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

Development of test method for determination of triglyceride (vegetable oils and used cooking oils (UCO)) in diesel and diesel-biodiesel blends 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.

Biodiesel, obtained from the esterification of vegetable oils, UCO, or animal fats, consists of mono-alkyl esters of long chain fatty acids. In the Indian Standard IS 15607, the term 'Biodiesel' refers to mono alkyl methyl esters of vegetable oils like rapeseed, soya bean, sunflower, jatropha curcas, karanja, palm etc., UCOs, waste vegetable oils, by-products of edible oil production like free fatty acids, palm stearin etc., and other fats. Biodiesel can be used for engine applications as a standalone fuel or as a blend with diesel (IS 15607 and IS 16531).

The oils and fats that have been used for cooking or frying in the food processing industry, bakery, restaurants, fast foods centers and at consumer level, in households are defined as Used Cooking Oil (UCO), which is one of the feedstock for production of the biodiesel.

Determination of vegetable oil and UCO content in biodiesel is an important requirement for its quality control, and its content (as triglyceride) is restricted up to 0.2 percent by mass in IS 15607. Method of test for determination of triglyceride in IS 15607 is ASTM D6584 which is Gas Chromatography based method. However, limitation of ASTM D6584 is that it is not applicable to triglyceride obtained from lauric oils, such as coconut oil and palm kernel oil.

A test method applicable for triglyceride derived from all kind of vegetable oil and UCO is not available. Such test method is highly required for determination of adulterants in the form of vegetable oil and UCO present in diesel and diesel – biodiesel blends. 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 develop HPLC based test method for the determination of vegetable oil and UCO (as triglyceride) in diesel and diesel-biodiesel blends.

4 Scope

4.1 Extensive and thorough examination of the available literature on HPLC based test methods for various parameters in diesel and diesel-biodiesel blends, 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 diesel and biodiesel in India along with categorization of large, medium, small and micro units. Collection of information on feedstock composition, manufacturing process, blending process, quality control, and analysis of information.

4.3 Experiments for separation of diesel hydrocarbons, biodiesel (FAME) and triglycerides (vegetable oil and UCO) as three distinct entities in a single HPLC chromatogram using a suitable detector and comparative analysis of overlap of FAME, and vegetable oiland UCO (as triglyceride) with diesel tri^{+}-aromatics and mono-aromatics, respectively.

4.4 Analysis of the effects of interferences due to overlap of FAME, and vegetable oil and UCO (triglyceride) 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 diesel and diesel-biodiesel blends to support regulatory bodies in formulating specifications and quality control. Samples of B8, B20, and any other five concentrations (between B8 to B20) 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 triglyceride (vegetable oils and used cooking oils (UCO)) in diesel and B8-B20 diesel-biodiesel blends 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 categorized into large, medium, small, and micro units. Contact the manufacturers 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 diesel and diesel-biodiesel blends 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 biodiesel that is blended with diesel and its composition;

b) Manufacturing process for biodiesel and& blending process utilized for preparation of B8 – B20 diesel-biodiesel blends;

c) In-process quality control in respect to presence triglyceride (vegetable oils and used cooking oils (UCO)) in diesel and diesel-biodiesel blends;

5.4 Based on the feasibility and relevance of the B8-B20 diesel testing, a scenario depicting their QA/QC and adulteration shall be prepared by blending various edible and non-edible vegetable oils, including UCO. Samples of B8, B20, and any other five concentrations (between B8 to B20) 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 hydrocarbons, FAME, and UCO.
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 bases test method for determination of triglyceride in *diesel and B8-B20 diesel-biodiesel blends 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) Identified manufacturers of biodiesel;

c) Information obtained through questionnaires from the above-mentioned stakeholders and visits to be carried out;

d) Laboratory where testing is to be carried out; and

e) Test method proposed to be used for determination of triglyceride (vegetable oils and used cooking oils (UCO)) in diesel and diesel-biodiesel blends and sampling plan.

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

7.2.2 Stage II – At the end of 4rd 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 and available literature with BIS

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.