Fuel Property Investigation: Jatropha Biodiesel, Used Cooking Oil Biodiesel and Fuel-grade Ethanol Blends

Tomesh Kumar Sahu1*, Pravesh Chandra Shukla1, Vikas Kumar Sahu1, Satyajit Gupta2 and Sumit Sarkar3

1 Department of Mechanical Engineering, Indian Institute of Technology Bhilai, India
2 Department of Chemistry, Indian Institute of Technology Bhilai, India
3 Chhattisgarh Biofuel Development Authority, Chhattisgarh, India
* Corresponding author’s e-mail ID: tomeshs@iitbhilai.ac.in

Abstract. Compression ignition (CI) engines are one of the promising power producing units which provide higher efficiency and durability. Increasing environmental pollution and depleting resources led the research in the field of alternative fuels such as biodiesels, ethanol etc. for utilization in CI engines. In the present study, two different types of biodiesels i.e. Jatropha Biodiesel (JBD), Used Cooking Oil (UCO) Biodiesel and Ethanol were investigated for the fuel properties and compared. Various fuel properties like density, kinematic viscosity, calorific value, oxidation stability, cold weather properties (CFPP, CF, and PP), and flash point temperature were measured and compared for pure form of alternative fuels. Different blends (5%, 10%, 15% and 20%) of JBD, UCO biodiesel and ethanol were also investigated. It has been observed that ethanol showed lower density, lower viscosity and superior cold weather properties compared to the tested fuels/blends. The average viscosity for ethanol was measured to be 1.08 mm²/sec which is ~61.8 % less compared to mineral diesel. Oxidation stability tests were also performed where mineral diesel shows 83.15 min for 10% pressure drop at 140°C and 700 kPa, UCO biodiesel and JBD shows 9.2 min and 8.32 min. 5% ethanol blend showed sharp reduction in flash point compared to mineral diesel, however, it remained almost at the same level with further blending.

1. Introduction
Diesel engines have significant importance in global goods transportation and heavy vehicle operations due to their higher efficiency and durability [1]. Limited reserves, uneven distribution of petroleum reserves among countries and increasing pollution level led to the research activities for alternative fuel options for mineral diesel. Biodiesel is an accepted alternative fuels of mineral diesel being used for a very long time in diesel engines [2]. In their early-stage research, biodiesels were produced and used using edible seeds oils as a first-generation (1G) biodiesels, however, second-generation (2G) biodiesel includes non-edible oil seeds for the production of biodiesel such as Jatropha, Karanja etc. [3,4]. Increasing global emission is a major concern these days and biodiesel are effective in reducing the pollution level. Another option for diesel engines are various alcohols, primarily methanol and ethanol which are relatively easier to produce and used as an alternative of diesel. In India, Jatropha is one of the abundantly available resources for feedstock oil. On the other hand, waste cooking oil (WCO) is an emerging alternative for biodiesel production [5,6]. The usage of vegetable oil is not desirable for cooking when its polar compound concentration increases beyond 25% [7]. Cooking oil with higher concentration of polar compounds can be alternatively used for biodiesel production and known as used
cooking oil (UCO). Ethanol is also an important possible alternative fuel with relatively lower calorific values (~27 MJ/kg) [8,9]. Biofuels such as biodiesels and ethanol possess different properties compared to mineral diesel in context of utilization diesel engines. Fuel properties like calorific value, density etc. largely affect the combustion and performance behaviour of the diesel engines [10]. Silitonga et al., 2013 [11] have reviewed fuel properties, ignition properties and cold weather properties of jatropha biodiesel (JBD)/mineral diesel blends (10%, 20%, 30%; v/v). They observed that higher proportion of JBD resulted into increased flash point (~18% increase for 30% blend), kinematic viscosity (~38% increase for 30% blend), density and cloud point temperature while calorific value of the blend decreased (~4.3% decrease for 30% blend) [11]. Chen et al., 2012 [12] have observed increase in the oxidation stability by blending the mixture of soapnut biodiesel (SNBD) and JBD (35:65 (w/w)) ratio to mineral diesel (with blends ratios of 1%, 2%, 5%, 7%, 10%, 20%, 40%, 60% and 80%; v/v). They obtained -6°C cold filter plugging point (CFPP), oxidation stability in the range of 9.1-17.3 hours and kinematic viscosity (at 40°C) in the range of 3.03-3.51 mm²/s up to 40% mixed biodiesel blends in mineral diesel [12]. Chen et al., 2013 [13] have recommended upto 40% blending of JBD (doped with 250 ppm pyrogallol) to counter the problems of oxidation stability [13]. National Renewable Energy Laboratory (NREL), USA has reported [14] that the use of JBD reduced the greenhouse gases (GHGs) emissions by 62% while testing in locomotives. According to their report, 5% biodiesel blend, 20% biodiesel blend and neat biodiesel may replace 4%, 17% and 86% petroleum use respectively [14]. UCO biodiesel’s total environment footprint is 40% lesser than first-generation biodiesel and 1/4th (3 times lower) of the mineral diesel’s total environmental footprint [15]. Singh et al., 2019 [16] studied the properties of pure diesel and diesel/ethanol blends with co-solvent oleic acid (7% ethanol, 1% oleic acid, 92% diesel; 13% ethanol, 5% oleic acid, 82% diesel; 19% ethanol, 7% oleic acid, 92% diesel; v/v). They concluded that decrease in density and viscosity due to blending leads to retarded injection timing and decreased sulphur content in the blend lower the toxic pollutants in the exhaust [16]. Jimenez et al., 2009 [17] blended ethanol with rapeseed biodiesel at 5%, 10% and 15% and investigated the effect on fuel properties. They suggested that low flash point and hygroscopic nature of ethanol in these blended fuel drawn a major setback for possible practical application [17]. Fernando and Hanna, 2004 [18] experimented two separate blends of ethanol-biodiesel-diesel in certain proportions (3.75%: 25%: 71.25%; 4.00%: 20%: 76.00%; v/v) and found minimum phase transition temperature (PTT) of 11°C in both LSD and ULSD [18]. Further characteristic’s influencing the lubrication, ignition and combustion of mineral diesel and its ethanol blends (5%, 10%, 15%; v/v) studied by Jimenez et al., 2011 [19]. Certain properties like Density, viscosity, Pour point, flash point, lower specific energy content, wear scar and filter plugging tendency decreased due to ethanol addition [19].

The objective of the present study is to investigate the physical and chemical properties of alternative fuel and look for their variation by varying percentage of alternative fuel into baseline diesel, to relate them with the desirable specifications of diesel fuel. Second generation (non-edible source) were used for in-house production of biodiesels. Fuel properties are important to understand the combustion chemistry and emission behaviour in IC engines. Calorific value, viscosity, cloud and pour point, density, oxidation stability, cold filter plugging point, the flash point were measured and compared for JBD, UCO biodiesel (UCO), and ethanol (E). These properties were also measured and analysed for their various blend ratios (JB05, JB10, JB15, JB20; U05, U10, U15, U20; E05, E10, E15, E20). Where 5-20 representing the percentage of respective alternative fuel into mineral diesel.

2. Methodology
In the present study, three alternative fuels i.e. JBD, UCO biodiesel and Ethanol, were chosen and investigated for various fuel property parameters of pure fuels and their blends. Methodology of the study adopted the selection and preparation of fuel blends, measurement of various property parameters and their comparison for the utilization suitability in compression ignition (CI) engines.

2.1. Preparation of Fuels
UCO was collected from the restaurants of Dhamtari city of Chhattisgarh, and Jatropha seeds were
collected from the locally available resources/fields. Further, two separate batches of biodiesel (UCO and JBD) were produced using the transesterification process in a Biodiesel production pilot plant of Chhattisgarh Biofuel Development Authority (CBDA), Raipur. Methanol as a reactant and sodium hydroxide (NaOH) as a catalyst was used for the same. Chemical grade ethanol (99.9%) and mineral diesel were procured from authorized supplier and government authorized diesel outlet respectively. UCO biodiesel, JBD and ethanol were blended with mineral diesel in the range of 5-20% (v/v) blend ratio. Prepared blends include, Ethanol-diesel blends (E5, E10, E15, and E20; v/v), JBD blends (J5, J10, J15, and J20; v/v), UCO biodiesel blends (U5, U10, U15, and U20; v/v), where the numeral values indicate the volume fraction of biofuel in mineral diesel. Figure 1 shows the chemical process of transesterification adopted in the laboratory for biodiesel making.

![Figure 1: Transesterification process for biodiesel production [20]](image-url)

2.2. Fuel Properties Measurement
Fuel properties of test fuels were determined as per the international standard of ASTM (Table 1). The knowledge about the fuel property parameters are the essential part for the biofuel utilization in CI engines as varying physico-chemical properties may largely affect the combustion and performance parameters. Measurement of fuel property parameters include density, calorific value, viscosity, flash point, cold filter plugging point (CFPP), cloud point (CP), pour point (PP), and oxidation stability.

2.2.1. Density. The density of fuels were measured according to the criteria specified by ASTM 4052 standard. Density of tested fuels were measured by keeping the room temperature and the device temperature at 25°C. The equipment used for the density measurement was Rudolf Research Analytical [Model: DDM2909]. Small amount of fuel is injected through a syringe in a temperature-controlled U tube to measure the density of fuel. Mechanical oscillation method was used to measure the density. The oscillation frequency \( f \) was measured, density was calculated using the following expression shown in equation 1 [16, 19]. Each measurement was repeated 3 times to reduce measurement error and average results are used for analysis.

\[
\rho = A \cdot \tau^2 + B \quad \text{............... (1)}
\]

Where \( \rho \) is the density of fuel, \( \tau \) is the time-period of oscillation (1/\( f \)) in seconds and A and B are the respective instrument constants.

2.2.2. Kinematic Viscosity. It is defined as a property due to which it offers resistance against motion. It was measured for the biofuels (fuels used in this study) and their blends as per the method specified in standard ASTM D445 at 40°C. Viscometer from OMNITEK B. V. [Model: U-Visc 110] was used with a measuring range of 0.5 to 10000 mm²/sec. The working principle of kinematic viscosity meter include
the measurement of the travel time required for the fixed volume of the given fuel through the capillary under the influence of gravity. The equation used for kinematic viscosity calculation is shown in equation 2 [19]. Each measurement was repeated 3 times to reduce measurement error and average results are used for analysis.

\[ \nu = C \cdot t \]  

(2)

Where, \( \nu \): kinematic viscosity (mm\(^2\)/s), \( C \): calibration constant of the viscometer (mm\(^2\)/s\(^2\)) and \( t \): mean flow time required to pass capillary.

2.2.3. Calorific Value. Calorific values were measured using bomb calorimeter for the chosen alternative fuels (UCO biodiesel, JBD and ethanol). The Bomb calorimeter offers a quick and precise calorific value calculation technique. Measurements of fuel sample calorific values were conducted in compliance with the procedure and parameters defined by the ASTM D240 standard. A small amount of fuel (1 gm) was taken into crucible and oxygen is supplies through the cylinder to fill the bomb till a pressure of 3 MPa. For the calculation of the calorific value of the fuel measured, the original temperature of the water in the calorimeter after stirring and the highest temperature indicated by the thermometer are used. The instrument used for measuring of cv value was from Advance research instruments co. [Model: ARICO IP-3].

2.2.4. CP, PP, and CFPP. For running the engines under cold weather conditions, cold flow characteristics are important. The temperatures of the cloud point shall be calculated as the temperature at which the wax crystal cloud is first appeared under a controlled condition in a liquid during standard testing (ASTM D2500). The temperature below which the fuel cannot be poured due to the forming of gel (ASTM D6892) is known as pour point, and CFPP is the lowest temperature at which the amount of sample fuel (70ml) is passes under standardized filtration unit within a specified time (60 sec) (ASTM D6371). ORBIS B. V. [Model: Air STAR cold block CPPP and Model: Air STAR cold block CFPP] were used for measurement.

2.2.5. Oxidation stability. Oxidation stability test of diesel and biodiesel have been performed to estimate its long term storage capability. Oxidation stability tests are normally performed at relatively higher temperature and also used to add oxygen to speed up the oxidation of the test fuels [21]. ASTM standard D7545 was adopted for performing oxidation stability test for the tested fuels. Test were performed in Anton Par GmbH small scale rapid ox apparatus [Model: RapidOxy 100].

2.2.6. Flash point. Flash point temperature is important for transportation and storage purposes. It was measured for pure alternative fuels used in this study and their blends as per criteria specified by ASTM D93-A. Pensky martin closed cup auto flash tester by Acute Instruments Pvt. Ltd. [Model: PMCC Auto Flash – 93] was used for measurement. The test involves the use of a sample volume of approximately 75 ml which is then placed in the closed cup of the tester, subsequently firing was performed with 10°C of interval till the flashpoint obtained.

3. Results and Discussion

In the present study, three alternative fuels i.e. JBD, UCO biodiesel and ethanol were chosen for the fuel property parameter measurement. Since, the objective of the current study is to compare the alternative fuel properties for the possible utilization in CI engine, fuel properties were measured for the neat fuels and their blends with mineral diesel. The discussion in this section is subdivided for the property measurement of pure and blends of these tested fuels with mineral diesel.

3.1. Properties of Pure Alternative Fuels

ASTM standards were referred for the methodology adopted for the measurement of fuel properties.
The evaluation of fuel properties is essential to understand their combustion and performance characteristics. Table 1 shows the measured properties of ethanol, UCO biodiesel and JBD along with mineral diesel, it was noted that UCO Biodiesel shows similar value compare to B100 Standard, Viscosity value is ranging on higher side for biodiesel, which may require extra pump power while injecting into engine. Flash point and density values of produced fuel were within limits, and cold weather properties shows superior compare to standard B100.

Table 1: Fuel properties of JBD, UCO biodiesel, ethanol and mineral diesel

| Properties                          | Method       | Standard (B100) | Diesel       | Ethanol     | UCO BD | JBD  |
|-------------------------------------|--------------|----------------|--------------|-------------|--------|------|
| Density at 25 °C, (kg/m³)           | ASTM D4052   | 860-900        | 822          | 795         | 863    | 892.5|
| Kinematic Viscosity at 40 °C, (mm²/sec) | ASTM D445    | 3.5-5          | 2.83         | 1.08        | 5.1    | 5.6  |
| Calorific value (MJ/kg)             | ASTM D240    | -              | 45.6         | 29.3        | 39     | 39.3 |
| Flash point, min (°C)               | ASTM D93A    | 101            | 56           | 12²         | 163    | 160  |
| Cloud point (°C)                    | ASTM D2500   | -              | -2           | -34         | 5      | 6    |
| Pour Point (°C)                     | ASTM D6892   | -              | -6           | -117.3³     | -3     | -2   |
| Cold filter plugging point (°C)     | ASTM D6371   | 6 °C for winter| -6           | -           | -2     | -1   |
|                                     |              | 18 °C for summer| -           | -           | -     |      |
| Oxidation Stability at 140 °C, (min)| ASTM D7545   | 8              | 83.1         | 5           | 8.32   | 9.25 |

³ Adapted from Li D et al., 2005 [23]

3.1.1 Viscosity, Density, and Calorific Value. Figure 2 illustrates the density, viscosity, and calorific value of pure JBD, UCO biodiesel and ethanol. It was observed that both biodiesels (863 kg/m³ and 892.5 kg/m³ for UCO biodiesel and JBD respectively) have higher density compared to mineral diesel (822 kg/m³), however, ethanol density (795 kg/m³) measured to be the lowest among tested fuels, lower density of ethanol were also observed by Jimenez et al [19]. The effect in density can affect start of ignition and combustion duration, which can adjusted by tuning the injection timing [19, 24]. Reduction in density reduces its sauter mean diameter (SMD) and improve the spray characteristics [19,25]. From Figure 2, it can be observed that the average viscosity for ethanol is 1.08 mm²/sec, which is ~61.8 % less compared to mineral diesel (2.83 mm²/sec), however, biodiesels show significantly higher viscosity (5.1 mm²/sec and 5.6 mm²/sec for UCO biodiesel and JBD). The lower viscosity of ethanol may cause pump and injector leakage [26,27] while using ethanol in conventional diesel engine.

3.1.2 Cold Weather Properties (CP, PP and CFPP). Figure 3 shows the cold flow properties of Diesel, Biodiesel, and ethanol. It includes CP, PP, and cold filter plugging point (CFPP) temperature for all tested fuels, which are essential for operating an engine in cold countries or in cold climate regions. CP is the maximum absolute temperature at which the first cloud of crystal appears during cooling. CFPP is the minimum temperature below which fuel is unable to pass through fuel filtration device due to gel formation. On the other hand, PP is the minimum temperature below which fluid can’t be poured in any system. Figure 3 shows that pure biodiesels possess inferior cold flow properties. CP, PP and CFPP temperatures for biodiesels (JBD and UCO) were found to be higher in comparison to mineral diesel.
Higher CP, PP and CFPP of biodiesels indicates that these fuels may not be suitable for extreme cold weather. Superior cold weather properties of ethanol make it suitable for these purpose (PP and CFPP of ethanol were found to be below -34°C).

3.1.3 Flash Point and Oxidation Stability. Figure 4 illustrates the flash point temperature and oxidation stability of pure biodiesels and ethanol. Flash point temperature is a very critical parameter since this plays an important role in handling and storage of the fuels. Biodiesels showed a much higher flash point (160°C and 163°C for JBD and UCO biodiesels respectively) in comparison to mineral diesel (56°C), signifies biodiesel handling and storage is safer and special management is thus not required.

Flash point temperature of ethanol is below room temperature (12°C), and it can catch the fire easily therefore it need special transportation and handling. Apart from the flash points determination, oxidation stability of the pure alternative fuels was also investigated. Oxidation stability tests were also performed where mineral diesel shows 83.15 min for 10% pressure drop at 140°C and 700 kPa, UCO Biodiesel and JBD shows 9.2 min and 8.32 min. Biodiesel oxidation time is 10 times lesser compare to mineral diesel, biodiesel standard oxidation time as per BIS standard is 8 min.
3.2. Properties of Fuel Blends of Alternative Fuels

Due to wide variation in the major properties of the alternative fuels, it becomes difficult to use the pure form of alternative fuels in the compression ignition engines. For example, ethanol shows very high autoignition value (~363°C) which cannot be ignited in conventional CI engine. Similarly, biodiesel shows high viscosity and density and therefore it is difficult to use biodiesel for a longer term in CI engines as it can clog the injector nozzles and fuels lines. To resolve these issues with alternative fuels, blending method has been adopted in which one or more alternative fuels can be blended with mineral diesel to keep the fuel properties closer to mineral diesel. However, it is essential to measure properties of blends for proper functioning of diesel engines because blending two different fuel can alter density, viscosity, stability, cold flow properties, and energy content of the fuel. Ethanol-diesel blends (E5, E10, E15, and E20; v/v), JBD blends (J5, J10, J15, and J20; v/v), UCO biodiesel blends (U5, U10, U15, and U20; v/v) where ethanol, JBD, and UCO biodiesel percentages are 5, 10, 15 and 20% respectively (v/v) into mineral diesel were prepared and tested. Properties of blended fuels were discussed below. Tested fuel properties were analyzed for their variation with blends percentage and alteration with baseline diesel properties.

3.2.1 Viscosity, Density and Calorific Value. Figure 5(a) shows the density variation for various blends of ethanol, UCO biodiesel, and JBD into diesel. E20 showed 0.24% reduction in density compared to mineral diesel while JBD20 and UCO20 showed 1.70% and 1.34% increase in the density respectively. Figure 5(b) shows the variation in viscosity of the blends of three alternative fuels (i.e. JBD, UCO biodiesel and ethanol) with mineral diesel.

![Figure 5](image-url)

**Figure 5**: Relative change in fuel properties with blend percentage (a) density variation (b) viscosity variation (c) variation in calorific value.

The increasing fraction of JBD and UCO biodiesel increased the viscosity. It was 2.8 mm²/sec for mineral diesel and gradually increased to the level of 3.5 mm²/sec for JBD20 and UCO20. Ethanol showed the opposite trend and its viscosity reduced just below 2 mm²/sec for E20. It should be noted that significant reduction in viscosity may add a lubrication problem to the engine, which will affect the performance of the engine. Similar to viscosity, density also showing the similar trend for the blends of three alternative fuels tested. Density affects the fuel injection spray behavior such as spray penetration length, spray area, atomization etc. Due to the conical and cylindrical design features of nozzle holes, higher density fuels also prone to create cavitation in the injection, thus reduces the fuel flow rate. Calorific value for a given fuel is also an important property as it influences the engine efficiency and fuel consumption rate. Figure 5(c) illustrates the calorific value of various blends of JBD, UCO biodiesel and ethanol blends. Blends for JBD, UCO biodiesel and ethanol showed reducing trend in calorific values unlike the viscosity and density where it increased for JBD and UCO biodiesel. Reduction in calorific value (~6.8% reduction for E20, ~2.6% reduction for JBD20 and UCO20) was observed with an increase in fraction of alternative fuel in the fuel blend.
3.2.2 Cloud Point (CP), Pour Point (PP), Cold Filter Plugging point (CFPP). Cold weather properties CP, PP, and cold filter plugging point were measured for all blends of ethanol, UCO biodiesel, and JBD is shown in Figure 6. For ethanol-diesel blends, it was observed that, ethanol addition into diesel improves cold weather properties. However, for biodiesel blends, CP appears at a much higher temperature, whereas PP and cold filter plugging point are not much affected, biodiesels possess inferior cold flow properties. From the above result, it can be concluded that ethanol blends can work at extremely lower weather conditions, however, the use of biodiesel blends for the same is not advisable.

![Figure 6](image.png)

**Figure 6**: Variation in fuel properties with blend percentage (a) cloud point variation (b) pour point variation (c) variation in CFPP.

3.2.3 Flash point and Oxidation Stability. Figure 7 (a) and (b) illustrate the measured flash point and oxidation stability of blended fuels. Flash point of any fluid is the minimum temperature at which it catches fire when the ignition source is provided.

![Figure 7](image.png)

**Figure 7**: Flash point and oxidation stability variation of blends.

Flash point is important for handling and storage purpose of any fluid. Diesel have flash point of 56°C and biodiesels have flashpoint in the range of 160°C, however, ethanol has flash point at 12°C (which is below room temperature for Indian climate condition). Ethanol needs safe transportation, handling, and storage methods compared to other fuels. Similarly, blending of ethanol into diesel will continue to reduce its flash point temperature shown in Figure 7(a), although biodiesel blending in diesel increases the flash point. The variation in flash point is sharp in the case of ethanol blends, only 5% ethanol reduces flash point from 56°C to 25°C, however beyond 5% of ethanol blend reduction in flash point is negligible. Figure 7(b) shows the oxidation stability test results performed at 140°C for biodiesel blends and ethanol blends. It should be noted that adding ethanol or biodiesel into mineral diesel reduces the oxidation stability of the fuel. However, ethanol shows less reduction compare to biodiesel blends.
4. Conclusions
Physico-chemical properties of trending alternatives (JBD, UCO biodiesel and ethanol) of mineral diesel were investigated and compared in their pure and blended forms. Biodiesel blends exhibit the nearer value for flash point, calorific value and PP while ethanol blends are favourable in terms of viscosity, density and CP. Based on the current study, following inferences may be summarized:

- Biodiesels (863 kg/m$^3$ and 892.5 kg/m$^3$ for UCO biodiesel and JBD respectively) have higher density compared to mineral diesel (822 kg/m$^3$) while ethanol density (795 kg/m$^3$) measured to be the lowest among tested fuels.
- Measurements showed that biodiesel and ethanol possess lower calorific values compared to mineral diesel (~15-20% lower for biodiesels and 35.74% lower for ethanol). On the other hand, cold weather properties for ethanol showed superior quality.
- Oxidation stability was measured to be 9.225 min and 8.32 min for JBD and UCO biodiesels respectively which was significantly lower compared to mineral diesel (83.15 min).
- Concerning to the blends of biodiesels, it showed increasing trend with higher fraction of biodiesels in blend while ethanol blends with diesel resulted in decreasing values of these properties. Cold whether properties of ethanol blends improved with increasing fraction of ethanol in the blend.

Overall, it was observed that biodiesel (pure and blended forms) may be suitable to use in CI engines when it comes to flash point, calorific value and PP. While ethanol (pure and blended forms) may be suitable for CI engines in terms of viscosity, density and CP. To overcome the demerits of these alternative fuels, blended form of these fuels may be recommended for the use in CI engines.

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Acknowledgments
The authors acknowledge the support of Mr. Puranchandra Sahu and Mr. Kanhaiya Yadav for the experimental work. The authors also would like to thank the CBDA, Chhattisgarh Government, for the resource arrangement. The authors would also like to thank DST-SERB for supplying funds for consumables and staff (under the project code: SRG/2019/001664). Some of the key results will also be used in the final report on the submission of the project to DST-SERB.