

**FINAL REPORT OF THE WORK DONE ON THE
MAJOR RESEARCH PROJECT [F.No.43-161/2014 (SR)]**

**INTENSIFICATION AND OPTIMIZATION OF CONVERSION
OF BIO-GLYCEROL INTO VALUE-ADDED PRODUCTS
USING ELECTROMAGNETICALLY IRRADIATED REACTOR
THROUGH NOVEL PROTOCOLS**

Submitted

To

UNIVERSITY GRANTS COMMISSION, NEW DELHI, INDIA

Submitted by

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**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE
FINAL REPORT OF THE WORK DONE ON THE PROJECT**

1.	Title of the Project	Intensification and optimization of conversion of bio-glycerol into value-added products using electromagnetically irradiated reactor through novel protocols
2.	NAME & ADDRESS OF THE PRINCIPAL INVESTIGATOR	Dr. Rajat Chakraborty, Chemical Engineering Department, Jadavpur University; Kolkata:70032 e-mail: rajat_chakraborty25@yahoo.com; Mobile No. 9831259201
3.	NAME & ADDRESS OF THE INSTITUTE	Jadavpur University; Kolkata:70032
4.	UGC APPROVAL LETTER NO. & DATE	F.No.43-161/2014 (SR) Dated. 03.12.2015
5.	DATE OF IMPLEMENTATION	01.07.2015
6.	TENURE OF THE PROJECT	3 years from 01.07.2015 to 30.06.2018
7.	TOTAL GRANT ALLOCATED	Total Allocation (Rs.):13,44,299/-
8.	TOTAL GRANT RECEIVED	Total received (Rs.):12,46,770/-
9.	FINAL EXPENDITURE	Total final expenditure (Rs.):13,31,379/-
10.	TITLE OF THE PROJECT	Intensification and optimization of conversion of bio-glycerol into value-added products using electromagnetically irradiated reactor through novel protocols
11.	OBJECTIVE OF THE PROJECT	Annexure I [Page 3]
12.	WHETHER OBJECTIVES WERE	Yes, all the objectives were achieved

	ACHIEVED (GIVE DETAILS)	successfully and the details were given in Annexure II [Page 4-33]
13.	ACHIEVEMENTS FROM THE PROJECT	Annexure III [Page 34-35]
14.	SUMMARY OF THE FINDINGS (IN 500 WORDS)	Annexure IV [Page 36-37]
15.	CONTRIBUTION TO THE SOCIETY (GIVE DETAILS)	Annexure V [Page 38-40]
16.	WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT	Project Fellow, Ms. Poulami Karan was registered (on 28.092016) for PhD at Jadavpur University
17.	NO. OF PUBLICATIONS OUT OF THE PROJECT (PLEASE ATTACH)	Annexure VI [Page 41-43]

(PRINCIPAL INVESTIGATOR)

(REGISTRAR/PRINCIPAL)
(Seal)

(CO-INVESTIGATOR)

ANNEXURE I

OBJECTIVES OF THE PROJECT

The objectives of the proposed project work are to develop a novel electromagnetic irradiation assisted reactor along with development and validation of novel operating protocols to accomplish the following:

OBJECTIVE 1: Intensification of reaction rate to reduce reactor operating time, temperature, catalyst and reactant requirements and to improve glycerol conversion and selectivity of monoglyceryl esters/glycerol carbonate

OBJECTIVE 2: Optimization of reaction conditions for batch/ semi-batch and continuous modes of reactor operations for maximum selectivity of desired product while minimizing reaction time, temperature, catalyst and reactant requirements

OBJECTIVE 3: Evaluation of reaction kinetic parameters under optimal process conditions

OBJECTIVE 4: Minimization of energy consumption & overall process while ensuring environmentally benign process

OBJECTIVE 5: Design of pilot/ industrial scale reactor using the evaluated optimized reaction conditions and kinetic parameters.

OBJECTIVE 6: Performing an elaborate techno-economical study to make the process energy-efficient, eco-friendly, economically profitable while achieving desired product quality.

ANNEXURE II

WHEATHER OBJECTIVES WERE ACHIEVED

OBJECTIVE 1: Intensification of reaction rate to reduce reactor operating time, temperature, catalyst and reactant requirements and to improve glycerol conversion and selectivity of monoglyceryl esters/glycerol carbonate.

Activity I: Intensification of monostearin (phase change material) synthesis in infrared radiated rotating reactor

➤ *Reduction in operating time*

In the present study rotating batch reactor (RBR) retrofitted with far infrared radiating Rotating (FIRR) system (150 W) was used to intensify monostearin yield (MSN). Under the identical operating condition, run was conducted in RBR equipped with a conventional heating (CH) system of similar power input (150 W) and abbreviated as CH-RBR.



Fig.1. Photograph of infrared radiated rotating Batch Reactor

Fig. 2 reveals the superiority of FIRR over conventional thermal sources in synthesis of MSN. IR activation has intensely promoted the MSN yield compared to CH only in 25 mins (Table 1). This phenomenon could be explained by the capacity of better propagation on FIRR through the reaction mixture compared to CH.

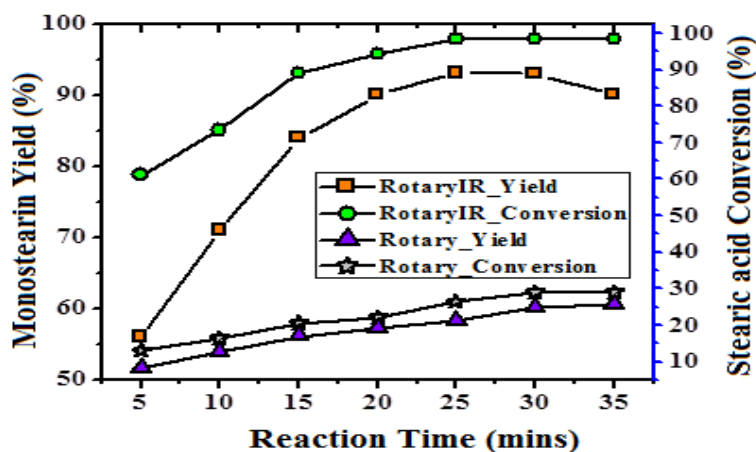


Fig.2. Comparative study between conventional heating and Far infrared radiation on stearic acid conversion and formation of monostearin yield

➤ *Reduction in reaction temperature*

It has been observed that incorporation of infrared along with rotating action has greatly improved the MSN yield and stearic acid (SA) conversion.

Table.1. Comparative Analysis between different reaction conditions for MSN synthesis.

Catalyst	Reactor Type	Heating	Solvent	Temperature (°C)	Time (h/ mins)	Stearic Acid Conversion (%)	MSN Yield (%)	Reference No.
NaOH	Batch	-	-	130	-	89	56	Kaufman et. al.1
Amberlyst 36	Rotating Batch	Conventional	-	90	25 mins	28	20	Present Work (Note)
	Batch	FIR	-			55	52	
	Rotating Batch	Radiation	-			97	92	

➤ *Reduction in Catalyst amount*

Previous literature reported either catalyst dosage or costly enzymatic or catalysts which has insignificant recyclable efficiency. In the present study, Amberlyst 36 (AW36) has been used which has good recyclability characteristics. In the study on 6 wt% catalyst gives promising stearic acid conversion and MSN yield (Fig. 3).

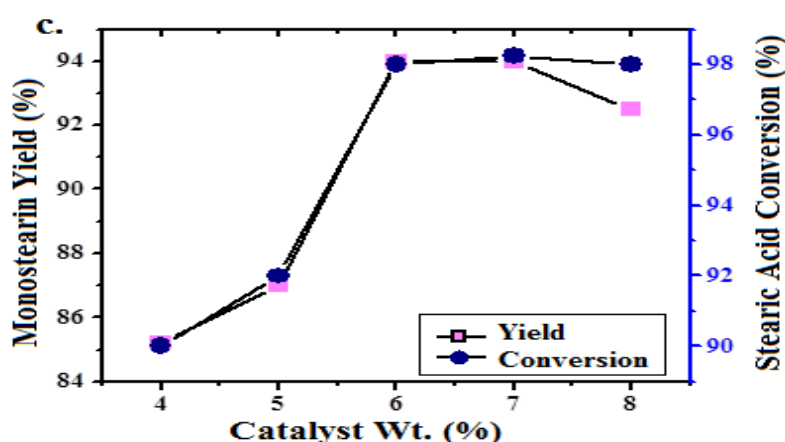


Fig.3. Effect of Catalyst loading on MSN yield and SA conversion

Note: For details see publication link (<https://doi.org/10.1016/j.enconman.2017.02.026>)

Activity II: Optimal Synthesis of Glyceryl Diacetin and Triacetin under far infrared radiation.

➤ *Reduction in reactor operating time*

Previous literature for diacetin and triacetin (DT) synthesis discussed the use of cost intensive commercial catalysts, coupled with lengthy reaction time and moderately high reaction temperature. Tungsto-phosphoric acid anchored to MCM-48 for acetic acid (AA) and glycerol (G) esterification and resulted 100 % G conversion with improved selectivity of diacetin (57%) and triacetin (31%) at the expense of lengthy 6h reaction time was reported [2].

In the present work, the study was conducted under far infrared radiation (150W; far infrared wavelength: 2700–30,000 μm) to expedite the entire process. IR activation has profoundly increased the DT selectivity compared to conventional heating. It has also been previously elucidated [3] that IRI can penetrate better through the reaction mixture compared to conventional heating. Accordingly, all reactive species undergo rigorous stretching and bending vibrations of the functional groups resulting in intense molecular collision; thus, rendering faster esterification rate leading to rapid formation of mono, di and triacetin compared to conventional heating. Notably, a close inspection of Fig. 4a and 4b enumerates that glycerol conversion has already reached $99\pm 1\%$ within 30 mins in case of IRI; thus, leaving only monoacetin in the IRRABR to react with excess acetic acid for DT formation. Even, in case of a blank run, it has been observed that IR activation resulted 13% more G conversion with 36.3% yield towards DT compared to conventional heating with only 10.3% DT yield under optimal condition.

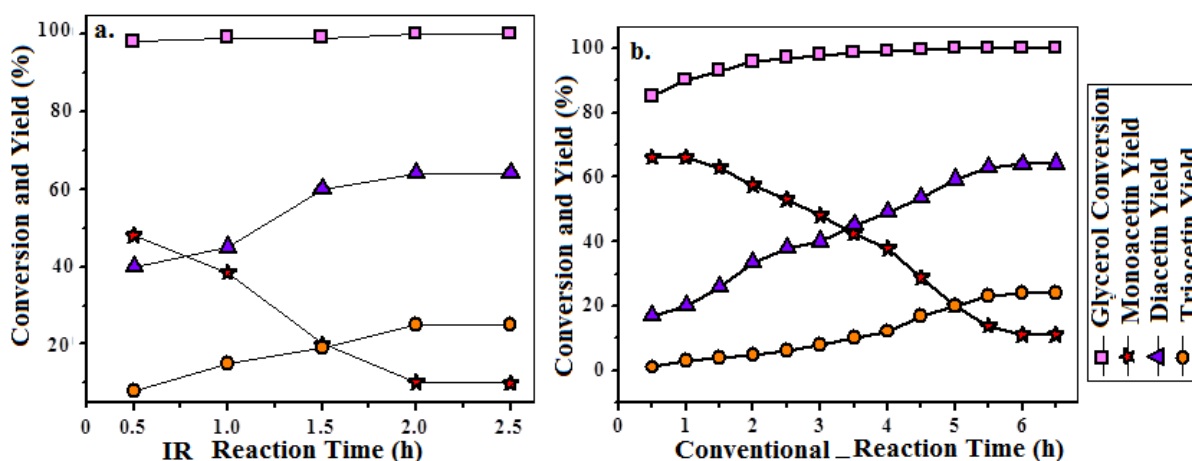


Fig.4. (a) IR (b) Conventional energy effect on G Conversion and DT Yield

It has been observed that increase in reaction time resulted consistent G conversion with increase in DT yield from $60\pm 1\%$ obtained at 1h to $88\pm 1\%$ at 2h and remained more or less constant with further increase in reaction time as depicted in Fig. 4a. Furthermore, in

comparison with Fig. 4b, 4a also exemplifies the energy efficacy of IRI over conventional heating (CH) protocol, consuming lower reaction time for maximum DT yield.

➤ *Reduction in Reactor Operating time*

At lower temperature, monoacetin availability is preponderant and as the temperature increased DT yield increased in expense of monoacetin yield (Fig.5). Successively, excess AA reacts with monoacetin and diacetin and forms triacetin. Therefore, to maximize DT yield, optimum reaction temperature has been selected at 110°C which substantiates the selection of process parameters for Taguchi prediction.

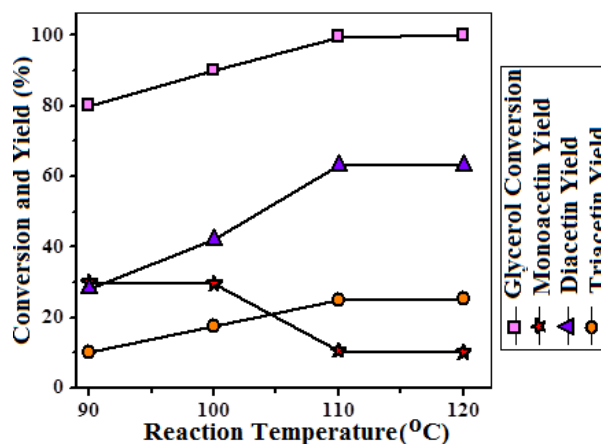


Fig.5. Effect of reaction temperature.

➤ *Reduction in reactant requirements*

Influence of AA:G mole ratio has been found maximum on DT yield. Fig.6. Shows AA:G mole ratio has been varied between 2:1 to 8:1 to maximize DT yield however further increase above 6:1 ratio resulted minimal change in G conversion and least alteration in DT yield. This explains the fact that under infrared radiation reactant requirements were comparatively less as reported in previous literatures [4].

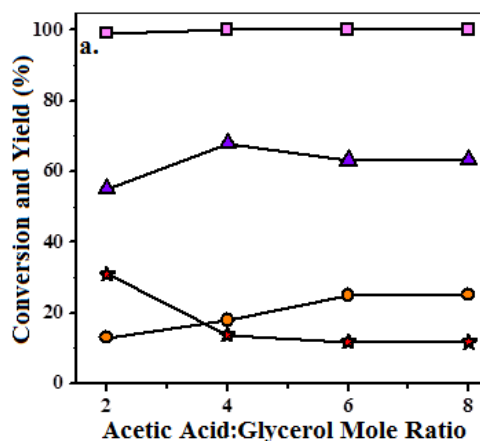


Fig.6. Reactants requirement.

Note: For details follow published paper: <https://doi.org/10.1016/j.enconman.2016.07.069>

Activity III: Intensification of monooleoyl glycerol synthesis under combined infrared and ultrasonic wave energised reactor

For the first time esterification kinetics of formation of monooleoyl glycerol(MOG) has been studied in an ultrasonic-infrared-wave (USIRW) promoted batch reactor using Amberlyst 36 (wet) catalyst. Esterification of Octadecanoic acid (ODA) with glycerol (G) have been conducted in three different reactors viz. traditional batch reactor (TBR), infrared wave (IRW) promoted batch reactor (IRWPBR) and ultrasonic-infrared-wave promoted batch reactor(USIRWPBR) to assess the relative efficacy.

➤ *Reduction in reactant consumption*

Primarily consumption of glycerol for production of value-added chemicals will improve the market price of biodiesel as glycerol is considered as by-product of biodiesel. However, in the present study only 5:1 (G:ODA) mole ratio of reactants are required to achieve desired product (Fig. 7a).

➤ *Reduction in operating temperature*

Previous reports enumerated the application of HPW/Cu₃(BTC)₂ (1 wt.%) as a catalyst which provided lower acid conversion (45%) with 62% monoglyceride selectivity in 8 h and 120 °C[5]. Thereby depicting high reaction time and temperature. Whereas in the present study incorporation of only infrared energy has resulted in maximum conversion of 80% only at 70°C (Fig. 7b).

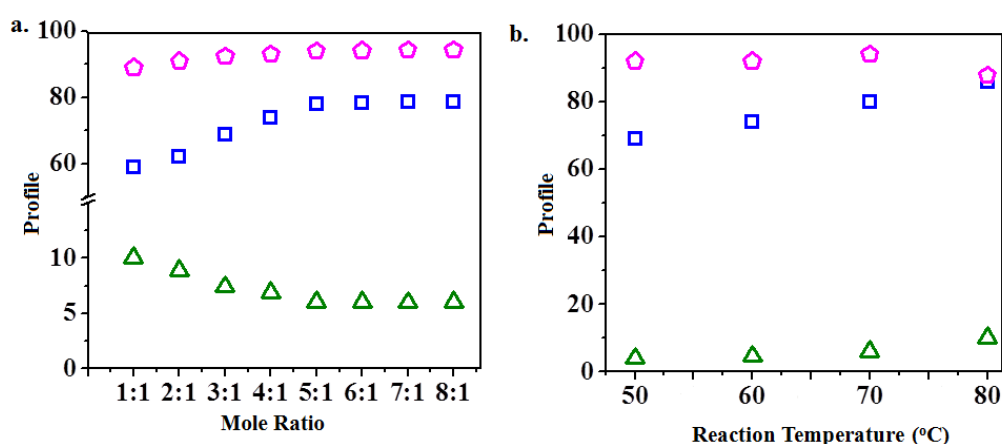


Fig.7. Effect of (a.) mole ratio MOG selectivity (b.) Reaction Temperature on acid Conversion.

➤ *Reduction in operating time*

USIRWPBR synergistically intensifies the ODA-G esterification as manifested through superior ODA conversion (92.5±1.25 %) compared to IRWPBR (79.8±1.2 %) and TBR (36.39±1.25 %). The improvement in ODA conversion and MOG selectivity upon application of electromagnetic energy can be explained (Fig. 8a-b) by the fact that FIR has a capacity to infiltrate into the reaction mixture and can transmit immense energy, thus, rendering intense molecular collision (due to stretching and bending vibrations) and excitation that promotes faster reactions. Whereas, ultrasonic energy results in intense turbulence, acoustic streaming and thus can remove the phase boundaries; hence, overcoming the effect of the diffusional hindrance. Therefore, it could be concluded that coupled effect of US and FIR energies can

immensely accelerate the G/ODA esterification, thereby, reaching equilibrium conversion within much shorter time compared to IRWPBR and TBR.

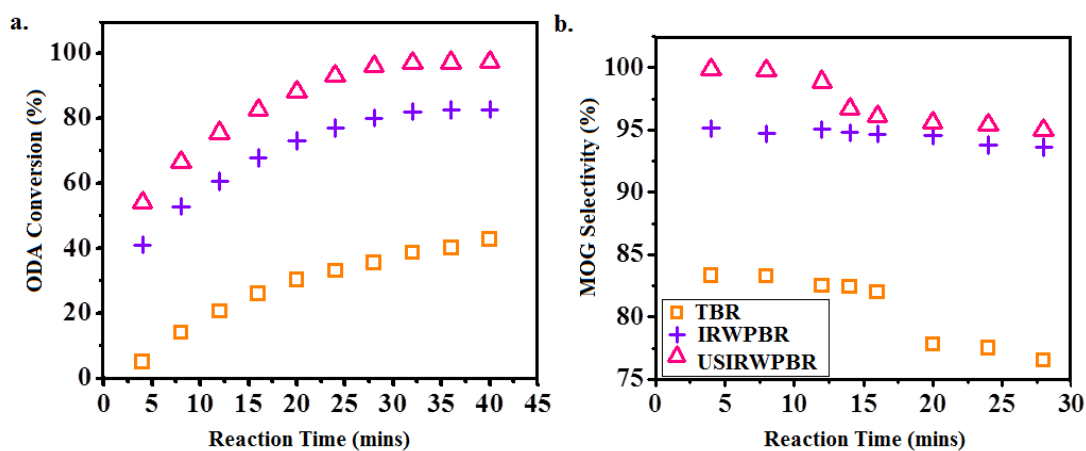


Fig.8. Performance of different reactors (a) ODA conversion (b) MOGselectivity wrt.reaction time.

Activity IV: Intensification of glycerylmonocaprin synthesis under concurrentelectromagnetic and ultrasonic energy

An intensification protocol for synthesis of glyceryl monocaprin (GMC) through inclusive application of different electromagnetic energies viz., far infrared radiation (FIR) and ultrasonic (US) cavitation in presence of Amberlyst 15 (A15) heterogeneous catalyst had been investigated under a precise rotating condition.

➤ Reduction in time

A capric acid (CA) conversion of $88 \pm 1.5\%$ could be asserted by employing the inclusive FIR and US energized rotating reactor (FIRUERR) operated under batch mode which was $9 \pm 1\%$ higher than far infrared energized rotating reactor (FIRERR) and $20 \pm 1\%$ higher than

conventionally energized rotating reactor (CERR) in optimum reaction time of 40mins (Fig. 9).

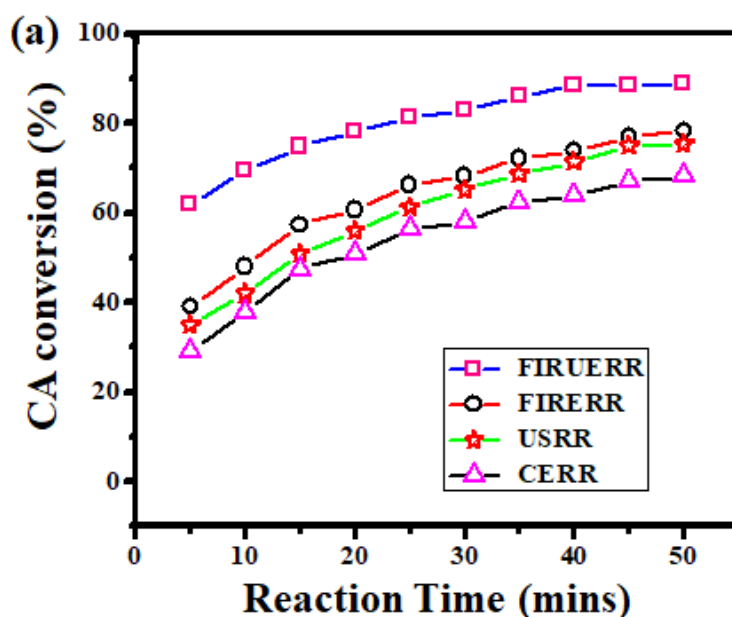


Fig. 9. CA conversion using different reactor combinations.

➤ *Recycle of Catalyst or Activity of catalyst*

Deactivation of A15 catalyst was investigated under optimal condition in all reactor configurations to understand the effect of different reactors on catalyst decay. Only 36% decay was observed in FIRUERR and more than 60% decay were observed both in FIRERR and CERR which was due to the agitation efficiency of ultrasonic wave. This has resulted in surface renewal of the catalyst, thereby, leading to less deterioration in the catalyst performance as exemplified in Fig 10. Moreover, catalyst in FIRUERR can sustain for 5 recycles whereas, in case of FIRERR and CERR catalyst can only withstand upto 4 recycles with complete deactivation after the 4th cycle. This also established the efficacy of the reactor performance of FIRUERR over other two systems. Therefore, the study also explains the recycling efficiency of catalyst in FIRUERR which has reduced the operating cost incurred

for catalyst. Thus the requirement of fresh catalyst for every batch has curtailed down with combined application of infrared and ultrasonic energy.

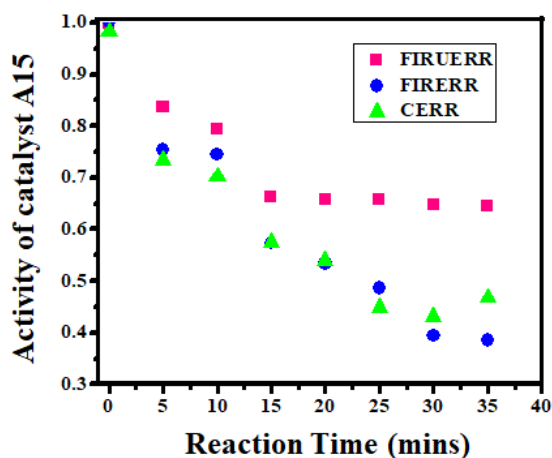


Fig. 10. Activity of catalyst.

Note: For details see manuscript list (“*Infrared radiation.....catalyst deactivation*”
Submission Date: 03.10.18)

OBJECTIVE 2: Optimization of reaction conditions for batch/ semi-batch and continuous modes of reactor operations for maximum selectivity of desired product while minimizing reaction time, temperature, catalyst and reactant requirements.

Activity I: Intensification of monostearin (phase change material) synthesis in infrared radiated rotating batch reactor

The independent factors and their corresponding levels were examined in an L_9 orthogonal array using standard TED [6]. Accordingly, the experiments were conducted in triplicates using three levels of the selected four operating factors viz. Glycerol: Stearic Acid mole ratio ($\theta_{G.SA}$), reaction temperature (θ_{RT}), reactor rotational speed (θ_{RPM}) and catalyst concentration (θ_C) in G-SA esterification. A customized set of nine experimental settings was presented in Table 2 with corresponding yields and SN ratios.

Table 2. Process factorial combinations as per TED with corresponding MSN yield and SN ratio in FIRR-RBR.

Run No.	$\theta_{G:SA}$	θ_{RT} , K	θ_{RPM} , rpm	θ_C , g/L	ϕ_{MSN} , %	SN Ratio
1	10	353	150	4	52.57	34.37
2	10	363	200	6	78.47	37.89
3	10	373	250	8	70.00	36.90
4	15	353	200	8	77.96	37.84
5	15	363	250	4	78.38	37.88
6	15	373	150	6	63.13	35.58
7	20	353	250	6	79.93	38.05
8	20	363	150	8	67.17	36.54
9	20	373	200	4	82.19	38.08

Table 2 depicts factorial ranks based on relative effects on output variable (ϕ_{MSN}) using ‘higher the better’ criterion for SN ratios. Notably, reactor rotational speed ranked 1st since it represented highest Δ -values followed by $\theta_{G:SA}$, θ_{RT} and θ_C . The asterisks in Table 3 represent the optimum levels of process factors that maximize MSN yield (ϕ_{MSN}).

Table 3. Relative ranks of process factors in maximizing MSN Yield in FIRR-RBR.

Level	$\theta_{G:SA}$	θ_{RT} , K	θ_{RPM} , rpm	θ_C , g/L
1	36.4	36.77	35.51	36.79
2	37.1	37.44*	37.94*	37.18*
3	37.56*	36.86	37.61	37.09
Delta	1.16	0.67	2.42	0.38
Rank	2	3	1	4

Note: For details see publication link (<https://doi.org/10.1016/j.enconman.2017.02.026>)

Activity II: Optimal Synthesis of Glyceryl Diacetin and Triacetin under far infrared radiation

In the present study a statistical tool, Taguchi L₉ orthogonal matrix (TOLM) had been applied in process optimization due to its advantages in revealing interactive effects

among process parameters, utilizing minimum experimental trials and hence, enhancing process robustness.

A standard Taguchi orthogonal L_9 matrix (TOLM) is used to execute the experiments in triplicates using three levels of the four process parameters viz., AA:G molar ratio (a_{MR}), Sb precursor loading (a_{CL}), catalyst concentration (a_{CC}) and reaction temperature (a_T) in AA-G esterification. The TOLM has been applied to understand the parametric effects and to determine a set of optimal process parameters corresponding to maximum combined yield of diacetin and triacetin (Y_{DT}) through SN ratios and analysis of variance (ANOVA) using MINITAB-16 (Minitab Inc. USA for Windows7) software. Fig. 11 depicts the plot generated by the statistical optimization technique. It describes the profile for different reaction parameters on the response variable.

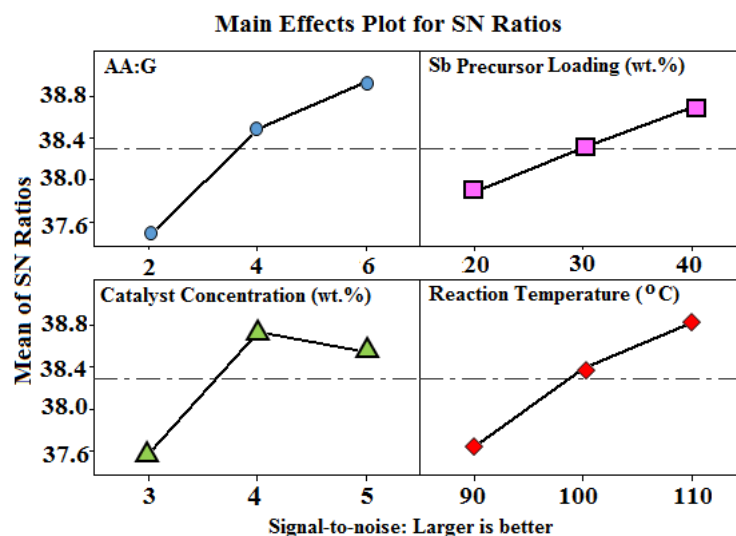


Fig.11. SN ratio plot

Note: For details see published paper link: <https://doi.org/10.1016/j.enconman.2016.07.069>

Activity III: Intensification of monooleoyl glycerol synthesis under combined infrared and ultrasonic wave energised reactor

The optimum parametric condition for maximum monoester yield has been evaluated through Taguchi design (TD) of experiments. G/OA mole ratio ($\alpha_{G/ODA}$), catalyst

concentration (α_{AC}), impeller speed (α_{RS}) and reaction temperature (α_T) were considered as process independent variables and their ranges were fixed between 3-5, 0.004-0.006 g/mL, 300-700 rpm and 333-353 K respectively. A statistical design array was developed using TD where MOG yield (β_{MOG}) was selected as the process response. From Table 4, it is evident that G/ODA mole ratio (Rank 1) has the greatest influence on β_{MOG} followed by reaction temperature, catalyst concentration and impeller speed as illustrated by the delta values and the parametric ranks. The individual level marked “a” represents the appropriate parametric level leading to maximum desired product yield. Therefore, from the Taguchi analyses, 5:1 G/ODA mole ratio, 700 rpm impeller speed, 70°C reaction temperature and 0.0066 g/mL catalyst concentration have been the optimum parametric combinations facilitating maximum β_{MOG} .

Table 4. Degree of influence of individual process variables on MOG yield.

Level	$\alpha_{G/ODA}$	α_{RS} (rpm)	α_T (°C)	α_{AC} (g/mL)
1	35.92	36.34	35.97	36.14
2	36.78	36.69	37.16 ^a	36.7
3	37.35 ^a	37.02 ^a	36.93	37.21 ^a
Delta	1.42	0.68	1.19	1.06
Rank	1	4	2	3

Note: For details (Follow manuscript ID: [ao-2018-025334](#))

Activity IV: Intensification of glyceryl monocaprin synthesis under concurrent electromagnetic and ultrasonic energy

GMC production had been experimentally maximized by designing suitable parametric arrangements using statistical optimization technique (Taguchi). Under the taguchi Orthogonal Design (TOD) predicted parametric combination for FIR energized rotating reactor (FIRERR), the performance of conventionally energized rotating reactor

(CERR) and inclusive FIR ultrasound energized rotating reactor (FIRUERR) had been compared. [Table 5](#) represents the orthogonal combinations of operating factors with corresponding GMC yield and SN ratios.

Table 5. Design Table for Taguchi Analysis with corresponding GMC yield and SN Ratios.

$f_{CA:G}$	f_{CC} (wt. %)	f_{RT} (°C)	f_{DL} (wt. %)	θ_{GMC} (%)	θ_{SN}
0.25	7	55	20	61.00 ± 0.8	35.70
0.25	11	75	30	77.89 ± 0.5	37.82
0.25	15	65	40	78.45 ± 1	37.89
0.35	7	75	40	66.00 ± 1.3	36.39
0.35	11	65	20	74.87 ± 0.6	37.48
0.35	15	55	30	71.45 ± 1.2	37.08
0.5	7	65	30	69.88 ± 1	36.88
0.5	11	55	40	63.00 ± 0.7	35.98
0.5	15	75	20	67.00 ± 0.5	36.52

From [Table 5](#) after evaluation of delta values and ranks depicted 0.25 CA:G mole ratio, 15 wt. % catalyst weight, 338K reaction temperature and 30 wt. % desiccant loads as the optimum parametric combination resulting in maximum GMC production.

Note: For details see manuscript list (“[Infrared radiation.....catalyst deactivation](#)”
Submission Date: 03.10.18)

Activity V: Synthesis of Glycerol Monooleate using Semi-batch reactor Operation equipped with far infrared Radiation

The present study inculcated the maximization of monoglyceride of oleic acid through semi-batch operation under far infrared radiation using macro porous acidic resin, Amberlyst 15. The influence of operating parameters viz., feed flow rate (0.5-2.5 mL/min), reaction temperature (75°C-95°C) and catalyst concentration (0.2-0.6 g/mL) on monoglyceride maximization had been investigated. The efficacy of semi-batch operation equipped with

electromagnetic radiation had been compared with conventional semi-batch reactor where presence of electromagnetic radiation had elevated the oleic acid conversion by 35% only in 40 mins.

Optimization was conducted through Taguchi analyses. Higher values of Signal-Noise ratio were taken as the response variable for maximization GMO selectivity. The values highlighted in bold letters represent the optimum levels of the process condition (Table 6).

Table 6. Response Values for SN ratio with GMO selectivity.

Level	Ol Flow Rate (mL/min)	Reaction Temperature (°C)	Amb15 Concentration (g/mL)
1	36.23	36.73	36.88
2	37.68	37.16	37.13
3	36.88	36.90	36.79
Δ -value	1.25	0.22	0.13
Rank	1	2	3

Note: For details see publication list CHEMCON (PAPER ID: [CRE00229](#))

Activity VI: Production of Glyceryl Monooleate using electromagnetically radiated rotating continuous flow packed bed reactor.

Reaction parameter optimization has been identified by Taguchi optimization technique in a far infrared energy equipped rotating batch reactor (FIRBR) and under the identified optimum condition far infrared radiated rotating packed bed reactor (FIRPR) was operated for optimum production of Glyceryl Monooleate (GMO).



Fig.12. Photograph of electromagnetically radiated rotating continuous flow packed bed reactor.

Three level four parameter L9 orthogonal arrays. Operating range for the selected parameters were reactant ratio, G:Ol ($\chi_{G/Ol}$) varied between 4-8; reactor rotational speed (χ_{RRS}) between 150-250 rpm; esterification temperature (χ_{ET}) between 348-368 K and catalyst weight between 4-8 wt.% (χ_{CW}). The levels corresponding to optimum values have been highlighted in Table 7 and the degree of parametric dependency could be also observed from the same table. It can be perceived from Table 7 that the order of dependency on reaction parameters was $\chi_{G/Ol} \succ \chi_{ET} \succ \chi_{RRS} \succ \chi_{CD}$.

Table 7. SN ratio table for determination of best parametric condition.

Level	$\chi_{G/Ol}$	χ_{RRS} (rpm)	χ_{ET} (K)	χ_{CD} (g/mL)
1	34.30	35.23	35.74	35.18
2	36.08	36.10	36.54	35.72
3	37.00	36.06	35.10	36.48
Delta	2.70	0.87	1.43	1.30
Rank	1	4	2	3

After identification of the best operating condition for Ol-G esterification reaction and best kinetic model describing the esterification reaction, continuous GMO production using FIRPR was studied. Therefore, during analyses, the reaction temperature was fixed at 358 K, catalyst weight has been varied below and above 8 wt. % in order to evaluate WHSV, molar flow rate of G and Ol was maintained at 12 mL/min and 6.6 mL/min respectively so that 8:1 G:Ol molar ratio could be maintained.

OBJECTIVE 3: Evaluation of reaction kinetic parameters under optimal process conditions.

BATCH REACTOR STUDY

Activity I: Reaction kinetics of monostearin (phase change material) synthesis in infrared radiated rotating batch reactor.

In the present study, Amberlyst 36 catalyzed heterogeneous esterification kinetics has been evaluated under both mass transfer and surface reaction-controlled regimes. Esterification activation energies under both the reactor configurations has been calculated for evaluating the advantage of rotating action (RBR) over conventional stirring under infrared radiation (SBR) (Table 8)

Table 8. Kinetic Parameter for G-SA esterification in FIRR-RBR and FIR-SBR

Reacto r Type	Mode l Type	Temperatur e, K	$k_{obs} \times 10^{-4}$ [L ² /mol.g.mi n]	K_1 $\times 10^{-3}$ [L/mol]	K_2 $\times 10^{-3}$ [L/mol]	K_3 $\times 10^3$ [mol/L]	R^2	R_{adj}^2	k_{obs}^o [L ² /mol.g.mi n]	E_A [kJ/mol]	
FIR- RBR	LH	353	6.80	51.49 \pm 3.82	1.92 \pm 0.14	8.82 \times 1 0 ⁻³ 0.014	0.87	0.80	0.235	21.84	
		363	8.83	36.11 \pm 3.7 \times 10 ⁻³	1.51 \pm 1.59 \times 1 0 ⁻⁴	1.0 \pm 0.31	0.98	0.94			
		373	10.83	19.64 \pm 1.29 \times 1 0 ⁻³	0.76 \pm 5.07 \times 10 ⁻⁵	1.01 \pm 0.18	0.90	0.85			
	ERS A	353	5.07	26.45 \pm 2.65 \times 1 0 ⁻³	-	1.01 \pm 0.47		0.80	0.70	3.225	31.72
		363	6.80	26.11 \pm 2.14 \times 1 0 ⁻³		1.011 \pm 0.38		0.87	0.83		
		373	6.93	16.45 \pm 1.37 \times 1 0 ⁻³		1.013 \pm 0.46		0.86	0.82		
	ERG	353	6.49	-	26.88 \pm 3.9 \times 10 ⁻³	1.092 \pm 0.69		0.74	0.70	1.147	24.825
		363	8.90		25.65 \pm 2.8 \times 10 ⁻³	1.0098 \pm 0.51		0.85	0.81		
		373	10.2		23.68 \pm 1.8 \times 10 ⁻³	1.0099 \pm 0.44		0.90	0.87		
	FIR- SBR	PH	353	4.95	-			0.75	0.75	0.140	22.622
			363	6.97				0.88	0.88		
			373	7.15				0.87	0.87		
LH		353	1.51	15.44 \pm 2.03 \times 1 0 ⁻²	1.01 \pm 1.59 \times 1 0 ⁻³	3.76 \times 1 0 ⁻⁴ \pm 1.91 \times 1 0 ⁻⁶		0.76	0.70	4.835	40.198
		363	1.608	12.64 \pm 3.81 \times 1 0 ⁻³	0.96 \pm 2.94 \times 1 0 ⁻⁴	1.0 \pm 0.012		0.93	0.82		
		373	2.61	11.09 \pm 6.1	0.72 \pm 0.40	7.75 \times 1 0 ⁻⁴ \pm 1.29 \times 1 0 ⁻⁴		0.91	0.80		

NOTE: K_1 : Adsorption equilibrium constant for Acid (L/mol); K_2 : Adsorption equilibrium constant for Glycerol (L/mol); K_3 : Desorption equilibrium constant (mol/L); k_{obs} : Kinetic constant (L²/mol g min); R^2 : Regression coefficient; R_{adj}^2 : Adjusted Regression coefficient; E_A : Activation Energy (kJ/mol)

Significantly, the energy-efficient behaviour of FIRR-RBR was evident from the reaction activation energy (Table 8) of FIRR-SBR ($E_A = 40.2$ kJ/mol) and FIRR-RBR ($E_A = 21.84$ kJ/mol) indicating 2 (two) times greater energy consumption in conventionally SBR.

Activity II: Reaction Kinetics of monooleoyl glycerol synthesis under combined infrared and ultrasonic wave energised reactor

The present study also envisages the formulation and validation of an innovative kinetic model i.e., concurrent non-catalytic and heterogeneously catalyzed (CNCHC) reaction mechanism in addition to the conventional heterogeneous kinetic models (LHHW and Eley-Rideal mechanisms). Under combined ultrasonic-infrared-wave, CNCHC esterification mechanism, could best describe ODA-G esterification ($R^2 = 0.98$) compared to LHHW ($R^2 = 0.97$) and Eley-Rideal ($R^2 = 0.88$) mechanisms. The kinetic data obtained in all reactor configurations viz., TBR, IRWPBR and USIRWPBR were assessed to evaluate the reaction kinetics. The mass transfer resistances viz., external and internal diffusional resistance have been evaluated under the derived optimum condition to identify the controlling regimes pertaining to the esterification.

All heterogeneous and non-catalytic models were correlated using non-linear regression with the kinetic data while satisfying 95% confidence level. Since, byproduct water was adsorbed by molecular sieves; hence, irreversible reaction was considered. Moreover, the combined yields of DOG and TOG were less than $8 \pm 1\%$ therefore, reactions pertaining to 2° and 3° ester formations have been neglected in the present study. Since, USIRWPBR resulted the maximum MOG yield and ODA conversion at much lower reaction time compared to other two reactors; therefore, initially LH and ER (ODA and G surface-adsorbed) models were fitted with the kinetic data obtained from USIRWPBR. It was

observed that LH mechanism could best describe (R^2 value=0.97) the G/ODA esterification in the case of USIRWPBR. Therefore, for comparative analyses, LH models have been also considered for other two reactor systems (TBR and IRWPBR). Activation energy was 114.45 kJ/mole for TBR, 20.286 kJ/mole for IRWPBR and 8.520 kJ/mol for USIRWPBR, thus, implying the requirement of lowest energy under combined influence of ultrasonic and far infrared energy (Fig. 11).

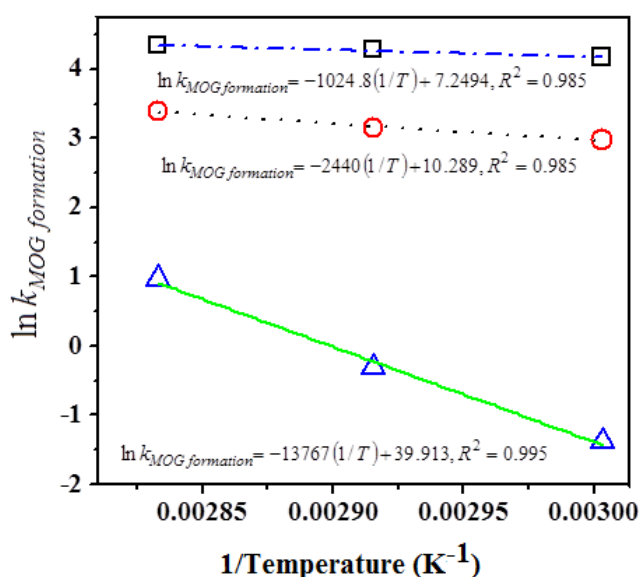


Fig. 11. Esterification rate constant profiles of ODA/G esterification in different batch reactors.

Now, after identification of the reaction mechanism for heterogeneous esterification reaction, non-catalytic experiments were conducted under optimal operating conditions in USIRWPBR. It was observed that the non-catalytic part contributed $30\pm 1\%$ to ODA conversion and the kinetic model also showed satisfactory R^2 values (≈ 0.98) at all reaction temperatures. Therefore, during heterogeneous experiments in USIRWPBR, non-catalytic effect prevailed synchronously and thereby the global reaction rate was influenced by concurrent non-catalytic and heterogeneously catalysed reaction pathway (Eq 1). The combined model was fitted well with experimental data, and the R^2 values (0.98) showed

better fitting compared to the LH model ($R^2 = 0.97$) alone for USIRWPBR; thereby, validating the concurrent model hypothesis.

On the other hand, the NC contribution as revealed from the rate constant values for IRWPBR and TBR were 3.02 and 9.2 times lower than USIRWPBR with corresponding lower ODA conversion (<13% and <8% ODA conversion in IRWPBR and TBR) under optimum condition. Again, CNCHC model showed comparatively lower R^2 values for both IRWPBR and TBR than their LH models as well as CNCHC model for USIRWPBR. This explains the fact that ultrasonic wave energy can facilitate reaction species to overcome phase boundaries; therefore, it was judicious to consider that both catalytic and non-catalytic esterification reaction has occurred simultaneously.

$$-r_{ODA(global)} = -r_{ODA(non-catalytic)} + -r_{ODA(AW36)} \quad (1)$$

Activity III: Reaction Kinetics of glyceryl monocaprin synthesis under concurrent electromagnetic and ultrasonic energy

Under the taguchi Orthogonal Design (TOD) predicted parametric combination for FIR energized rotating reactor (FIRERR), the performance of conventionally energized rotating reactor (CERR) and inclusive FIR ultrasound energized rotating reactor (FIRUERR) had been compared. Reaction kinetic analyses using both pseudo-homogeneous and heterogeneous (Langmuir Hinshelwood and Eley Rideal) models were performed in order to ascertain the underlying CA-G esterification mechanism. Accordingly, pseudo homogeneous and heterogeneous esterification rate equations considering surface kinetics as the limiting step, were expressed by Eqs3, 4 and 5 respectively; while, pseudo homogeneous rate law was represented by Eq2. The rate expression for the batch reactor was given by Eq6. Also, the surface reaction as the rate limiting step was considered only after evaluating the bulk and internal diffusional resistance.

$$-r_{CA} = k_{forward}(C_{CA} \times C_G) \quad (2)$$

$$-r_{CA} = \frac{k_{forward}(K_{ads,CA}C_{CA} \times K_{ads,G}C_G)}{\left(1 + K_{ads,CA}C_{CA} + K_{ads,G}C_G + \frac{C_{GMC}}{K_{des,GMC}}\right)^2} \quad (3)$$

$$-r_{CA} = \frac{k_{forward}(K_{ads,CA}C_{CA} \times C_G)}{\left(1 + K_{ads,CA}C_{CA} + \frac{C_{GMC}}{K_{des,GMC}}\right)^2} \quad (4)$$

$$-r_{CA} = \frac{k_{forward}(C_{CA} \times K_{ads,G}C_G)}{\left(1 + K_{ads,G}C_G + \frac{C_{GMC}}{K_{des,GMC}}\right)^2} \quad (5)$$

$$-r_{CA} = -\frac{d(CA)}{dt} \quad (6)$$

Where, $-r_{CA}$ was calculated from Eq. (6)

Table 9. Kinetic Parameters for IFUER, FIRER and CERR reactor set-ups

Reactor Type	Kinetic Model	Temperature, K	$k_{forward}$ [mol/gcat.min]	$K_{ads,CA}$ [L/mol]	$\times 10^3$	$K_{ads,G}$ [L/mol]	$\times 10^3$	$K_{des,GMC}$ [mol/L]	$\times 10^{-3}$	R^2	R_{adj}^2
FIRUERR	LH	328	2.1493 ± 0.6104	31.2996 ± 8.9219		1.766 ± 0.5928		1.317 × 10 ⁻⁴ ± 2.296 × 10 ⁻⁵		0.97	0.90
		338	2.332 ± 0.1485	29.2796 ± 1.8758		0.7347 ± 0.0525		2.436 × 10 ⁻⁴ ± 1.02 × 10 ⁻⁵		0.99	0.98
		348	2.63 ± 0.02	7.49 ± 0.058		9.0798 ± 0.24		1.94 × 10 ⁻⁴ ± 1.37 × 10 ⁻⁶		0.97	0.93
	ERCA	328	2.0099 ± 0.0338	1.7870 ± 0.0301		-		5.688 × 10 ⁻⁴ ± 1.477 × 10 ⁻⁵		0.86	0.72
		338	1.8103 ± 0.03608	2.0099 ± 0.0400				8.082 × 10 ⁻⁴ ± 2.841 × 10 ⁻⁵		0.91	0.86
		348	1.8106 ± 0.0320	2.0099 ± 0.0356				9.627 × 10 ⁻⁴ ± 3.146 × 10 ⁻⁵		0.92	0.89
		328	3.0199 ± 0.0573	-		1.2281 ± 0.0280		7.197 × 10 ⁻⁴ ± 2.752 × 10 ⁻⁵		0.82	0.64
	ERG	338	9.0799 ± 0.1344			1.941 ± 0.0309		1.13 × 10 ⁻⁴ ± 2.002 × 10 ⁻⁶		0.95	0.92
		348	3.0199 ± 0.0528			2.6916 ± 0.0608		4.1 × 10 ⁻⁴ ± 1.261 × 10 ⁻⁵		0.92	0.89
		328	1.2243 ± 0.4546							0.68	0.68
PH	338	1.5438 ± 0.3490			-		-		0.78	0.78	
	348	1.6429 ± 0.2744							0.85	0.85	
	328	0.7640 ± 0.0047	14.1299 ± 0.0890		1.4146 ± 0.0138		1.491 × 10 ⁻⁴ ± 9.214 × 10 ⁻⁷		0.95	0.92	
FIRERR	LH	338	1.0907 ± 0.0293	14.1299 ± 0.3837		1.5271 ± 0.0688		2.487 × 10 ⁻⁴ ± 7.078 × 10 ⁻⁶		0.98	0.95
		348	2.0128 ± 0.6824	13.1199 ± 4.4638		1.0676 ± 0.4398		2.349 × 10 ⁻⁴ ± 5.63 × 10 ⁻⁵		0.97	0.86
	ERCA	338	1.9089 ± 0.0071	1.9063 ± 0.00712		-		9.0 × 10 ⁻⁴ ± 1.983 × 10 ⁻⁶		0.96	0.94
		338	1.9998 ± 0.0260	-		1.8981 ± 0.0325		5.214 × 10 ⁻⁴ ± 1.487 × 10 ⁻⁵		0.95	0.92
CERR	PH	338	1.1403 ± 0.1975			-		-		0.83	0.83
		328	2.0025 ± 0.0064	3.415 ± 0.0109		9.8879 ± 0.199		3.893 × 10 ⁻⁵ ± 1.644 × 10 ⁻⁷		0.97	0.93
	LH	338	3.0199 ± 0.4511	1.761 ± 0.2637		1.6081 ± 0.5632		3.624 × 10 ⁻⁴ ± 7.663 × 10 ⁻⁵		0.99	0.99
		348	3.9888 ± 0.1445	4.2319 ± 0.1536		1.2152 ± 0.0551		1.731 × 10 ⁻⁴ ± 4.5 × 10 ⁻⁶		0.94	0.86
	ERCA	338	1.4646 ± 0.0251	1.7069 ± 0.0293		-		2.91 × 10 ⁻⁴ ± 7.731 × 10 ⁻⁶		0.92	0.87
		338	1.7372 ± 0.0307	-		1.8079 ± 0.0403		2.927 × 10 ⁻⁴ ± 1.001 × 10 ⁻⁵		0.90	0.85
PH	338	0.7549 ± 0.0987			-		-		0.87	0.87	

All the kinetic constants were evaluated by non linear regression using Levenberg Marquardt algorithm (Polymath 7.0)

From Table 9, LH model was found to be the best representative model for all three reactors viz., FIRUERR, FIRERR and CERR. On the other hand, PH model had shown lowest R^2 values; thus, justifying the heterogeneous characteristics of CA:G esterification reaction. Furthermore, highest R^2 values were observed at reaction temperature 338K, thus, 338K has been confirmed as the optimum temperature for maximum GMC production. Moreover, the reaction activation energy required in case of FIRUERR was 9.63 kJ/mol whereas, for FIRERR was 27.5 kJ/mol and for CERR was 32.74 kJ/mol which also evidenced the energy efficiency of FIRUERR over FIRERR and CERR.

Activity V: Reaction Kinetics of Glyceryl Monooleate synthesis by using Semi-batch reactor Operation equipped with far infrared Radiation.

Pseudo-homogeneous kinetics (Eq.7) was applied in order to understand the reaction behavior. Table 8 revealed that kinetic constant for far infrared emitted semi batch reactor (FIRESBR) was twice than conventional semi batch reactor (CSBR) (Table 10).

$$-r_{OA} = k_{forward} C_{Ol} C_G \quad (7)$$

Table 10. Kinetic parameters for Ol-G esterification.

Heating Mode	$k_{forward}$	R^2	RMSD $\times 10^{-5}$
FIR	0.00246	0.96	5.4
Conventional	0.00156	0.96	5.5

Activity VI: Reaction Kinetics study for production of Glyceryl Monooleate using electromagnetically radiated rotating batch and rotating packed bed reactor.

Various kinetic models including non-catalytic, heterogeneous (Langmuir Hinshelwood and Eley-Rideal models) were under statistically optimized condition. Non catalytic under identical condition resulted 36% conversion therefore coupled non-catalytic and catalytic kinetics was fitted with to the experimental data ($R^2 = 0.98$) (Table 11).

Using k_{NC} (Table 11), activation energy was determined (Eq. 8) and 57 kJ/mol K was obtained for the non-catalytic system. In the similar way, reactions were performed with Amberlyst 15 catalyst and corresponding heterogeneous models (Eq. 9-11) were fitted to the kinetic data using optimum condition derived from Taguchi design.

It has been observed from the experimental analyses that under optimum reaction condition, although addition of Amberlyst 15 has greatly improved Oleic acid(OI) conversion ($86\pm 1\%$) whereas, non-catalytic mechanism was also prevalent, showing $28\pm 2\%$ OI conversion. Hence, for this esterification study non-catalytic/catalytic coupled kinetic models have been developed and were fitted with the experimental data. Along with NC model two different ER models (Eq. 13 and Eq. 14) and LH model (Eq. 12) and here also coupled NC and LH model represented the best fitted model (R^2 value: 0.98). This could be explained by the fact that under electromagnetic radiation the entire reaction mix gets excited and thus apart from the catalytic action.

Table 11. FIRBR kinetic analyses for pure non-catalytic, catalytic and coupled reaction

Model	Temperature (K)	k_{NC} (L/mol.min) $\times 10^{-3}$	k_C (L ² /mol.g.min) $\times 10^{-6}$	K_G (L/mol) $\times 10^{-3}$	K_{OI} (L/mol) $\times 10^{-3}$	K_{GMO} (mol/L) $\times 10^3$	R^2	RMSD
Eq. (8)	348	0.56 \pm 0.0006	-	0.98	12×10^{-8}			
	358	0.98 \pm 0.015		0.99	4.8×10^{-8}			

	368	1.64 ± 0.04		0.97	2.3×10 ⁻⁸			
Eq. (9)	358	-	35.33 ± 0.04	2.09 ± 0.003	10.38 ± 0.012	6.43 ×10 ⁻⁴	0.975	5.3 ×10 ⁻⁵
Eq. (10)			35.33 ± 0.14	17.12 ± 0.074	-	± 1.38 ×10 ⁻⁶ 5.99 ×10 ⁻⁴	0.92	9.4 ×10 ⁻⁵
Eq. (11)			35.33 ± 0.24	-	10.41 ± 0.07	± 8.02 ×10 ⁻⁶ 3.48 ×10 ⁻³	0.80	14.8×10 ⁻⁵
Eq. (12)	348	0.56 ± 0.0235	3.696 ± 0.011	13.166 ± 0.048	10.796 ± 0.032	± 2.913 ×10 ⁻⁴ ± 4.16 ×10 ⁻⁶	0.96	8.29×10 ⁻⁵
	358	1.004 ± 0.041	9.535 ± 0.247	12.87 ± 0.379	10.702 ± 0.279	3 ×10 ⁻⁴ ± 1.0 ×10 ⁻⁵	0.994	2.68×10 ⁻⁵
	368	1.639 ± 0.288	10.02 ± 0.007	8.407 ± 0.006	6.85 ± 0.005	3.11×10 ⁻⁴ ± 1.53 ×10 ⁻⁶	0.99	5.9×10 ⁻⁵
Eq. (13)	358	1.004 ± 0.025	15.5 ± 0.06	34.17 ± 0.15	-	± 4.66 ×10 ⁻⁴ ± 5.34 ×10 ⁻⁶	0.863	1.3 ×10 ⁻⁴
Eq. (14)		1.004 ± 0.028	21.42 ± 0.09	-	16.68 ± 0.07	± 9.57 ×10 ⁻⁴ ± 1.68 ×10 ⁻⁵	0.82	1.4 ×10 ⁻⁴

$$-r_{Ol} = k_{NC}(C_{Ol})^{\phi} \times (C_G)^{\varphi} \quad (8)$$

Again, heterogeneous reaction kinetics have been represented by the following model equations viz. Langmuir Hinshelwood (Eq.9), Eley-Rideal for Glycerol (Gly) (Eq.10) adsorbed and Eley-Rideal for Ol adsorbed (Eq.11) on the active site of the catalyst.

$$-r_{Ol} = \frac{k_c(K_{Ol}C_{Ol} \times K_G C_G)}{\left(1 + K_{Ol}C_{Ol} + K_G C_G + \frac{C_{GMO}}{K_{GMO}}\right)^2} \quad (9)$$

$$-r_{Ol} = \frac{k_C \times K_G (C_{Ol} C_G)}{\left(1 + K_G C_G + \frac{C_{GMO}}{K_{GMO}}\right)} \quad (10)$$

$$-r_{Ol} = \frac{k_C \times K_{Ol} (C_{Ol} C_G)}{\left(1 + K_{Ol} C_{Ol} + \frac{C_{GMO}}{K_{GMO}}\right)} \quad (11)$$

For coupled kinetics, the following models (Eqs. 12-14) can be developed by combining non-catalytic model equation (Eq. 8) with the heterogeneous kinetic equations (Eqs. 9-11)

$$-r_{Ol(global)} = (k_{NC} (C_{Ol})^\phi \times (C_G)^\varphi) + \frac{k_C (K_{Ol} C_{Ol} \times K_G C_G)}{\left(1 + K_{Ol} C_{Ol} + K_G C_G + \frac{C_{GMO}}{K_{GMO}}\right)^2} \quad (12)$$

$$-r_{Ol(global)} = (k_{NC} (C_{Ol})^\phi \times (C_G)^\varphi) + \frac{k_C \times K_{Gly} (C_{Ol} C_G)}{\left(1 + K_G C_G + \frac{C_{GMO}}{K_{GMO}}\right)} \quad (13)$$

$$-r_{Ol(global)} = -r_{Ol(NC)} + -r_{Ol(C)} = (k_{NC} (C_{Ol})^\phi \times (C_G)^\varphi) + \frac{k_C \times K_{Ol} (C_{Ol} C_G)}{\left(1 + K_{Ol} C_{Ol} + \frac{C_{GMO}}{K_{GMO}}\right)} \quad (14)$$

For batch reactor, r_{Ol} can be calculated from Eq. (15)

$$-r_{Ol} = \frac{d(Ol)}{dt} \quad (15)$$

The kinetic parameters were measured by non linear regression employing Levenberg Marquardt algorithm subroutine in Polymath® program.

Activation energy of the catalyst have been computed using Arrhenius equation represented

by Eq. 16.:

$$k_{NC/C} = k_{0(NC/C)} e^{-\left(\frac{E_{NC/C}}{RT}\right)} \quad (16)$$

OBJECTIVE 4: Minimization of energy consumption & overall process while ensuring environmentally benign process.

		ACTIVITIES				
		I: Intensification of monostearin (phase-change material) synthesis in infrared radiated rotating reactor	II. Intensification of glycerylmonocaprin synthesis under concurrent electromagnetic and ultrasonic energy	III: Intensification of monooleoyl glycerol synthesis under combined infrared and ultrasonic radiation	IV. Intensification of isopropyl oleate synthesis under near infrared radiation	V. Biodiesel synthesis from waste cooking oil under far-infrared radiation
Maximum Limiting Reactant Conversion		98±1% stearic acid conversion	88±1% capric acid conversion	93% oleic acid conversion	94% oleic acid conversion	
Maximum Desired Product Yield/Selectivity		92±2% monostearin yield	79.5±1% glyceryl monocaprin yield	84.6% monooleoyl glycerol yield	90% yield of Isopropyl oleate	97% yield of Fatty acid methyl ester
Energy consumed	Conventionally heated stirred batch reactor		Activation-Energy: 33 kJ/mol Energy-Input: 1857 kJ	Activation Energy: 114kJ/mol Energy-Input: 1650 kJ	Activation Energy: 67kJ/mol Energy-Input: 2700 kJ	Energy-Input: 720 kJ
	FIR-SBR	Activation Energy: 40.18 kJ/mol Energy Input: 300 kJ	-X-	Activation Energy: 20.28kJ/mol Energy-Input: 72 kJ	Activation Energy: 48kJ/mol Energy-Input: 360 kJ	Energy-Input: 180 kJ
	FIR-RBR	Activation Energy: 21.84 kJ/mol Energy Input: 120 kJ	Activation Energy: 27 kJ/mol Energy-Input: 170 kJ	-X-	-X-	-X-
	US-FIR-SBR	-X-	-X-	Activation Energy: 8.52kJ/mol Energy-Input: 60 kJ		
	US-FIR-RBR		Activation Energy: 9.6 kJ/mol Energy-Input: 150 kJ	-X-		
	US-RBR		Energy-Input: 208 kJ			
	Environmental Sustainability	1. Rotating action coupled with far infrared radiation consumed 2.5 times less energy than FIR-SBR 2. Monostearin showed desirable properties of an environmentally benign phase change material.	1. Application of acoustic-cavitation with far infrared radiation greatly reduced energy consumption. 2. Glycerylmonocaprin acts as a bio lubricants for low sulphur diesel fuel.	1. Application of ultrasonic energy with far-infrared radiation was resulted more than 45% conversion than conventional reactors. 2. Product can act as a fuel lubricant.	1. FIR radiation consumed 7.5 times less energy than conventional reactor. 2. The product isopropyl oleate has performed as a biodiesel additive in reducing pour point and HC emission of biodiesel	1. Use of used frying mustard oil for eco-friendly biodiesel production. 2. FIR consumed 1/4 th energy than conventional system 3. Low HC and CO emission.

OBJECTIVE 5: Design of pilot/ industrial scale reactor using the evaluated optimized reaction conditions and kinetic parameters.

- In all the experimental activities, different optimization techniques (Taguchi design of experiments and Response surface methodology) were employed and the best condition for maximum production of the desired product was evaluated. Under that derived optimum condition, kinetic assessments (pseudo-homogeneous and heterogeneous models) were conducted and kinetic parameters were estimated. These kinetic parameters can be utilized to scale-up efficient reactors.
- To fulfil the objective, glyceryl monooleate (ester of glycerol and oleic acid) production has been carried out to continuous reactor (rotating packed bed reactor) study from rotating batch reactor analyses under far-infrared radiation.
- Reactor scale-up is still under progress by using software viz., UniSim design suite (Honeywell) and Aspen plus provided by our departmental facility.

OBJECTIVE 6: Performing an elaborate techno-economical study to make the process energy-efficient, eco-friendly, economically profitable while achieving desired product quality.

6.1 Energy Efficient Process

- Experimental activities pertaining to the project enumerate the fact that application of different kinds of electromagnetic radiation involving infrared and ultrasonic energy has expedited the synthesis process of the value added chemicals while maintaining desired quality of the product.

- Electromagnetically energized process consumed much less energy and has given comparatively higher limiting reactant conversion in considerably shorter reaction time and mild reaction condition than the conventionally heated reactors.

6.2 Economic Sustainability

- **Less Production Time:** As observed from the experimental activities that the time required to achieve target quality product in electromagnetically energized reactor were significantly lower which implies less electricity/power consumption for the desired product production. This saves the overall operational cost.
- **Catalyst Recycling:** For all the experimental studies different heterogeneous catalysts have been used which was separated from the reaction mix by vacuum-filtration method. The recovered has been recycled for 4-5 batches without significant loss in catalytic activity. Therefore, no requirement of fresh catalyst (in case of specific product) for every set of experimental runs makes the overall process economical lucrative.
- **Molecular Sieves Recycling:** Molecular sieves used as desiccants for by-product water removal during esterification reaction has been collected and reused again for the next batch cycle after oven drying. This also curtailed down the cost related to molecular sieves and has increased the cost effectiveness of the production process.
- **Reactants Utilization:** Leftover glycerol obtained after the reaction was separated by gravity-decantation method due to its substantial density difference from the esters and fatty acid. Water from the glycerol was removed through distillation method using the boiling point difference.

Therefore, the recovery of glycerol incurred minimum cost for reactant separation which adds to the economic cost-effectiveness of the synthesis process.

6.3 Eco-friendliness/Environmentally Benign.

➤ *Reuse of Glycerol, Catalyst and Molecular Sieves*

Reutilization of reactants, desiccants and catalysts results in minimization of solid waste disposal problem. Since, no waste stream (liquid/water) disposal was observed in the studies hence the overall process represents near “zero waste” philosophy.

➤ *Minimum Energy Requirement*

Application of electromagnetic radiation resulted in less consumption of electrical energy thereby reducing the carbon footprint.

➤ *Glycerol conversion to valuable products*

Glycerol is obtained as a by-product of biodiesel so, utilization of glycerol for production of value added chemicals is of utmost requirement. Moreover, accumulation of glycerol has plunged down the market price of biodiesel. Hence, the present study focuses on transformation of by-product glycerol into valuable fuel additives. This has greatly promoted the market for biodiesel production which in-turn has reduced the harmful emissions from conventional fuel.

ANNEXTURE III

ACHIVEMENTS FROM THE PROJECT

Achievements from the Projects

1. Successful application of electromagnetic radiation viz., infrared radiation (far and near) and ultrasonic radiation either conjointly or individually has immensely intensified esterification reaction for production of valuable glyceryl esters.(Follow manuscript ID: [ao-2018-025334](#))
2. Infrared radiation has also expedited the production process of esters from monohydric alcohols (isopropyl oleate) and resulted desirable fatty acid conversion in less than an hour. The product could perform as an efficient biodiesel blend; the blended biodiesel showed lower pour point and reduced carbon monoxide and hydrocarbon emission thereby mitigating the inherent problem of the conventional biodiesel.(Follow manuscript ID: [GCEC-2018-0239.R1](#))
3. Effect of infrared radiation was also investigated in the production of biodiesel from used frying mustard oil. Results showed 46% more ester yield in case of infrared radiation than conventional heating. Additionally, the biodiesel showed sufficient reduction in carbon monoxide and hydrocarbon emission compared to neat diesel. (Follow link: [DOI: 10.1016/j.energy.2018.08.181](#))
4. Employment of far and near infrared radiation has been successively studied in hydrolyses of lignocellulosic biomass for production of an alternative fuel i.e., bio-ethanol. (Publication link: [DOI: 10.1007/s12649-018-0220-2](#))

5. Application of infrared radiation was also studied in development of hydroxyapatite supported cobalt catalyst. The catalyst prepared under infrared radiation exhibited superior characteristics (specific surface area and surface acidity) compared to catalyst prepared through conventional wet-impregnation methods. (Follow link: [DOI: 10.1016/j.catcom.2017.02.020](https://doi.org/10.1016/j.catcom.2017.02.020))

ANNEXTURE IV

SUMMARY OF THE FINDINGS

Bio-glycerol is a key by-product generated during the biodiesel production. Therefore, valorisation of bio-glycerol is of utmost importance for sustainability of biodiesel industry. The present project envisaged intensification and optimization of bio-glycerol conversion into value-added products using electromagnetically irradiated energy-efficient reactor. The major outcomes are summarised below:

- I. Glycerol was esterified with fatty acids viz. oleic acid, stearic acid and capric acid into esters (viz., monooleoyl glycerol, monostearin and monocaprine) in presence of different heterogeneous catalysts viz. Amberlyst 36 (wet) and Amberlyst 15 (dry) under different electromagnetic waves (viz. far infrared, near infrared radiation and ultrasonication) to intensify the overall reaction rate while minimising energy and resource consumption. Performance of different reactor configurations viz. batch, semi batch and packed bed flow reactors have also been investigated for maximum selectivity of desired product through process optimization.
- II. Esterification of Octadecanoic acid (ODA) with glycerol (G) in presence of Amberlyst 36 catalyst had been performed and the relative effectiveness based on monooleoyl glycerol (MOG) yield was assessed in three different reactors viz. traditional batch reactor (TBR), infrared wave (IRW) promoted batch reactor (IRWPBR) and synergistic ultrasonic-infrared-wave promoted batch reactor (USIRWPBR). USIRWPBR could intensify the reaction with superior ODA conversion (92.5%) compared to IRWPBR (79.8%) and TBR (36.39%). The derived product (MOG) can be used as a plasticizer/fuel additives.

- III. The formation of monostearin (MSN) was executed over heterogeneous solid acid catalyst Amberlyst 36 in a far infrared radiation assisted rotating batch reactor (RBR) and stirred batch reactor (SBR). This work established the advantage of RBR over SBR. In the intensification of MSN synthesis, RBR depicted 92 % MSN yields, which was 40% higher than the yield obtained in SBR.
- IV. Catalysts prepared under infrared activation (IRC) possessed excellent catalytic properties and demonstrated noteworthy catalytic efficacy in accelerating oleic acid (OA) conversion to monoolein, rendering 98% conversion within much shorter time (80 mins) in a conventional semi-batch reactor setup.
- V. A novel “Far Infrared Radiation (FIR) with Ultrasonication (US)” energized rotating reactor (FIRUERR) for maximization of glyceryl monocaprin (GMC) yield in presence of Amberlyst 15 (A15) heterogeneous catalyst had been investigated. A capric acid (CA) conversion of 88% could be asserted in FIRUERR operated under batch mode which was 9% higher than FIR energized rotating reactor (FIRERR) and 20% higher than conventionally energized rotating reactor (CERR). Deactivation of A15 catalyst was investigated with only 36% decay in FIRUERR and more than 60% decay was observed both in FIRERR and CER.
- VI. The sustainable synthesis of biodiesel (96.85% FAME yield) from used frying mustard oil was achieved in far infrared (FIR) radiated reactor within only 30 min reaction time, which was remarkably higher than 40.22% FAME yield employing conventional heating system. The FIR reactor demonstrated high energy-efficiency.
- VII. Heterogeneous kinetics of esterification of G with ODA was investigated in a novel continuous flow rotating packed bed reactor (RPBR) under electromagnetic waves. The kinetic data obtained from RPBR can be useful for process simulation by using standard software viz., UniSim design suite (Honeywell) and Aspen Plus.

ANNEXTURE V

CONTRIBUTION TO THE SOCIETY

Rapid industrialization has increased the demand of fossil fuels. Air pollution can result from the burning of fossil fuels and responsible for several major problems like global warming, acid rain, and the deterioration of the ozone layer. Biodiesel has received considerable attention in recent years as a biodegradable, renewable, non-toxic, environment friendly substitute for commercial diesel. Glycerol is a major by-product in the biodiesel manufacturing process. As the biodiesel industry is rapidly expanding, a glut of crude glycerol is being created. Because this glycerol is expensive to purify for use in food, pharmaceutical, or cosmetic industries, biodiesel producers must seek alternative methods for its utilisation.

Notably, energy-efficient and cost-effective reactors and technologies developed in the present project, would facilitate sustainable thermo-chemical conversion of bio-glycerol to value added products fostering overall economic growth.

Everyday several tons of waste cooking oils are generated from restaurants, homes, and wafer industries. The sustainable synthesis of biodiesel from this used frying mustard oil was achieved through application of far infrared radiated reactor which would facilitate minimising energy consumption and recurring costs; which in turn may boost growth of biodiesel industry; thus, promoting development of rural and urban economies.

Besides, India is an agriculture based country. A huge amount of lignocellulosic waste generated from agricultural production of various crops like sugarcane, sorghum, sweet sorghum, pulses, etc. which do not find any alternative use and are either left in the fields or burned. Hence, these could be used in bio-ethanol production which is a good alternative to

use it in an environmentally friendly manner. Use of agricultural residues helps in reduction of deforestation as our reliance on forest woody biomass decreases. Non ionizing excitation (Far Infrared radiation) has a stupendous influence on the pre-treatment and hydrolyses of lignocellulosic biomass for its high energy-efficiency and time saving characteristics. The application of near infrared radiation could efficiently produce total reducing sugar (TRS)[for subsequent conversion to biofuel] from waste papaya epidermis through a sustainable process which will help in solid waste valorisation and sustainable biofuel production .

The hydroxyapatite (HAP) derived from naturally available resources (including waste animal bones) could be used as catalyst support; thereby, reducing the cost incurred in catalyst preparation. Application of electromagnetic radiation for catalyst preparation has immensely improved the catalyst quality (specific surface area and surface acidity) compared to conventional method. Therefore, sustainable utilization of natural HAP (i.e. animal bone/ fish scale) as green support for catalysis expected to mitigate the solid-waste disposal problem while creating employment opportunity through rural/urban entrepreneurship.

Esters of Glycerol (G) are important synthetic chemicals which find their application in various fields such as plasticizer, food additive, fuel additive etc. Glycerol reacts with fatty acids (FA) like oleic acid, stearic acid, capric acid through the process of esterification and produced several value added products (like monoolein, monostearin, monocaprin). However, esterification between G and FA consumes high reaction time and temperature as revealed from previous reports. So the aim was to intensify the overall esterification process to reduce the cost of the reaction process using indigenously developed electromagnetically radiated energy-efficient reactor. Electromagnetic radiations (viz., far infrared radiation and near infrared radiation) could synergistically intensify the esterification reaction compared to other conventional heating methods. The application of ultrasonication in combination with far infrared radiation has synergistically promoted esterification reaction that reduced the

time and temperature of the reaction making the process energy-efficient and economically and environmentally sustainable.

Efficient utilization of waste biomass for sustainable biodiesel vis-à-vis bio-glycerol production and subsequent conversion of bio-glycerol to valuable products through the application of energy-efficient reactor developed in the present project would certainly improve the rural and urban economy of our country through possible entrepreneurship/industrialisation.

ANNEXTURE VI

Details of Publications

Paper published/Accepted in Journal:

1. P Karan, P Mukhopadhyay, R Chakraborty, 2017 Intensification of monostearin (phase change material) synthesis in infrared radiated rotating reactor: Optimization and heterogeneous kinetics; Energy Conversion and Management(ELSEVIER) 138, 577-586 (Impact Factor:4.801)<http://dx.doi.org/10.1016/j.enconman.2017.02.026>(Impact Factor: 6.377).
2. P Mukhopadhyay, R Chakraborty, 2017; Infrared radiation promoted preparation of cost-effective lamb bone supported cobalt catalyst: Efficacy in semi-batch monoolein synthesis; Catalysis Communications (Elsevier); 94 (2017) 73–76. (Impact Factor:3.646)
3. Rajat Chakraborty, Punam Mukhopadhyay, Bipin Kumar, Optimal biodiesel-additive synthesis under infrared excitation using pork bone supported-Sb catalyst: Engine performance and emission analyses. Energy Conversion and Management (2016), 126, 32-41. <https://doi.org/10.1016/j.enconman.2016.07.069>.
4. Piasy Pradhan, Rajat Chakraborty, 2018; Optimal efficient biodiesel synthesis from used oil employing low-cost ram bone supported Cr catalyst: Engine performance and exhaust assessment; Energy (ELSEVIER) Volume 164, 1 December 2018, Pages 35-45. (Impact Factor: 5.582)
5. Swapnendu Chatterjee, Sourav Barman and Rajat Chakraborty, 2018, Combined Effects of Ionic Liquid and Tungsten–Halogen Radiation on Heterogeneous Hydrolysis Kinetics of Waste Papaya Epidermis for Production of Total Reducing Sugar; Waste and Biomass Valorization (Springer Netherlands) February 2018; DOI 10.1007/s12649-018-0220-2.(Impact Factor: 1.874)

6. Punam Mukhopadhyay, RajatChakraborty,2018; Heterogeneous esterification kinetics of isopropyl oleate synthesis under non-ionizing excitation using nano-anatase imbued mesoporous catalyst. Chemical Engineering Communications. (Taylor & Francis)(Accepted ; In Press; DOI:10.1080/00986445.2018.1534230)..(Impact Factor: 1.282)

Paper submitted to Journal:

1. Megha Srivastava, Punam Mukhopadhyay, Rajat Chakraborty, Efficient monooleoyl glycerol synthesis employing hybrid ultrasonic-infrared-wave promoted reactor: Concurrent catalytic and non-catalytic esterification kinetics, Submitted to ACS Omega, Manuscript ID: ao-2018-025334.[under Review]
2. Poulami Karan, Punam Mukhopadhyay, Rajat Chakraborty, 2018 “Infrared radiation-ultrasonication integrated rotating reactor for efficient synthesis of glyceryl monocaprin: Kinetics of heterogeneous esterification and catalyst deactivation", submitted to Journal of the Taiwan Institute of Chemical Engineers (ELSVIER).[under Review]

Paper published in proceedings of international conference:

1. P. Karan, R. Chakraborty; 2016; Utilization of Waste Biomass derived Bioglycerol for Synthesis of Industrially Important Products; 6th International Conference on Solid Waste Management, 6thIconSWM (November 2016).

Paper presented at national conference:

1. Megha Srivastava, Punam Mukhopadhyay, Rajat Chakraborty, Synthesis of Glycerol Monooleate using Semi Batch reactor operation equipped with Far Infrared Radiation, CHEMCON, December 2017, Department of Chemical Engineering, HIT.
2. Poulami Karan, Punam Mukhopadhyay, Rajat Chakraborty, 2016,Recent trends in synthesis of fatty acid esters applied as phase change energy storage materials, National

Conference on Renewable Energy- NCRE 2016(TEQIP-II sponsored); Heritage Institute of Technology, Kolkata; July 27-28, 2016.

3. Punam Mukhopadhyay. Rajat Chakraborty, Contributed Talk on Stearic Acid Esterification using semi batch reactor, 2018, National Conference organized by IICHE & CGCRI.

Reference:

- 1) Kaufman V. R., and N. Garti. "Organic reactions in emulsions—Preparation of glycerol and polyglycerol esters of fatty acids by transesterification reaction." *Journal of the American Oil Chemists Society* 59, no. 11 (1982): 471-474.
- 2) Singh S, Patel A. Selective green esterification and oxidation of glycerol over 12 tungstophosphoric acid anchored to MCM-48. *IndEng Chem Res* 2014;53:14592–600.
- 3) Chakraborty R, Mandal E. Fast and energy efficient glycerol esterification with lauric acid by near and far-infrared irradiation: Taguchi optimization and kinetics evaluation. *J Taiwan Inst Chem Eng* 2015;50:93–9.
- 4) Mallesham B, Sudarsanam P, Reddy BM. Production of biofuel additives from esterification and acetalization of bioglycerol over SnO₂-based solid acids. *IndEng Chem Res* 2014;53:18775–85.
- 5) Wee, L. H.; Lescouet, T.; Fritsch, J.; Bonino, F.; Rose, M.; Sui, Z.; Garrier, E.; Packet, D.; Bordiga, S.; Kaskel, S.; Herskowitz, M. Synthesis of monoglycerides by esterification of oleic acid with glycerol in heterogeneous catalytic process using tin–organic framework catalyst. *Catal. Lett.* 2013, 143(4), 356-363.
- 6) Chakraborty, Rajat, PunamMukhopadhyay, and Bipin Kumar. "Optimal biodiesel-additive synthesis under infrared excitation using pork bone supported-Sb catalyst: Engine performance and emission analyses." *Energy Conversion and Management* 126 (2016): 32-41.