

TERMS OF REFERENCE FOR THE R&D PROJECT
PETROLEUM, COAL AND RELATED PRODUCTS DEPARTMENT
Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen), PCD 01

1 Title of the Project

To provide inputs for development of test method for determination of wide-range FAME (C8 & above) as total FAME content in Aviation Turbine Fuels containing synthesized hydrocarbons using High Performance Liquid Chromatography (HPLC)

2 Background

Biofuels are fuels derived from organic materials such as biomass and natural waste; they are available in gaseous, solid, and liquid form. Biofuels are a renewable and sustainable alternative to conventional petroleum and coal derived fuels and also contribute in reducing environmental emissions. Moreover, liquid biofuels have the additional advantage that they can be used as “drop-in” fuels, implying that they can be used directly in existing engines with minimum or no change in design.

Aviation turbine fuel containing synthesized hydrocarbons is a complex mixture of hydrocarbons that varies depending on crude oil and renewable feed source and manufacturing process. There is an Indian Standard IS 17081: 2019 ‘Aviation turbine fuel (kerosene type, Jet A-1) containing synthesized hydrocarbons’. The fuel shall consist of synthetic blending components and additives as prescribed in Indian Standard. Synthesized paraffinic kerosene (SPK) produced from hydroprocessed esters and fatty acids (HEFA) is used as a synthetic blending component in aviation turbine fuels (ATF) for use in civil aircraft and engines. These comprise bio-derived hydrocarbons, free fatty acids, and fatty acid methyl esters (FAME) that have been hydroprocessed to saturate the hydrocarbon molecules and remove all oxygen. Majority of feedstocks for biofuel production contain mainly C16 and C18 FAMES (95% or more), however, some exceptional feedstocks such as palm kernel oil, coconut oil, and used cooking oil (UCO) contain significantly high amounts (around 80%) of C8, C10, C12, and C14 glycerides.

Determination of fatty acid methyl esters (FAME) content in biodiesel is an important requirement for its quality control, and its content is restricted up to 5 ppm in IS 17081. Method of test for determination of FAME in IS 17081 are IP 590 and IP 585. IP 590 is HPLC based test method which is applicable between 3 mg/kg to 140 mg/kg and IP 585 is GC-MS based test method which is applicable between 4.5 mg/kg -150 mg/kg. Both these test methods are capable to determine the following FAMES:

- i. Methyl Palmitate (C16:0),
- ii. Methyl Margarate (C17:0) (*IP 585 only*),
- iii. Methyl Stearate(C18:0),
- iv. Methyl Oleate(C18:1),
- v. Methyl Linoleate(C18:2), and
- vi. Methyl Linolenate(C18:3).

The limitations of IP 590 and IP 585 are that these test methods are:

- a) Not applicable to determine the FAME content below 3 mg/kg.
- b) Capable to determine only 5-6 individual FAME between C16-C18 and not the total FAME content.
- c) Not applicable to C8-C16 FAME obtained from coconut oil, palm kernel oil, and used cooking oil.

A test method applicable for FAME below 3 mg/kg, and for FAME derived from all kind of feedstocks is not available. Need has been felt to determine wide-range FAME (C8 & above) as total FAME content with less than 3 ppm detection limits in ATF. Since HPLC does not separate hydrocarbons individually but combines them in the form of groups of saturates and aromatics, thus, is important from the QA/QC viewpoint of these finished products.

3 Objective

To provide inputs for developing HPLC based test method for the determination of wide-range FAME (C8 & above) as total FAME content in Aviation Turbine Fuels containing synthesized hydrocarbons.

4 Scope

4.1 Extensive and thorough examination of the available literature on HPLC based test methods for various parameters in Aviation Turbine Fuels containing synthesized hydrocarbons, including but not restricted to the following and provide comparative analysis:

- a) International standards;
- b) Research papers;
- d) Any studies being conducted by any organization; and
- e) Any other sources.

4.2 Identification of manufacturing base of Aviation Turbine Fuels containing synthesized hydrocarbons in India. Collection of information on feedstock composition, manufacturing process, blending process, quality control, and analysis of information.

4.3 Experiments for detection of FAME (C8 & above) below the 3 ppm using various FAMES derived from palm kernel oil, coconut oil, and UCO.

4.4 Analysis of the effects of interferences, if any, in the chromatographic separation. For this, different stationary phases shall be screened along with combination of different eluting solvents.

4.5 Thoroughly optimize all chromatographic conditions of HPLC as given in 5.5

4.6 Validation of optimized analytical protocol through rigorous internal, external, and statistical data using different concentrations of the Aviation Turbine Fuels containing synthesized hydrocarbons to support regulatory bodies in formulating specifications and quality control. Samples of Aviation Turbine Fuels containing synthesized hydrocarbons and suitable calibration

standards shall be taken for analysis and validation.

4.7 Based on the test reports of experiments and information collected through questionnaires, visits and discussion, analyze and provide inputs for development of HPLC based test method for determination of wide-range FAME (C8 & above) as total FAME content in Aviation Turbine Fuels containing synthesized hydrocarbons and submit project report.

5 Research Methodology

5.1 Undertake thorough literature review as per 4.1 and prepare summary report including comparative analysis, if any;

5.2 Identify manufacturing base and collect information on feedstock composition, manufacturing process, blending process, and quality control using a structured questionnaire. Inform them about requirement of industry visit and collection of Aviation Turbine Fuels containing synthesized hydrocarbons samples.

5.3 Undertake visit to identified manufacturing units as per 4.2. Following activities shall be carried out and report prepared:

5.31 Observation on

- a) Feedstock being used for production of Aviation Turbine Fuels containing synthesized hydrocarbons and its composition;
- b) Manufacturing process for aviation turbine fuels that consists of conventional and synthetic blending components and blending process utilized for preparation of blends;
- c) In-process quality control in respect to presence fatty acid methyl esters (FAME) in Aviation Turbine Fuels containing synthesized hydrocarbons;

5.4 Based on the inputs collated and relevance of the ATF-HEFA blend testing of FAME, various concentrations of total FAME (instead of individual) shall be prepared by blending various FAMES (C8-C16) in ATF. Samples of at least ten concentrations from range 1 mg/kg to 140 mg/kg (including 1 mg/kg and 140 mg/kg) shall be prepared for analysis and validation.

5.5 Thoroughly optimize all chromatographic conditions of HPLC involving the following activities;

- a) Selection and optimization of stationary phase(s).
- b) Optimization of mobile phase and elution parameters, including:
 - i) The polarity of the mobile phase,
 - ii) Isocratic or gradient elution,
 - iii) Modifier needed, if any,
 - iv) Resolution between various FAMES,
- c) Selection and optimization of detector response.
- d) Determination of analytical figures of merit.
- e) Validation of optimized analytical protocol using real-world samples.

5.6 The experimental results shall be quantitatively generated using model FAME compounds, and their calibration standards shall be prepared at different concentrations.

5.7 The final quantifiable method outcomes as given below shall be calculated.

- a) Applicable range of testing;
- b) Linearity; and
- c) Precision

5.8 Based on the test reports of experiments and information collected through questionnaires, visits and discussion, analyze and provide inputs for development of HPLC based test method for determination of wide-range FAME (C8 & above) as total FAME content in Aviation Turbine Fuels containing synthesized hydrocarbons *and* submit project report.

6 Deliverables

6.1 Project report, in hard copy and digital formats, covering all aspects mentioned in scope

6.2 Questionnaires, discussion and visit reports, test reports, to be appended with the project report

7 Timeline and Method of Progress Review

7.1 Timeline for the project is 5 months from the date of award of the project.

7.2 Stages for Review:

7.2.1 **Stage I:** At the end of 1st month, prepare a comprehensive plan identifying the following:

- a) Details of literature review carried out and summarized report;
- b) Information obtained through questionnaires from the above-mentioned stakeholders and visits to be carried out;
- c) Laboratory where testing is to be carried out; and
- d) Test method proposed to be used for determination of wide-range FAME (C8 & above) as total FAME content in Aviation Turbine Fuels containing synthesized hydrocarbons and sampling plan.

Member Secretary will evaluate the plan and provide feedback, if any.

7.2.2 **Stage II** – At the end of 4th month, submit draft report with the following information:

- a) Reports of visits carried out to manufacturing units;
- b) Details of analysis processes being used as given in 5.5;
- c) Number of samples collected with information related to source of the samples;
- d) Test reports; and
- e) Analysis of data and validation of optimized analytical protocol using real-world samples.

Sectional Committee will evaluate the draft report and provide feedback/recommend changes, if required. Project allottee to submit final project report incorporating recommendations/feedback of Committee by end of 5th month.

8 Support from BIS

- 8.1** BIS will provide access to latest editions of Indian and International Standards.
- 8.2** BIS will facilitate introduction to manufacturing industries, laboratories, and user industries for carrying out the project

9 Nodal Officer

Mr. Hari Mohan Meena, Sc. C/Deputy Director, PCD, BIS, may be contacted at pcd1@bis.gov.in for any queries on the research project.