CHAPTER-7

7.1 Summary of present work

The dwindling reserve of conventional fossil fuels and their adverse impacts on human beings and surroundings in current environment have pressurized the research fraternity to seek environmentally benign and renewable alternatives. Presently biodiesel is being scaled up to industry level to fulfill the energy demand of growing population and commercial units across the globe. Additionally, biodiesel is safer, non-toxic, and biodegradable with low noxious emission profile. Biodiesel is chemically fatty acid methyl ester (FAME) and is derived from plants and animal fats. Furthermore, biodiesel is more oxygenated than conventional diesel and hence its combustion results in less emission of hydrocarbons, carbon dioxide, and particulate matter. Biodiesel is economically produced by transesterification, an economically viable method where methanol is used as acyl acceptor in process catalyzed by either homogeneous and heterogeneous acids or bases. This is a catalysed chemical reaction in which triglyceride molecule reacts with three molecules of methanol to form three molecules of FAME and one glycerol molecule stoichiometrically. Methyl esters are primarily manufactured from edible or non edible oil feedstock. Catalyst plays major role in transesterification which provides a new path of lower activation energy. Both homogeneous and heterogeneous catalysts have been effectively used in this process but application of heterogeneous catalysts in biodiesel production is highly encouraged as they are sustainable for reusability, making transesterification cost effective. Therefore, both acidic and basic heterogeneous catalysts are found to be potential substitutes for homogeneous catalysts. Nevertheless, heterogeneous basic catalysis overweighs its acidic counterpart as the former is irreversible in nature and also approximately 4000 times faster than latter one. The metal oxide is composed of positive metal ions (cations) and negative oxygen ions (anions) as Lewis and Brønsted base sites, respectively, where methanolysis begins with sufficient adsorption of methanol on active sites followed by the cleavage of O-H bonds into methoxide anions coined as acyl acceptor. The methoxide anions then react with the acyl moiety from triglyceride molecules to form the corresponding FAME. In present study, Ba and Sr based heterogeneous base catalysts were employed in transesterification reaction. Further, rare earth metals and transition metals are known for their catalytic activity owing to thermal stability and excellent oxidation activity ameliorating the catalytic potency of base catalyst due to its variable valences. Regarding aforementioned characteristics of dopants, active Ba and Sr metals were doped with La, Ce, and Ti metals to form highly stable and basic mixed metal oxides as heterogeneous base catalyst for transesterification reaction. Several characterizations of synthesized solid base catalyst were executed through thermal analysis (TGA/DTA/DTG), PXRD, XPS, SEM-EDX, FT-IR, and BET surface area analysis along with basic strength to analyze physicochemical properties. In present study, non-edible feedstocks have been selected as they don’t compete with food security. *Madhuca longifolia* oil, *Millettia pinnata* oil, *Schleichera oleosa* oil, and waste cooking oil were employed as non edible feedstocks for biodiesel production using doped Ba and Sr mixed metal oxides. The process was optimized through analyzing the impact of various process variables such as catalyst dose, oil to methanol molar ratio, reaction temperature, reaction time, and stirring speed along with endurance capacity of catalyst. Additionally, kinetics and thermodynamics of transesterification were also carried out to comprehend the reaction rate and mechanism involved in transesterification reaction. The greenness approach of reaction and catalyst sustainability were ascertained by E-factor and TOF study. Later, the prepared methyl esters were characterized by GC-MS, ^{1}H-NMR, ^{13}C-NMR, and ATR FT-IR spectroscopy. Ultimately, physicochemical properties of prepared methyl esters were checked to ensure their compatibility with conventional fuel.

Overall, the extensive experimental work has been well-drafted in this thesis which clearly depicts the successful application of efficient heterogeneous base catalysts in transesterification reaction for FAME production using non-edible feedstocks. Additionally, kinetic as well as thermodynamic investigation was also executed to deeply analyze the mechanism of reaction alongwith E-factor and TOF.

The essence of the thesis has been mentioned below:

Chapter 1 consists general introduction regarding present work where candidate has introduced the topic, general terms, definitions and facts. A brief literature review on the topic has also been given here. Basic and latest references have been presented authentically. Objectives of the work reported have been clearly presented.

Chapter 2 manifests the materials and methods adopted to carry out the work as presented in the objectives. The characterization techniques were used to analyze the physicochemical properties of catalyst and prepared methyl esters as well. The prepared novel catalysts applied in transesterification were characterized by PXRD, XPS, SEM-EDX, FT-IR, and BET surface area analysis. The basic strength of prepared catalyst was evaluated through Hammett indicator-benzoic acid titration method. Synthesized biodiesel was also characterized by GC-MS analysis, ^{1}H-NMR, ^{13}C-NMR, and FT-IR analysis but methyl ester conversion was quantified by^{1}H-NMR analysis. Additionally, kinetics and thermodynamics of transesterification were also carried out to comprehend the reaction rate and mechanism involved in transesterification reaction. The greenness approach of reaction and catalyst sustainability were ascertained by E-factor and TOF study.

In **Chapter 3,** Ba-La mixed metal oxide has been emphasized as heterogeneous base catalyst for methyl ester production from *Madhuca longifolia* (Mahua) oil feedstock using transesterification reaction. Four samples of novel catalyst (BLOA1, BLOA2, BLOC, and BLOS) were prepared by four different synthesis protocols, i.e., sol-gel auto-combustion (BLOA1: 7-8 pH; BLOA2: 2.31pH), co-precipitation and solid-state route. Co-precipitation route and solid route did not prove to be significant enough to produce the efficient catalyst. BLOA1 was also not the suitable candidate as a catalyst for transesterification as surface passivation was observed with carbonate adsorption. BLOA2 was perceived to be most catalytically active with the highest purity and high crystallinity in the absence of carbonate species. Hence BLOA2 was used as a novel heterogeneous basic catalyst. The MOME was characterized by ^{1}H-NMR for FAME conversion. All important process variables were optimized to obtain maximum 97.5±0.5% FAME conversion; the optimized conditions were as follows: catalyst concentration (1.5wt %), oil to alcohol molar ratio (1:18), stirring speed (500 rpm), temperature (65˚C), reaction time (2 h). The reaction mechanism followed first-order kinetics. The activation energy (E_A) was 34.64kJmol^{-1} and the frequency factor (A) was 2.4×10^{3} min^{-1}. The thermodynamic functions such as ΔH°, ΔS°, and ΔG° and were also calculated and found to be 32.12 kJ/mol, -188.33 J/mol, and 95.78 kJ/mol at 65˚C. The positive value of Gibbs free energy (ΔG°) suggested the transesterification reaction as non-spontaneous viz. external force driven reaction which validates the need of heterogeneous catalysis. The E-factor and turn over frequency (TOF) were also determined and found to be 0.089 and 23×10^{-2} s^{-1}. The physicochemical properties of the synthesized biodiesel were measured according to ASTM D 6751 and found to be within the permissible range.

In **Chapter 4**, application of Ba-Ce mixed metal oxide is emphasized heterogeneous base catalyst for methyl ester production from *Millettia pinnata* (Karanja) oil feedstock using transesterification reaction. The perovskite barium cerate ($BaCeO_3$) was successfully prepared by sol-gel polymer precursor method. The desired structure was ascertained by powder PXRD, SEM, EDX, and FT-IR analysis. Various Ba/Ce stoichiometric ratios were inspected for catalytic activity. Among all, perovskite barium cerate ($BaCeO_3$) was proved to be an active and stable catalyst for the methanolysis of karanja oil. The surface area analysis of $BaCeO_3$ showed that specific surface area (S_{BET}) was determined as $32m^2/g$, and its pore size distribution confirmed it as mesoporous catalyst. The influence of various parameters such as catalyst dose, oil to alcohol molar ratio, reaction temperature, reaction time and agitation speed were thoroughly studied and the KOME with remarkable 98.41±0.45 % conversion was synthesized at following optimum reaction conditions: catalyst dose; 1.2 wt %, oil to methanol molar ratio; 1:19, reaction temperature; 65˚C, reaction time;100 min, and agitation speed; 600 rpm. The reaction mechanism followed pseudo-first order kinetics. The activation energy (E_a) of the reaction process was found to be $42.77 kJmol^{-1}$. Barium cerate has got the excellent reusability till sixth cycles with KOME conversion capacity greater than 81%. In present study, green chemistry metrics such as E-factor value of 0.088 illustrated $BaCeO_3$ catalysed transesterification reaction as a clean biodiesel production technique. TOF was also quantified as $21\times10^{-2}s^{-1}$ classifying the perovskite $BaCeO_3$ as efficient and sustainable catalyst for transesterification to produce biodiesel. The prepared KOME with the highest KOME conversion underwent for physicochemical analysis to assure its suitability for engines without modification. All the physicochemical properties accounted in this study were well within the permissible range as prescribed by ASTM which made the produced biodiesel as a clean and efficient alternative for conventional diesel fuel.

In **Chapter 5**, Sr-La mixed metal oxide has been emphasized as heterogeneous base catalyst for methyl ester production from *Schleichera oleosa* (Kusum) oil feedstock using transesterification. The solid Sr-La mixed metal oxide as heterogeneous base catalyst was synthesized via co-precipitation route. The catalyst was characterized by PXRD, FT-IR, SEM, EDX and XPS. The free fatty acid content of the feedstock was assuaged by esterification process followed by transesterification for the synthesis of biodiesel. Effect of various factors including calcination time, temperature, reaction time, molar ratio (methanol: oil), and catalyst dose were also taken into account using OVAT (one variable at a time). High quality and pure biodiesel was synthesized at optimized condition viz. Alcohol to oil molar ratio (14:1), catalyst dose (1.5 %), temperature (65˚C), stirring speed (600 rpm) for 40 min in presence of DPE (co-solvent to alcohol molar ratio, 1:1) and was characterized by ^1H NMR and FT-IR analysis. Reusability of catalyst was checked and the catalyst was found stable up to eight runs with more than 75% FAME conversion. The pseudo-first order kinetic model successfully established the kinetics of transesterification reaction having activation energy (E_a) of 65.23kJmol^{-1}. Furthermore, thermodynamics was also explored and important thermodynamic functions (ΔH°, ΔS°, and ΔG°) were evaluated using Eyring equation. The Environment-factor (E-factor) and turn over frequency (TOF) were enumerated as 0.091and $24\times10^{-2}s^{-1}$, respectively. The physicochemical properties of the synthesized *Schleichera oleosa* oil methyl ester were measured according to ASTM D 6751 and were found to be within the permissible range.

In **Chapter 6**, Sr-Ti mixed metal oxide has been emphasized as heterogeneous base catalyst for methyl ester production from waste cooking oil feedstock using transesterification reaction. PXRD, XPS, SEM, EDX, FT-IR, and BET surface area analysis were used to determine the physicochemical properties of catalyst. Moreover, the highest FAME conversion was obtained by optimizing the process through RSM using CCD. The above mentioned design used in RSM statistically optimized the concerned reaction parameters i.e. catalyst dose (1.09wt %), methanol to oil molar ratio (10.76:1), reaction time (77.8min) offering 98.15% methyl ester conversion. However, the confirmatory tests declared 97.9% FAME conversion using optimized reaction conditions as catalyst dose (1.0wt %), methanol to oil molar ratio (11:1), reaction time (80min). The closeness in optimized value of anticipated and confirmatory results perceived the efficiency of CCD and approving its potency as successful tool to estimate the reaction process for highest FAME conversion. Next, a pseudo-first-order kinetic model was applied on transesterification reaction and the activation energy (E_a) of the reaction process was found to be 29.67 kJ/mol. Furthermore, thermodynamic of the same was also explored and important thermodynamic functions (ΔH°, ΔS°, and ΔG°) were reckoned to be 27.58 kJ/mol, -188.81J/mol and $91.39 kJmol^{-1}$ respectively. The Environment-factor and turn over frequency (TOF) were enumerated as 0.089 and $28\times10^{-2}\ s^{-1}$. Lastly all the critically important fuel properties of FAME produced from WCO was found to be within the permissible limit laid by ASTM standards for biodiesel. Finally, the prepared catalyst was found qualified for its application in CI engines as a substitute of conventional fossil fuel, i.e. diesel.

On the basis of outcome of this thesis work, it is concluded that all the four prepared catalysts i.e. Ba and Sr doped mixed metal oxides were efficient for methyl ester production using non-edible feedstocks. Moreover, among all the prepared catalyst samples, the last Sr-Ti mixed metal oxide was found to be the most efficient heterogeneous base catalyst attributing to its high basic strength and surface area. It provided the new path to reaction with lowest activation energy and catalysed the reaction at faster rate as compared with others for methyl ester conversion.

The key results of the work have been summarised in nutshell as in Table 7.1, 7.2, and 7.3.

Table 7.1

Comparison of optimum values of process parameters studied in the objectives.

Prepared Solid base catalysts	Catalyst dose wt%	Feedstocks	O/M molar ratio	Temperature (˚C)	Time (min)	FAME conversion (%)	Reusability runs
Ba-La mixed metals oxide	1.5	*M. longifolia* oil	1:18	65	120	97.5	5 (83.5%)
Ba-Ce mixed metal oxide	1.2	*M. pinnatta* oil	1:19	65	100	98.3	6(81.2%)
Sr-La mixed metals oxide	1.5	*S. Oleosa* oil	1:14	65	40	96.7	8(79.3%)
Sr-Ti mixed metal oxide	1.0	Waste cooking oil	1:10	65	80	98.1	8(83.0%)

Table 7.2

An illustration over compatibility check of the prepared catalysts with individual feedstocks.

Prepared Solid base catalysts	**Catalyst dose wt%**	**Oil /M molar ratio**	**Temperature (˚C)**	**Time (min)**	**FAME conversion (%) with different Feedstocks**			
					***M. longifolia* oil**	***M. pinnatta* oil**	***S. Oleosa* oil**	**WCO**
Ba-La mixed metaloxide **($Ba_2La_2O_5$)**	1.5	1:18	65	120	98.7	98.1	95.9	91.1
Ba-Ce mixed metal oxide **($BaCeO_3$)**	1.2	1:18	65	100	93.6	97.9	95.2	94.1
Sr-La mixed metals oxide **($Sr_2La_2O_5$)**	1.5	1:14	65	40	96.2	96.4	96.6	93.0
Sr-Ti mixed metal oxide **($SrO/SrTiO_3$)**	**1.0**	**1:10**	**65**	**80**	**96.7**	**97.3**	**96.9**	**98.3**

Table 7.3

Comparison of determined kinetic and thermodynamic parameters along with E-Factor and TOF.

Prepared Solid base catalysts	Feedstocks	E_a (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol/K)	E – factor	TOF (s^{-1})
Ba-La mixed metals oxide	*Madhuca longifolia* oil	34.64	32.12	-188.3	95.78	0.089	23×10^{-2}
Ba-Ce mixed metals oxide	*Millettia pinnata* oil	42.77	33.21	-177.9	93.38	0.088	21×10^{-2}
Sr-La mixed metals oxide	*Schleichera oleosa* oil	65.23	62.5	-77.6	88.73	0.091	24×10^{-2}
Sr-Ti mixed metals oxide	**Waste cooking oil**	**29.67**	**27.58**	**-188.8**	**91.39**	**0.087**	$\mathbf{28\times10^{-1}}$

7.2. Economic feasibility and cost analysis

Economic feasibility is a very critical factor of the process of biodiesel production which governs biodiesel sustainability. Though biodiesel has got many advantages and environmentally benign characteristics still biodiesel could not replace the conventional petroleum fuel so far completely due to its relatively higher cost. The commercial cost of biodiesel production is primarily contributed by the feedstock used, equipment, and catalyst (Gebremariam and Marchetti, 2018). 70–95% of total production cost is coming from feedstock to be used for biodiesel production affecting the economic viability of the process (Singh et al., 2018).In present study, the high-quality biodiesel has been produced by employing non-edible feedstocks (*Madhuca longifolia* oil, *Millettia pinnatta* oil, *Schliechera oleosa* oil and waste cooking oil) and efficient catalysts (Ba and Sr doped mixed metal oxides), so the overall cost of the production method has been mitigated to great extent accordingly. Moreover, the purification process also affects the economics of biodiesel production method. Here, the application of heterogeneous catalyst has given the concession of the cost involved in the purification of biodiesel by reducing the production cost up to 5-10% and equipment costs about 25% (Anuar and Abdullah, 2016; Singh et al., 2018). Furthermore, heterogeneous base catalyst might be reused which ultimately make the process sustainable. Hence, in present work, Ba and Sr doped mixed metal oxides were applied which could be effectively used in ceramics after their deactivation in the transesterification reaction. Apart from FAME production, transesterification also results in the glycerol as side product which has tremendous industrial application in commercial sectors. The fixed capital investments (FCI) involved in biodiesel production was determined by using the standards methodology in the literature (Apostolakou et al., 2009). This prescribed cost analysis included the cost of raw materials, chemicals, equipment and utility cost (electricity and water). During cost analysis, the reusability factor was taken into consideration. Owing to the solid-liquid separation method, excess methanol was recovered thoroughly. After careful investigation of physicochemical properties, the purity of produced biodiesel was anticipated to be 99% after thorough purification. The glycerol credit was also taken into overall cost analysis where the purity of produced glycerol was assumed to be >95% after extensive purification process and quality check. Finally, keeping all above-mentioned factors into account, the tentative cost of biodiesel production from *Madhuca longifolia* oil, *Millettia pinnatta* oil, *Schliechera oleosa* oil was estimated to be 0.81-1.19 USD/L whereas the cost of biodiesel from waste cooking oil was found to be 0.55-0.64 USD/L which was appreciably low in comparison to others. The discrepancy in cost of biodiesel produced corresponds to feedstock type owing to the abundance of WCO with zero investment. The current economic analysis illustrates that the process of biodiesel production can be scaled up at the commercial level using extensive and precise simulation technique.

7.3. Future scope of present work

Present study prefaces the production of high quality methyl ester from *Madhuca longifolia* oil, *Millettia pinnata* oil, *Schleichera oleosa* oil, and waste cooking oil using Sr and Ba doped mixed metal oxides as solid base catalysts. The extended work of present study could be to check the emission profile of prepared FAME. Apart from the FAME i.e. main product of transesterification, glycerol which is sole side product can also be used for further value addition into various environmentally benign chemicals. In this direction, appropriate methodology can be devised and its value addition can be executed further.