
Freezing point	°C	−47 max	−49.6	−57.5	−56
Smoke point	mm	25 max or 19 max (*)	21	> 50	41
Viscosity at −20°C	mm ² /s	8.0 max	4.04	7.517	6.335
Flash point	°C	38 min	40.5	68.0	58.0
Specific energy, net	MJ/kg	42.8 min	43.25	44.11	43.89

(*) and Naphthalenes < 3.0 wt% (D1840).

component. Its freezing point of −64.9°C is the highest reported for the fuel; analysts sometimes prefer not to determine freezing points accurately below an arbitrary temperature in the range −60 to −75°C as this takes more time and/or more effort to control such low temperatures. With this greater than 15°C improvement in freezing point compared to Jet fuel A, it was possible to consider higher levels of HEFA in the two sets of blends created. Table 7 summarises data for the seven blends created with HEFA1 and Table 8 provides data for the 5 blends with HEFA2; data for the neat HEFA and Jet fuel A and B are in Table 3, and Table 4.

As shown in Figure 7, Jet fuel B has extended the range over which HEFA1 can be blended and still achieve Jet A-1 requirements. The best fit for HEFA1 is now polynomial, with freezing points being higher (poorer) than a linear blend rule would expect. Based on the fit the highest level of HEFA1 to pass the Jet A-1 freezing point would be about 35% volume (or 30% based on actual data points). This is higher than seen with Jet fuel A. If only a Jet A freezing point needed to be met (−40°C maximum), the fit and actual data points would both suggest upper limits of 51% volume. For the HEFA2 blends the results are best described as “scattered”; there may or may not be a sweet spot

around 60% volume with an exceptionally low freezing point (similar to behaviour seen with some GTL SPK [14]); many of the results are likely to be affected by the analyst’s observation preference and the overriding message is that all the HEFA2 blends in Jet fuel B have very good freezing points, with no limits on HEFA2 content being caused by freeze point.

Viscosity data repeat the patterns seen with Jet fuel A: Figure 8 shows that the HEFA2 blends follow an approximately linear by volume behaviour while the HEFA2 blends are better fitted by a polynomial fit. HEFA1 blends above 63% volume fail the 8 mm²/s limit, while all HEFA2 blends pass.

The limiting factor for HEFA2 blends would be set by the 8.8% volume total aromatics by hplc method, if the 50% maximum were not applied.

In summary, the maximum volume percentages of the HEFA in the two Jet A-1 are as in Table 9, Figure 9 and Figure 10. Given that in a country using Jet A rather than Jet A-1 there may not be many very good freezing point fuels like Jet fuel B, this does indicate that HEFA1 will probably have an upper limit of 30 to 35% volume; more typically HEFA1 be limited to values in the range 15 to 20% volume for Jet A-1 production.

TABLE 7
Properties of blends of HEFA1 with Jet fuel B

%vol. HEFA1 in Jet fuel B		20	30	40	50	60	70
Analysis	Unit						
Density 15°C	kg/m ³	811.3	806.7	802.1	797.4	792.7	788.1
Total aromatics (hplc)	vol%	17.5	15.1	12.9	10.8	8.8	6.7
Distillation Initial	°C	153.9	155.4	157.1	159.6	161.9	165.7
T10	°C	172.5	174.4	176.3	179.1	182.2	185.7
T20	°C	179.9	182.6	185.6	188.5	192.9	197.0
T50	°C	208.9	213.9	219.4	227.0	234.3	243.1
T90	°C	264.3	273.2	277.4	282.1	283.7	285.4
Final	°C	283.5	286.7	289.1	289.6	290.6	290.9
T90-T10	°C	91.8	98.8	101.1	103.0	101.5	99.7
Freezing point	°C	-58.8	-47.8	-42.8	-40.2	-37.1	-34.6
Smoke point	mm	21.5	22.0	24.5	25.5	30.0	34.0
Viscosity at -20°C	mm ² /s	5.063	5.504	6.059	6.100	7.412	8.229
Flash point	°C	44.0	46.0	47.0	49.5	51.0	53.5
Specific energy, net	MJ/kg	43.215	43.325	43.426	43.535	43.636	43.741

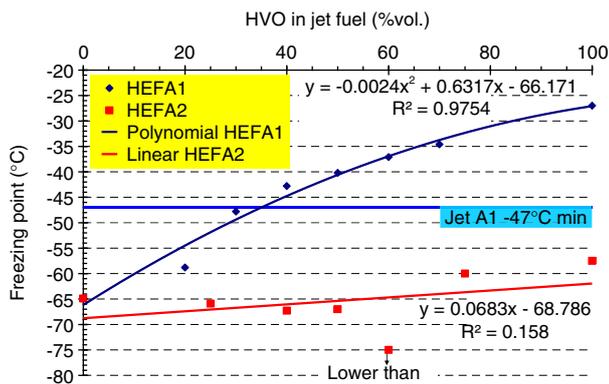


Figure 7

Freezing points for blends of HEFA1 and HEFA2 with Jet fuel B.

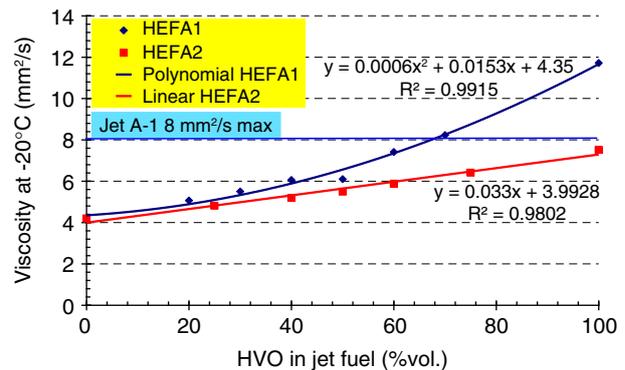


Figure 8

Viscosity for HEFA blends made with Jet fuel B.

2.3 Production Yield

Figure 11 shows the yield improvement for HEFA1 and HEFA2 production. It appears that lowering the severity of HIS operation, for production of HEFA1, leads to a gain of jet and Diesel fuel yield and particularly a gain of jet fuel yield to more than +10 points of mass yield relative to the oil.

For a given quantity of jet fuel produced, this potentially allows a reduction in the land surface area necessary for cultivation of the HEFA feedstock by at least 10%.

SUMMARY AND CONCLUSIONS

World wide air traffic has been steadily increasing for many years and is predicted to grow in the future.

TABLE 8
Properties of blends of HEFA2 with Jet fuel B

%vol. HEFA2 in Jet fuel B		25	40	50	60	75
Analysis	Unit					
Density 15°C	kg/m ³	807.0	799.0	793.6	788.0	779.6
Total aromatics (hplc)	vol%	16.2	13.1	11.0	9.1	5.5
Distillation Initial	°C	157.0	159.9	165.1	168.2	175.7
T10	°C	174.9	178.5	181.7	185.4	191.0
T20	°C	182.3	186.4	189.5	192.4	197.2
T50	°C	205.6	209.1	211.3	213.9	217.4
T90	°C	251.7	260.3	263.5	268.2	272.8
Final	°C	275.7	280.1	282.2	283.2	284.5
T90-T10	°C	76.8	81.8	81.8	82.8	81.8
Freezing point	°C	-65.9	-67.3	-67.0	< -75.0	-60.0
Smoke point	mm	20.5	22.0	26.0	33.0	34.0
Viscosity at -20°C	mm ² /s	4.811	5.190	5.495	5.876	6.412
Flash point	°C	45.5	47.5	49.5	52.0	56.0
Specific energy, net	MJ/kg	43.262	43.423	43.531	43.642	43.819

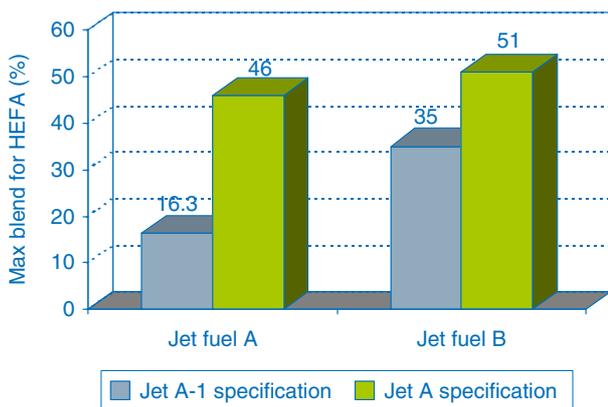


Figure 9

Maximum blend % volumes for HEFA1 / Jet fuels combinations neglecting current 50% specification limit.

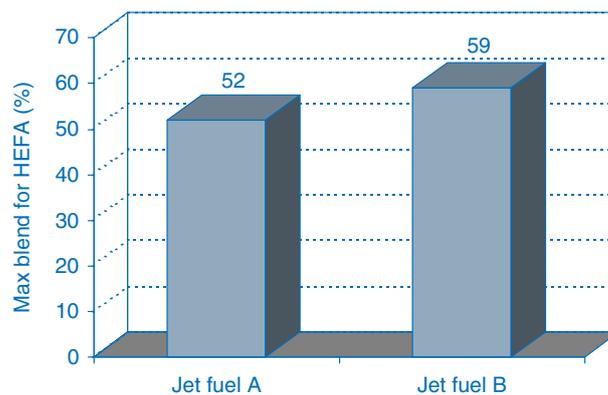


Figure 10

Maximum blend % volumes for HEFA2 / Jet fuels combinations neglecting current 50% specification limit.

Besides, the increased focus on climate change over the last decade has created pressure to reduce greenhouse gases emissions. One solution for the aeronautics sector to satisfy the objective of CO₂ reduction is the use of alternative fuel such as HEFA.

HEFA are produced from hydrogenation of mainly vegetable oils. This process generally comprises two

steps: hydrotreatment and hydroisomerization. The process yield for HEFA remains limited because of the isomerisation step that allows production of a bio-fuel with very good cold flow properties. This work proposes to relax the freezing point requirement for the neat HEFA component (by decreasing the severity of the isomerisation step) in order to minimize the

TABLE 9
Maximum blend % volumes for HEFA/Jet A-1 combinations neglecting current 50% specification limit

HEFA	Jet A-1	Limit %vol.	Limiting property	Blend rule
HEFA1	Jet fuel A	16.3	Freezing point Jet A-1	
		46	Freezing point Jet A	
HEFA1	Jet fuel B	35 (fit) or 30 (data point)	Freezing point Jet A-1	
		51	Freezing point Jet A	
HEFA2	Jet fuel A	52	Total aromatics	Linear by volume
HEFA2	Jet fuel B	59	Total aromatics (hplc)	Linear by volume

production of less valuable light compounds. This strategy could lead to a significant additional biofuel yield with respect to the oil. Then this experimental study determines if a combination of processing/blending is possible to optimise HEFA incorporation for industry benefit.

A rapeseed oil was used for this study. The choice of this oil has been done for reasons of feedstock availability. It was decided to set two distinct freezing point targets for the jet fuel candidate HEFA: one HEFA to have a freezing point close to -20°C and the other one HEFA to have a freezing point below -47°C . Moreover two different jet fuels were used for the blends. A first Jet A-1 with conventional characteristics and a second Jet A-1, with some more extreme but still “on spec” properties (in particular, exceptionally good freezing point).

It has been shown that these HEFA can be blended in significant volumes in a conventional Jet A-1. The upper limits in terms of incorporation are:

- the freezing point for the HEFA1 (-27°C). HEFA1 can be incorporated at up to 30-35% volume before failing Jet A-1 freezing point. The incorporation ratio is dependant of the jet fuel quality regarding cold flow behavior;
- the aromatic content of the final blend for the introduction of HEFA2 (-57.5°C). However, HEFA2 can be incorporated at up to 59% before failing to achieve the minimum total aromatics content. With a higher aromatics jet fuel that has excellent freezing point characteristics, higher levels of HEFA can be incorporated, though the limiting properties remain the same.

These preliminary tests have shown that by combining processing conditions in combination with blending strategies there is a potential to enhance the incorporation of HEFA in conventional jet fuel. The blending of a high amount of a low freezing point HEFA could allow higher incorporation rates in the long term, while the

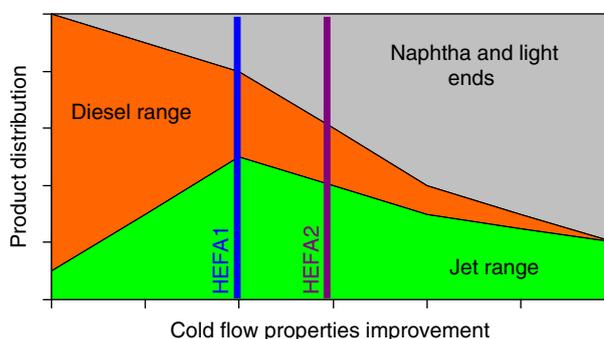


Figure 11

Yield improvement for HEFA production (source: IFP Energies nouvelles).

incorporation of high freezing point HEFA in smaller %vol. could allow HEFA incorporation to be started in the shorter term, while optimizing the process yield. This strategy is more in accordance with biomass availability. Nevertheless, it has to be stressed that these are only preliminary results and need important validation work, such as fitness for purpose tests recommended in ASTM D4054, before going into the certification process and being industrially used.

ACKNOWLEDGMENTS

This work was done as an additional contribution to the SWAFAEA Project and the contributors are Shell Global Solutions and IFP Energies nouvelles.

REFERENCES

- 1 Advisory Council on Aeronautics Research in Europe (ACARE (2010) *Aeronautics and air transport: beyond vision 2020 (towards 2050)*).

- 2 <http://www.airbus.com>, Airbus Global market forecast 2010-2029.
- 3 Pachauri R.K., Reisinger A. (2007) *Contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change*, Intergovernmental Panel on Climate Change (IPCC), Geneva Switzerland.
- 4 American Society for Testing and Materials (2009) Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, ASTM D7566 – 10.
- 5 Moses C.A. (2008) Comparative evaluation of semi-synthetic jet fuels, *CRC project No. AV-02-04a*, Sept.
- 6 American Society for Testing and Materials (2011) *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*, ASTM D7566 – 11a.
- 7 <http://www.swafea.eu>.
- 8 Simacek P., Kubicka D., Sebor G., Pospisil M. (2010) Fuel properties of hydroprocessed rapeseed oil, *Fuel* **89**, 609-615.
- 9 Lapuerta M., Villajos M., Agudelo J.R., Boehman A.L. (2011) Key properties and blending strategies of hydro-treated vegetable oil as biodiesel for Diesel engines, *Fuel Processing Technology* **92**, 2406-2411.
- 10 Ballerini D. (2011) *Les Biocarburants – Répondre aux défis énergétiques et environnementaux des transports*, Éditions Technip, Paris, France.
- 11 Huber G.W., O'Connor P., Corma A. (2007) Processing biomass in conventional oil refineries: production of high quality Diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures, *Applied Catalysis A: General* **329**, 120-129.
- 12 Simacek P., Kubicka D., Kubicková I., Homola F., Pospisil M., Chudoba J. (2011) Premium quality renewable Diesel by hydroprocessed of sunflower oil, *Fuel* **90**, 2473-2479.
- 13 Bloch M. (2010) State-of-the-Art BTL and HVO Production Processes and the Challenges for the Production of Bio-based Jet Fuel, *SWAFEA 2nd European Stakeholder Conference*, Munich Germany, July.
- 14 Bauldreay J.M., Heins R.J., Smith J. (2003) Synthetic jet fuels and their role in the future, *8th International Conference on Stability, Handling and Use of Liquid Fuels*, Steamboat Springs, CO, USA, 14-19 Sept.

Manuscript accepted in January 2014

Published online in June 2014