SYNERGY OF BLENDING HYDROTREATED AND HYDROCRACKED KEROSENE IN THE PRODUCTION OF JET FUEL

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Aviation kerosene is the fastest growing transportation fuel. Regardless of the ambition to replace it by SAF, consumption of the mineral component in JET fuel will grow. In oil refineries, kerosene fractions are used to produce JET fuel and as a component of diesel fuel. These fractions can differ in origin and composition. In this article the possibility of blending hydrocracked kerosene used for JET production and hydrotreated kerosene used for diesel fuel production was investigated. It was concluded that significant synergies can be achieved by blending of these fractions in terms of increasing JET fuel production by up to 2.5 times, controlling the aromatics content of hydrocracked kerosene and obtaining a fraction for blending of diesel fuel with improved low temperature properties.

1. Introduction

Air travel is developing rapidly, especially with respect to population growth, business activities of low-cost airlines, the growth of convenient direct connections instead of more cumbersome connecting flights and with regard to speed and comfort this form of transport. Moreover, unlike piston combustion engines, there is as yet no efficient alternative for aircraft turbines. In 2019, global air travel accounted for 16% of transportation energy consumption. In 2019, aviation fuel consumption was 331 Mt. JET fuel consumption is projected to increase by 3.7 % per year until 2050, the most of any transportation fuel [1]. Based on the EIA´s estimate, consumption will return to its 2019 pre-pandemic level in 2023 [2]. With the increasing consumption of JET fuel, there is a need to find new sources and methods of its production.

The quality standards classify the components of JET fuel according to technological origin into non-hydroprocessed (meroxed), mildly hydroprocessed (hydrotreated), severely hydroprocessed (hydrocracked), and synthetic products (primarily Sustainable Aviation Fuels, SAF) [3]. The standard practice is to produce JET fuel from pure mineral oil fractions. When using hydrotreated kerosene fraction the freezing point must be monitored, when using hydrocracked kerosene the aromatics content must be monitored. The use of SAF mainly in the form of drop-in fuels (it can be blended with mineral oil JET fuel and the final product requires no infrastructure or equipment changes) is currently in pilot testing. The mandatory use of 2 wt % SAF in 2025 and 5 wt % in 2030 is foreseen [4]. This means that the increase in JET fuel consumption in this decade will rely mainly on standard mineral oil hydrocarbons. Since crude oil refining will certainly not increase in developed countries (OECD), the use of kerosene fractions from conversion processes (hydrocracking in the first place) is of great interest to oil refiners.

In oil refineries, kerosene fractions are used to produce JET or diesel fuel. In each of these products the kerosene fraction plays a different role. JET fuel is pure kerosene. In diesel fuel, on the other hand, it represents only a minor part and its role here is to improve its low-temperature properties, especially in the winter period when diesel fuel class F and Arctic diesel class 2 are produced, in line with ČSN EN 590 standard [5]. The basic properties of JET [3] and diesel fuel [5], discussed further in this article, are listed in Table 1.

Table 1 Comparison of selected properties of JET A-1 (JIG AFQRJOS) and diesel fuel (EN 590)

Parameter	JET A-1	Diesel F	Diesel Arctic 2
Freezing point (°C)	max -47		
Cloud point (°C)	-	max -8	max -22
CFPP	-	max -20	max -32
Aromatics (vol. %)	max 26.5	-	
Naphthalenes (vol. %)	max 3[*]		
Polyaromatics (wt %)	-	max 8	max 8
Smoke point (mm)	min 18[*] or 25	-	-
Sulfur (mg·kg^{-1})	max 3000	max 10	max 10
Density (kg·m^{-3})	775-840	820-845	800-840
Distillation			
10% (°C)	max 205	-	-
95 % (°C)	-	max 360	-
End (°C)	max 300	-	-
At 180 °C (vol. %)	-	-	max 10
At 250 °C (vol. %)	-	<65	
At 340 °C (vol. %.)	-	-	min 95
At 350 °C (vol. %)	-	min 85	-
Cetane index	-	min 46	min 46

*For naphthalenes max. 3 vol. %, smoke point min 18 mm

The freezing point of JET A-1 of -47 °C represents a challenging requirement for a middle distillate fraction. The cloud point of diesel fuel has a similar significance as the freezing point for JET A-1. However, while diesel fuel can be used at temperatures 10-12 °C lower (CFPP) then the cloud point is, JET A-1 cannot be used under such conditions. The limitation of the total aromatics and naphthalenes content in JET A-1 is related to the combustion of the fuel in an aircraft turbine without black smoke formation, i.e. to the smoke point. The higher the aromatics content of JET fuel the lower is the smoke point. Such a correlation was described, for example, for hydrocracked kerosene (kerosene as a product of hydrocracking of vacuum distillates) [6]. Only the content of polyaromatics is limited in a diesel fuel (max 8 wt %), in order to prevent the formation of black particles during combustion in a diesel engine and to reduce the aromatics content in these particles. The sulfur content shall not exceed 0.3 wt % for kerosene fraction meroxed; however, such fraction shall not be blended directly into "clean diesel fuel" (max. 10 mg·kg^{-1} sulfur). Density is a complex physical property and depends on both fractional and chemical composition. The density limits of JET A-1 are much more liberal than those of diesel fuel, which can be beneficially used. As far as the distillation curve is concerned, different control points are set for JET A-1 and diesel fuel. The cetane index is calculated from the density and ASTM D86 distillation curve of the fraction. Both of these parameters depend on the chemical composition of the fraction.

In view of the facts above, the properties of a kerosene fraction differ for the production of JET A-1 or blending into diesel. There are a number of ways to control the above parameters in an oil refinery, for example utilizing a different withdraw tray in the main distillation column, different reaction conditions of hydrotreating, utilization of fraction from conversion processes, different blending recipes and specific additivation [7]. For an oil refinery, the preferred blending of the kerosene fractions depends on sales demand and is subject to optimization calculations.

The production of JET fuel in oil refineries is well described in the literature [8-10].

The standard fraction used in the modern oil refineries to produce JET fuel is straight-run (virgin) kerosene refined by hydrotreating. For a given crude oil, the yield and quality of the fraction is relatively stable. Hydrotreating can control the sulfur and aromatics content of kerosene but not the low temperature properties, because the n-alkanes contained in the feedstock are not affected by hydrotreating. For a straight-run fraction, this can be controlled by the distillation range. The lower its mean boiling point is and the narrower the fraction is, the more favorable its low-temperature properties are. Considering the extremely low freezing point of JET A-1 of -47 °C, the narrow and light kerosene fractions are utilized to produce JET fuel. Hence, heavy naphtha, also used as feedstock for catalytic reforming, is part of the JET fuel

fraction. A wide-cut kerosene with a higher initial boiling point is blended into diesel fuel.

Refineries operating a deep hydrocracking unit of vacuum distillates have available another interesting fraction to produce JET fuel – hydrocracked kerosene [11-14]. JET fuel produced on this basis represents a special product category [3] and, in comparison with a similar straight-run fraction it is characterized by higher density, high cycloalkane content, minimal sulfur content (units of mg·kg^{-1}) and extremely low freezing point of about -80 °C, because the n-alkanes contained in the feedstock are easily cracked and isomerized under hydrocracking conditions. With respect to current quality standards, the extremely low freezing point of the hydrocracked kerosene is not necessary to produce JET A-1 and represents a situation referred to in the refinery terminology as a "giveaway". However, as the hydrocracker catalytic system deactivates, it is necessary to increase gradually the reaction temperature. As a result, the aromatics content grows and the related smoke point drops up to values outside those allowed by JET fuel standards [6]. The yield of the hydrocracked kerosene has to be finally reduced.

Considering a standard paraffinic crude oil, the yield of primary straight-run kerosene used for diesel blending is approximately 14-15 wt %, the yield of hydrocracked kerosene from deep hydrocracking of vacuum distillates is 2.5-4.3 wt % of crude oil processed at the same time.

With respect to the increasing market demand for JET fuel, the question is, whether the blending of straight-run hydrotreated kerosene fraction in the quality used to produce diesel fuel and hydrocracked kerosene can increase the production of JET fuel in a hydrocracking type of oil refinery. Furthermore, such blending could mitigate the giveaways related to the cold flow properties and fluctuation in the quality of hydrocracked kerosene and at the same time increase flexibility and optimize blending of the middle distillates in a such refinery.

2. Methods and materials

To monitor the properties of the kerosene the following analytical methods were used:

- Freezing point – according to ASTM D5972, in the automatic analyzer Phase Technology type FPA - 70Xi.
- Aromatics content – according to ASTM D6379, a high performance liquid chromatography method (HPLC), in the AGILENT 1100 liquid chromatograph.
- Smoke point – according to ASTM D1322 method, in the automatic AD systems SP 10 device and utilizing a Greisinger digital barometer.
- Density – according to EN ISO 12185, in the Anton Paar DMA-48 density analyzer with an oscillating U-tube.
- Distillation – according to ASTM D86, in the Herzog HDA 628 distillation facility with an externally connected PC.

- Cetane index – calculated in line with ASTM D4737, using the experimental results of ASTM D87 distillation and density.
- The following fractions were investigated:
- Kerosene hydrotreated on a conventional Co-Mo/Al_2O_3 sulfidic catalyst, at 340 °C and 3.5 MPa, with sulfur content < 10 mg·kg^{-1}, used for blending of clean diesel fuel in line with the ČSN EN 590 standard [5].
- Kerosene hydrocracked on a tailor-made Ni-Mo/Al_2O_3 sulfidic catalyst, at 410 °C and 16.5 MPa, of quality corresponding to JET A-1.

Fractions were taken directly from the production facilities at a real oil refinery processing the Russian Export Blend crude oil (API gravity 32.3°, S 1.34 wt %) in a blend of up to 25 vol. % Caspian CPC crude oil (API gravity 42.7°, S 0.7 wt %) [6]. Two sets of samples were taken, hydrocracked kerosene samples from two following operating cycles of the hydrocracking catalyst. Mixtures of 30, 50, and 70 vol. % of both kerosene fractions were prepared in the laboratory in quantities of 500 ml and analyzed, together with the pure components, by the methods and instrumentation mentioned above, used for the attestation of the real product.

3.   Result and discussion

Attention was preferentially paid to the freezing point of the available fractions and the blends thereof (Figure 1).
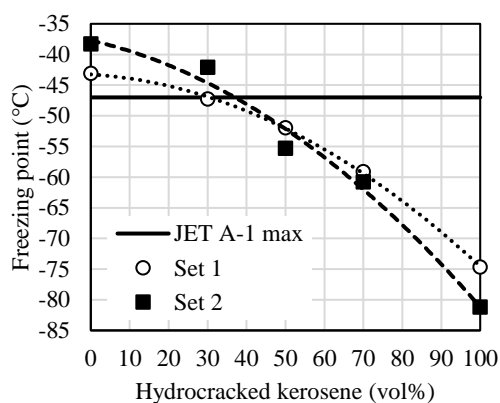

Fig 1 Freezing point of hydrotreated and hydrocracked kerosene and blends thereof

For hydrocracked kerosene, the freezing points of -74.7 °C (set 1) and -81.2 °C (set 2) were significantly lower than the required -47 °C for JET A-1. In contrast, for hydrotreated kerosene, neither of the samples met this value (-43.1 °C, set 1, and -38.3 °C, set 2). The freezing point of -47 °C was achieved with blending of 31 vol. % (set 1) and 37 vol. % (set 2) hydrocracked kerosene and hydrotreated one. This means that a blend of 40 vol. % hydrocracked kerosene and 60 vol. % hydrotreated kerosene would reliably provide the freezing point required for JET A-1 and the production of JET fuel can be operatively increased by up to 2.5 times compared to using

hydrocracked kerosene only or, at the same time, the low-temperature properties of the fraction blended into diesel fuel were improved. Importantly, the freezing point of the blend was found to be non-linearly dependent on the concentration of hydrocracked kerosene. When blending hydrocracked kerosene into hydrotreated one, the initial drop in the freezing point was slow. This is important from the point of view of a refinery blending optimization program.

The aromatics concentration in the studied samples ranged from 19.7 to 24.9 vol. % (Figure 2).
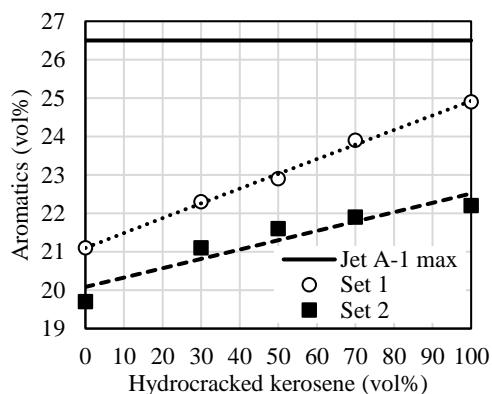

Fig 2 Aromatics content of hydrotreated and hydrocracked kerosene and blends thereof

The aromatic content of hydrotreated kerosene samples taken at different times was relatively stable, unlike in the hydrocracked kerosene samples, see also [6]. The limit for aromatics content in JET A-1 of 26.5 vol. % was not exceeded in any of the samples used. Therefore, the aromatics content did not limit the blending of the considered two fractions. Moreover, the aromatics content of the hydrotreated kerosene (19.7 and 21.1 vol. % only), which in terms of the JET A-1 specification (26.5 vol. %) is again a giveaway, may compensate for any real aromatics content above 26.5 vol. % in hydrocracked kerosene at the end of the operating cycle of the hydrocracking catalyst. The aromatics content of individual samples in vol. % should be additive in volume, which was confirmed in particular by set 1 of the samples.

Smoke point of the analyzed samples was as per Figure 3. The smoke point ranged from 18.7 to 22.7 mm. The direction of the correlation curves of the smoke point as a function of the hydrocracked kerosene content of the analyzed samples is opposite to the one for aromatics. Only one sample can be characterized as a critical, but not exceeding the limit, in terms of smoke point, i.e. pure hydrocracked kerosene in set 2 (smoke point 18.7 mm for aromatics content 24.9 vol. %).

The aromatics content and smoke point of the individual samples was of interest in order to study the relation between these important properties of JET fuel. This relation was researched for both sets of samples independently and subsequently also for all the data obtained (Figure 4).
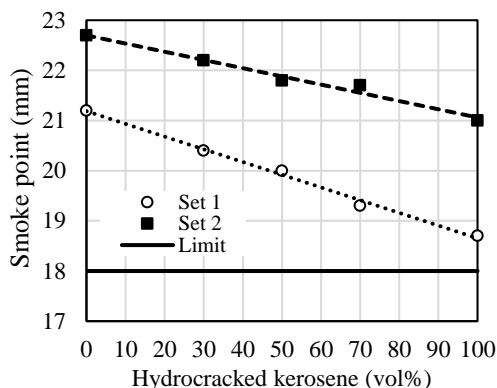
Fig 3 Aromatics content of hydrotreated and hydrocracked kerosene and blends thereof

Fig 5 Distillation curve of hydrotreated and hydrocracked kerosene and their blends
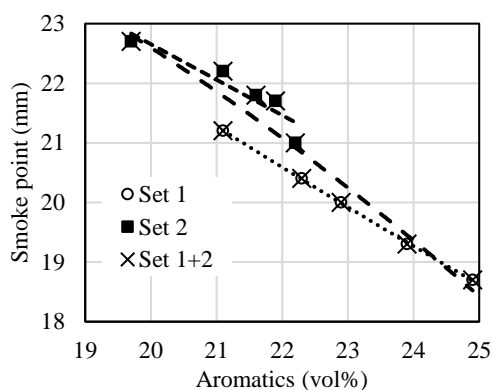

Fig 4 Smoke point relation to aromatics content of kerosene fractions

The results confirmed that there is a good correlation between both parameters for various blends of hydrotreated and hydrocracked kerosene, which is close to a linear function.

The sulfur content of both hydrotreated and hydrocracked kerosene was less than 10 mg·kg^{-1}, i.e. also of all blends. Sulfur did not represent a limit for considered blending of the two kerosene fractions.

The density of the researched samples of hydrotreated kerosene was 817.9 kg·m^{-3} (set 1) and 813.1 kg·m^{-3} (set 2), and 820.5 kg·m^{-3} (set 1) and 812.0 kg·m^{-3} (set 2) for hydrocracked kerosene samples. Therefore, all researched samples met the JET A-1 specification with sufficient reserve. The density of kerosene fractions was lower than the minimum 825 kg·m^{-3} for standard diesel fuel. In respect of the similar density of hydrotreated and hydrocracked kerosene, also the blending of hydrocracked kerosene into diesel fuel was not a problem for any mixture of the two fractions in terms of this parameter, because another component used for blending of diesel fuel, gas oil, has a density greater than this limit.

For set 2 ASTM D86 distillation curves were measured (Figure 5). Compared to the hydrotreated kerosene fraction used for diesel fuel blending (distillation range 176-287 °C, mean boiling point 224 °C), hydrocracked kerosene was a relatively light and narrow middle distillate cut (distillation range 160-220 °C, mean boiling point 186 °C).

Compared to the hydrotreated kerosene fraction used for diesel fuel blending (distillation range 176-287 °C, mean boiling point 224 °C), hydrocracked kerosene was a relatively light and narrow middle distillate cut (distillation range 160-220 °C, mean boiling point 186 °C). By blending these two fractions, the distillation curve gradually broadened. The blended samples tended to retain the initial boiling point of the light component (the hydrocracked kerosene) and the final boiling point of the heavier component (the hydrotreated kerosene) in the blend. The samples did not meet the maximum distilled volume requirements at 180 °C for Arctic diesel and at 250 °C for standard diesel (Table 2). However, this is not a problem because the kerosene fraction in diesel fuel is blended with heavier gas oil.

In terms of diesel blending, the cetane index of hydrotreated kerosene (49.9) was significantly higher than that of hydrocracked kerosene (35.1). This is one of the reasons why a different fraction of kerosene is used for the production of diesel fuel than for JET fuel. The relation of the cetane index to the hydrocracked kerosene content was significantly linear (Figure 6).
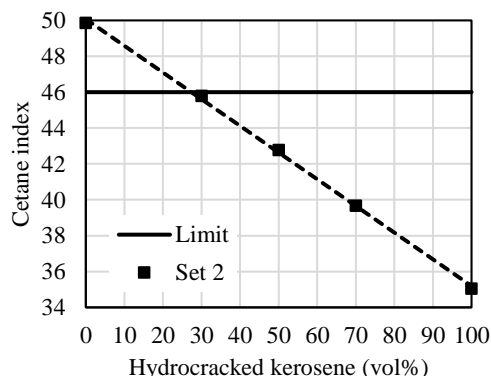

Fig 6 Cetane index of hydrotreated and hydrocracked kerosene and their blends

The low cetane index of hydrocracked kerosene alone, and consequently also in a blend with hydrotreated kerosene, would not jeopardize compliance with the diesel fuel limit, as hydrocracked kerosene would form only

Table 2 Compliance with the distillation requirements of JIQ AFQRJOS (JET A-1) and ČSN EN 590 (diesel fuel), respectively

Parameter	JET A-1	Diesel F	Diesel Arctic 2	Composition of samples				
Hydrotreated kerosene (vol. %)				100	70	50	30	0
Hydrocracked kerosene (vol. %)				0	30	50	70	100
Distillation								
10% (°C)	max 205	-	-	Yes	Yes	Yes	Yes	Yes
95% (°C)	-	max 360	-	Yes	Yes	Yes	Yes	Yes
End (°C)	max 300	-	-	Yes	Yes	Yes	Yes	Yes
At 180 °C	-		max 10	Yes	Yes	Yes	No	No
At 250 °C vol. %)	-	<65		No	No	No	No	No
At 340 °C vol. %)	-	-	min 95	Yes	Yes	Yes	Yes	Yes
At 350 °C (vol. %)	-	min 85	-	Yes	Yes	Yes	Yes	Yes

a small part of the final product. However, the effect of blending hydrocracked kerosene into diesel fuel on the cetane index and cetane number would deserve further attention.

4. Conclusion

In oil refineries, kerosene fractions of various origins and with different distillation curves are used for the production of JET fuel and as a component of diesel fuel. In this article, the properties of hydrocracked kerosene used for the production of JET A-1 and hydrotreated kerosene used for the production of diesel fuel and the properties of their blends were studied. Hydrocracked kerosene was characterized by an extremely low freezing point, and by variable and high aromatics content. In contrast, hydrotreated kerosene had a high freezing point but a stable lower aromatics content. It was shown that by blending hydrocracked and hydrotreated kerosene interesting synergies could be achieved in the refinery. The production of JET fuel may be increased by up to 2.5 times by blending hydrocracked and hydrotreated kerosene in a ratio of 40/60, controlling the high aromatics content of hydrocracked kerosene and the high freezing point of the hydrotreated kerosene at the same time. At the same time, the kerosene fraction with improved low temperature properties will be available for diesel fuel production. A possible negative impact of the cetane index of such blends on the properties of diesel fuel will have to be further researched. The proposed solution is of interest in order to reduce the so called "giveaways" in the area of low-temperature properties and balance of aromatics in kerosene fractions of hydrocracker-type oil refineries. However, the proposed solution would require an estimated investment of units of millions US$ in modifying the refinery's piping system, in adapting the JET fuel additivation, measurement and control system to this solution.

Acknowledgments

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