Copy to Dean R&D Dhanapati Deka

Annexure-III

UTILISATION CERTIFICATE (2 COPIES)

FOR THE FINANCIAL YEAR 2013-2014 (ENDING 31ST MARCH, 2014)

1. **Title of the Project**: Synthesis of platform biofuels from Renewable sources using acid modified supported ionic liquid catalysts.

OFFICE OF DEAN R&D
TEZPUR UNIVERSITY
DATE OF RECEIPT 9/12/2022
RECEIPT NO 3285
SIGNATURE

2. **Name of the Institution**: Tezpur University

3. **Principal Investigator**: Dr. Dhanapati Deka

4. **Department of Science & Technology sanction order No & date sanctioning the project:**
   i) DST sanction letter no. INT/FINLAND/P-02 dtd. 10-Mar-2011 –original sanction order
   ii) DST sanction letter no. INT/Finland/P-02 dtd. 13-August-2012 for 2nd year
   iii) DST sanction letter no. INT/Finland/P-02 dtd. 26-06-2013 for 3rd year

5. **Head of account as given in the original sanction order**:
   (i) Major Head-3425 B-other Scientific Research
   (ii) 60 other Minor Head 60.798 International Co-operation S&T Co-operation with other countries.

6. **Amount brought forward from the previous Financial year quoting DST letter no. and date in which the authority to carry forward the said amount was given**.
   Amount Rs. 1,28,187- (Rupees one lakh twenty eight thousand one hundred eighty seven only). Letter no. INT/Finland/P-02 dtd: 26-06-2013

7. **Amount received during the financial year (01-04-2013 till 31.03.2014)** (Please give DST letter/order no and date)
   i. Amount: Rs. 8,00,000/- (Rupees eight lakh) only for 3nd Year.
   ii. Letter/Order No : INT/FINLAND/P-02
   iii. Date: 26th -June-2013

8. **Total amount that was available for expenditure (excluding commitments) during the financial year (01-04-2013 till 31.03.2014)** (Sr. No. 6+7)
   Rs. 9,28,187/- (Rupees nine lakh twenty eight thousand one hundred eighty seven) only.

9. **Actual Expenditure (excluding commitments) incurred during the financial year (01-04-2013 till 31.03.2014)**
   Rs. 7,13,604/- (Rupees Seven lakh thirteen thousand six hundred four) only.

10. **Balance amount available at the end of the financial year**: Rs. 2,14,583/-- (Rupees two lakh fourteen thousand five hundred eighty three only)

11. **Unspent balance refunded, if any (please give details of cheque no etc.):**

Prof. Dhanapati Deka
Principal Investigator
Department of Energy

12. **Amount to be carried forward to the next financial year (2014-2015):** NA
The project has completed on 31.3.2014 and unspent amount of Rs. 2,14,583/-- (Rupees two lakh fourteen thousand five hundred eighty three only) is refunded to DST, India

UTILISATION CERTIFICATE

Certified that out of Rs. 8,00,000/- (Rupees eight lakh) only of grants-in-aid sanctioned during the year 2013-2014 in favour of the Registrar, Tezpur University under this Ministry/ Department letter No : INT/FINLAND/P-02 dtd. 26th June, 2013 and Rs. 1,28,187/- (Rupees one lakh twenty eight thousand one hundred eighty seven) only as unspent balance of the previous year, a sum of Rs. 7,13,604/- (Rupees seven lakh thirteen thousand six hundred four) only has been utilized for the purpose of purchasing consumables, salary of manpower, contingency, exchange visit of scientists from both collaborating countries and for which it was sanctioned and that the balance of Rs 2,14,583/-(Rupees two lakh fourteen thousand five hundred eighty three) only is refunded to DST, India as unspent balance after completion of the project through Cheque No.

Signature of PI	Accounts Officer of the Institute	Signature of Registrar/ Signature of Head the Institute
Prof. Dhanapati Deka Principal Investigator Department of Energy Tezpur University Tezpur-784028	Finance Officer Tezpur University	Registrar Tezpur University
Date: 15/7/2014	Date: 17/07/14	Date: 17/7/14

~~Provisional~~ Statement of Expenditure
For the financial year, 01-04-2013 till 31.03.2014)

Sr. No. (I)	Sanctioned Heads (II)	Funds Allocated (indicate sanctioned) (III)	1st year grant released	2nd year grant released	3rd year grant released	Expenditure Incurred			Total expenditure IV + V + VI (VII) (1st April, 2011 to 31st March, 2014)	Balance as on 31-3-2014 (VIII)	Remarks (if any)
						1st Year (1st April, 2011 to 31st March, 2012) (IV)	2nd Year (1st April, 2012 to 31st March, 2013) (V)	3rd Year (VI) (1st April, 2013 to 31st March, 2014)			
1.	Manpower costs	7,20,000/-	2,30,400/-	1,27,935/-	2,20,800/-	1,27,935/-	1,92,000/-	1,90,715	5,10,650/-	68,485/-	
2.	Consumables	8,00,000/-	5,00,000/-	1,66,009/-	91,701/-	4,66,009/-	1,94,701/-	86,462/-	7,47,172/-	10,538/-	
3.	Contingencies	90,000/-	30,000/-	30,211/-	28,005/-	30,211/-	30,597/-	27,408/-	88,216/-	nil	
4.	Exchange visit (Indian Scientist)	4,50,000/-	1,80,000/-	1,29,875/-	44,291/--	1,29,875/-	1,46,373/-	31,361/-	3,07,609/-	46,557/-	
5.	Exchange visit (Finland Scientist)	2,35,000/-	94,000/-	42,416/-	nil	42,416/-	34,000/-	nil	76,416/-	60,000/-	
6.	Workshop in Finland	4,50,000/-	4,50,000/-	nil	Nil	4,50,000/-	nil	nil	4,50,000/-	nil	
7.	Workshop in India	4,00,000/-	nil	nil	3,39,773/-	nil	nil	3,13,709/-	3,13,709/-	26,064/-	
8.	Internal travel within India	75,000/-	25,000/-	Carry over	Carry over	nil	nil	22,061/-	22,061/-	2,939/-	
9.	Overhead expenses	2,41,500/-	1,13,490/-	33,833/-	75,430/-	86,333/-	94,532/-	41888/-	2,22,753/-	nil	
	Total	34,61,500/-	16,22,890/-	5,30,279/-	8,00,000/-	13,32,779/-	6,92,203/-	7,13,604/-	27,38,586/-	2,14,583/-	

Rs. 2,14,583 (Rupees two Lach fourteen thousand five hundred eighty three) is refundable to DST, New Delhi, India as unspent amount after completion of the project on 31.03.2014.

(Dhanapati Deka)
Name and Signature of Principal Investigator:
Date: 16-5-2014

17/05/14
Signature of Competent financial authority: _____
(With seal) Finance Officer Tezpur University Date: _____

* DOS – Date of Start of project

Note:
1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III).
2. Utilisation Certificate (Annexure III) for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.

Annual Progress Report (2013-2014), Third Year

Of

DST sponsored collaborative Indo-Finnish Research Project on Green Chemistry of Department of Science and Technology (DST) and Academy of Finland

Title: "*Synthesis of platform biofuels from renewable sources using acid modified Supported Ionic Liquid Catalysts (SILCA) –FUSILCA*"

Submitted to

Department of Science and Technology, DST,
Technology Bhawan, New Mehrauli Road, New Delhi-110016 (India)

Submitted by

Dr. Dhanapati Deka
Professor (PI)
Department of Energy

Dr. Ashim J. Thakur
Associate Professor (Co-PI)
Department of Chemical Sciences

Tezpur University (a central University)
Napaam, Tezpur, Assam, India
Pin-784028

Annexure-V

PROGRESS REPORT

1. **Project Title**: Synthesis of platform biofuels from Renewable sources using acid modified supported ionic liquid catalysts.	DST sanction letter no. INT/FINLAND/P-02 dtd. 10-Mar-2011
2. **PI (Name & Address):** Dr. Dhanapati Deka Department of Energy Tezpur University Napaam, Tezpur- 784 028, Assam **Telephone No.** : **(Office)** +91 3712 275305 **(Residence)** +91 3712 273675 **Fax No. :** +91 3712 267006 **E-Mail**: dhanapati@tezu.ernet.in	**Date of Birth** 02-10-1965
3. **Co-PI (Name & Address)**: Dr. Ashim J. Thakur Department of Chemical Sciences Tezpur University Napaam, Tezpur- 784 028, Assam **Telephone No.** : **(Office)** +91 3712 275059 **Fax No. :** +91 3712 267006 **E-Mail**: ashim@tezu.ernet.in	**Date of Birth** 20-08-1974

Annexure-V

PROGRESS REPORT

1. **Project Title**: Synthesis of platform biofuels from Renewable sources using acid modified supported ionic liquid catalysts.	DST sanction letter no. INT/FINLAND/P-02 dtd. 10-Mar-2011
2. **PI (Name & Address):** Dr. Dhanapati Deka Department of Energy Tezpur University Napaam, Tezpur- 784 028, Assam **Telephone No.** : **(Office)** +91 3712 275305 **(Residence)** +91 3712 273675 **Fax No. :** +91 3712 267006 **E-Mail**: dhanapati@tezu.ernet.in	**Date of Birth** 02-10-1965
3. **Co-PI (Name & Address)**: Dr. Ashim J. Thakur Department of Chemical Sciences Tezpur University Napaam, Tezpur- 784 028, Assam **Telephone No.** : **(Office)** +91 3712 275059 **Fax No. :** +91 3712 267006 **E-Mail**: ashim@tezu.ernet.in	**Date of Birth** 20-08-1974

4. **Broad area of Research**: Green Chemistry/Green energy
4.1 **Sub Area**: Biofuel (Biodiesel production)

5. Approved Objectives of the Proposal:

In this research plan, novel heterogeneous acid/alkali catalysts – Supported Ionic Liquid Catalysts (SILCA) is proposed to be synthesized and applied for the production of biodiesel, furfural and bio-diethyl ether. The research project has been undertaken in close collaboration between Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University (AAU) and, Department of Energy, Tezpur University (TU), India.

Objectives of the proposed project include

1. to prepare different types of acid modified Supported Ionic Liquid Catalysts (SILCA) at AAU, Finland.
2. to investigate the influence of different acids as well as ionic liquids for preparation of SILCAs and their physico-chemical and catalytic properties at AAU, Finland.
3. to study the application of prepared SILCAs in the synthesis of biodiesel at TU, India and AAU, Finland along with its application in the synthesis of furfurals and their derivatives from renewable sources at AAU, Finland.
4. to collaborate research exchange with the researchers of both the countries.
5. to carry out practical synthesis test and optimization of the biodiesel production utilizing supported alkaline ionic liquids catalysts at TU, India delivered by Åbo Akademi University.
6. to investigate the use of novel, supported alkaline ionic liquids as the catalyst in biodiesel synthesis at TU.

Date of Start: 1st April, 2011	**Total cost of Project**: Rs. 29,53,169/- for three years (Indian side)
Date of completion: Completed on 31st March, 2014.	**Expenditure as on 31st March, 2014:** Rs. 27,38,586/-for three years

6. Materials and methods:

(a) **Ionic liquids catalyst supplied by Åbo Akademi University, Finland-** Please see the Final report of the project attached.

(b) **Synthesis of Ionic liquid Catalysts at Tezpur University-** Please see the Final report of the project attached.

(c) **Transesterification reaction for biodiesel production:**

The catalysts were tested for the transesterification reaction for the production of biodiesel from non edible oils. The reaction condition was: catalyst 1.0 wt% of oil, jatropha oil 10g, oil: methanol molar ratio of 1:6, reaction time 6 hours, magnetic stirring 700 rpm, temperature 70 °C. The catalysts were tested under different reaction conditions to check their influence in transesterification reaction. After reaction, catalysts were separated from the reaction mixture by ~~using~~ centrifugation. The

biodiesel conversions were calculated according to the ^{1}HNMR spectroscopic method. Also ^{13}CNMR spectra were taken for consideration. The catalysts show less activity in transesterification as compared to conventional catalysts.

(d) Catalysts characterization: Catalysts synthesized at Tezpur University were tested as per standard methods and details are presented in the Final report presented herewith.

7. **Salient Research Achievements**:

Summary of Progress:

The progresses made so far under this project during 2013-14 are summarized as follows.

1. Experiments continued from the previous year.
2. A two-day Indo-Finnish Workshop on Green Chemistry under this project was organized during December 13-14, 2013. (Please see details in **Enclosure-1**).
3. Mr. Subrata Das, Junior Research Fellow, Indo- Finnish Project and Mr. Lakhya Jyoti Konwar, Associated Researcher visited the laboratory of Industrial Chemistry and Reaction Engineering, Department of Chemical Engineering, Faculty of Technology, Åbo Akademi University, Biskopsgatan 8 FI-20500 Åbo-Turku, Finland during 29.3.2013 to 12.4.2014 as Visiting Researchers and they were associated with the Scientists of Åbo Akademi University and research works were carried out on the relevant field.
4. Research publications came out from the project have been credited with acknowledgement to DST (please see **Enclosure-2).**
5. Exchange visit under workshop components: As informed by PI-Finland, nobody was participated during the period from Finland under this component due to financial crisis at Åbo Akademi University, Finland. However, Dr. Paivi Maki-Arvela, Dr. Narendra Kumar and Prof. Jery Pekka-Mikkola delivered their talks via video conferencing.

8. New Observations:

Ionic liquid Catalysts and metal modified zeolite catalysts delivered by Åbo Akademi University, Finland have not shown promising result on biodiesel production. The basic reason behind this observation is that the zeolites are not good catalysts for biodiesel production from oils. It may be due to the fact that the larger triglyceride molecules can't enter into the small pores of zeolites and reactions occurred only on the surface. Besides, following observations were made:

a) Ionic liquids (IL) are prone to leaching from SILCA in reactions with methanol.
b) Microporous zeolites are ineffective as catalyst support due to their narrow pore structures preventing interaction of substrate molecules with acid sites.
c) Esterification/transesterification activity depends on IL acidity. It was possible to enhance catalytic performance by increasing/tuning IL acidity.

a) Innovations:

i. Acidic ionic liquid catalysts [BSMIM]Cl was synthesized and applied as catalyst

for the pretreatment of *Jatropha curcas* oil. Very few studies are reported elsewhere in literature for the use of this particular ionic liquid as catalyst for pretreatment of vegetable oil having high FFA. In addition, for the first time, we have reported the reusability study of ionic liquid in esterification followed by transesterification with KOH as base catalyst.

ii. [BSMIM]Cl-$FeCl_3$, [MSIM]Cl, [MSIM]HSO_4, [MSIM]CH_3SO_3, [MSIM]CF_3SO_3, and [MSIM]PTSA, Acidic ionic liquid catalysts, were prepared and tested for esterification of oleic acid for biodiesel production. From the results, it was found that both [MSIM]CH_3SO_3 and [MSIM]CF_3SO_3 were equally effective in esterification of oleic acid. Out of the two, [MSIM]CH_3SO_3 was selected for further optimization. It is because the ionic liquid with methanesulphonate ion is halogen free and hence less toxic and hazardous as compared to trifluoromethanesulphate ion.

iii. [DSIM]Cl having double sulphonic acid group directly attached to the ring nitrogen of the imidazole was synthesized and applied for esterification of oleic acid. An optimum molar ratio of oleic acid to methanol (1:6) and temperature at 600C-700 °C, 98.25% oleic acid conversion was observed. The IL was recovered and then reused for the oleic acid esterification at the optimum reaction conditions mentioned above. IL was reusable up to four times and maintained up to 92% of its activity.

b) **Application Potential**:

i. Long Term: Acidic ionic liquid catalysts synthesized at Tezpur University might be potential for industrial application, but further investigation is necessary.

ii. Immediate: The catalyst may replace conventional catalysts for application in biodiesel and other platform chemical production.

c) **Any other**: nil

9. Research work which remains to be done under the project (for on-going projects)

Research project was completed on 31st March, 2014 with achievement of major objectives and novel catalyst development. However, the project may be extended for exploring the application of prepared acidic ionic liquids at Tezpur University for One pot transformation of biomass to fuel and chemicals (e.g. Biomass/cellulose to levulinic acid).

Ph.Ds Produced no:	**Technical Personnel trained:**	**Research Publications arising out of the present project:**
Mr. Subrata Das, JRF of the project is carrying out Ph.D. research (Now in 5th Semester) in the Department of Energy, Tezpur University under Prof. D. Deka, (PI-India of the Project) as Supervisor and Dr. A. J. Thakur (Co-PI) as Co-Supervisor.	1) Mr. Subrata Das, Junior Research Fellow, Indo-Finnish Project, TU 2) Mr. Lakhya Jyoti Konwar, Associated Researcher, TU. 3) Mr. Lakhya Jyoti Konwar was awarded prestigious CIMO fellowship at Abo Akademi University, Finland during November 1, 2013 to January 31, 2014 to carry out his part of Ph.D. research at AAU, Finland.	1. Nos. of Journal paper published: 2 i. Indian partner only- 01 ii. Joint publication with Finland counterpart-01 2. Journal paper submitted -01 (under review) 3. Conference proceedings: 03 4. Book Chapter: 01

10. List of Publications from this Project (including title, author(s), journals & year(s)

(A) Papers published only in cited Journals (SCI):

1. Das S, Thakur AJ and **Deka D**. Two-Stage Conversion of High Free Fatty Acid Jatropha curcas Oil to Biodiesel using Brønsted Acidic Ionic Liquid and KOH as Catalysts. The Scientific World Journal, Volume 2014, pp 1-9, Article ID 180983, http://dx.doi.org/10.1155/2014/180983.

2. Das S, Thakur AJ, Borah RK, Dutta N and **Deka D.** Production of biodiesel by esterification of oleic acid over a highly efficient and environmentally benign Brønsted acidic ionic liquid catalyst. International Journal of Green Energy, submitted (under review).

3. **Konwar LJ***, Das R, Thakur AJ, Salminen E, Mäki-Arvela P, Kumar N, Mikkola J-P and **Deka D**. Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste. Journal of Molecular Catalysis A: Chemical, 388-389, 167-176, 2014.

Note: *Konwar LJ was the Associated Researcher of the project and visited Abo Akademi University, Finland two times as part of the project under DST approval. Mr. Konwar has duly acknowledged DST, India and Academy of Finland on his joint publication with Finland counterpart.

(B) Papers published in Conference Proceedings.

1. Das S, Thakur AJ, and **Deka D**. Esterification of oleic acid with methanol using a new imidazolium based bronsted acidic ioinic liquid catalyst for biodiesel synthesis. *In the proceedings of the International conference on Green Energy & Smart materials through Science, Technology and Management* held on 21-23 January, 2014 at Gauhati University jointly organized by Gauhati University, Guwahati, Assam, India and University of South Africa, Florida, South Africa in association with SECONE.

2. Das S, Thakur AJ, and **Deka D**. Biodiesel production by esterification of oleic acid over a Brønsted acidic ionic liquid catalyst. *In the proceedings of the International conference on Harnessing natural Resources for Sustainable Development- Global Trend* held on January 29-31, 2014 in Cotton College, Guwahati, Assam – 781 001, India.

3. Das S, Thakur AJ, and **Deka D.** Ionic liquid based catalysts for biodiesel production via transesterification-A review. *In the proceedings of the International Seminar and Workshop on Energy, Sustainability and Nanotechnology* held on October 12-14, 2012 in Sibsagar College, Joysagar, Assam.

(C) Book Chapter:

Das S, Thakur A J and **Deka D**. Influence of free fatty acids content in catalytic activities of [BSMIM]Cl ionic liquid for biodiesel production from non-edible acidic oils. In: *Recent Advances in Bioenergy Research, Vol. III* CHAPTER 33. Editors: Sachin Kumar, A.K. Sarma, S.K. Tyagi, Y.K. Yadav. ISBN 978-81-927097-2-7© Sardar Swaran Singh National Institute of Renewable Energy, Kapurthala-144601 (Punjab), Electronic version published by© SSS-NIRE-2014, Kapurthala, India, PP 349-356.

Patents filed/ to be filed: Not applicable

Major Equipment (Model and Make) : Does not arise.