BIODIESEL PRODUCTION FROM NON-EDIBLE OIL VIA TRANSESTERIFICATION REACTION USING HETEROGENEOUS CATALYST DERIVED FROM POST-HARVEST PLANTS

A THESIS
SUBMITTED TO BODOLAND UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE FACULTY OF SCIENCE AND TECHNOLOGY

SUBMITTED BY
BIDANGSHRI BASUMATARY
DEPARTMENT OF CHEMISTRY
BODOLAND UNIVERSITY, KOKRAJHAR–783370, INDIA
APRIL, 2024

Chapter 6

Summary and Conclusion

6.1 Summary

In this study, a variety of catalysts were derived from four different agricultural wastes or post-harvest materials. The catalysts derived from the four different post-harvest materials are *Musa paradisiaca* plant (**Chapter 2**), *Musa champa* plant (**Chapter 3**), sugarcane bagasse (**Chapter 4**), and Bharatmoni (*Musa* AAA) plant (**Chapter 5**). The elemental composition of all these catalysts from the EDX study is summarized in **Table 6.1**. It can be disclosed that all the catalysts prepared have the highest K than the composition of other metals. Similarly, the result of XPS analyses also exhibited the dominance of potassium in all the catalysts of this study which are shown in **Table 6.2**. From the data, it can be confirmed that calcined material possesses a higher concentration of K than the uncalcined material. The recycled catalysts lose their active components, like potassium, as can be seen from the XPS analysis data (**Table 6.2**). The XRD analyses revealed the existence of metal oxides and carbonates in the catalysts prepared from agricultural post-harvest materials. The common and significant compounds exhibited in the catalysts are K_2CO_3, K_2O, KCl, MgO, $CaCO_3$ and CaO. The FT-IR analysis results are also in accordance with XRD analysis data.

Conclusively, from the FESEM analyses of all the catalysts, it can be noted that the heterogeneous base catalyst prepared from the mentioned banana species and sugarcane bagasse have porous and agglomerated particles and depicting different irregular shapes and sizes of crystalline. Moreover, the HRTEM study interpreted that the surface morphology of the present catalysts is mostly polycrystalline in nature. The BET analyses confirmed the porosity nature of the present catalysts as summarized in **Table 6.3**. The catalysts derived from *Musa paradisiaca*, *Musa champa* and sugarcane bagasse are micro-mesoporous. On the other hand, the catalyst from *Musa* AAA has mesoporous material. The N_2 adsorption-desorption isotherm of all the calcined catalysts is found to be a type IV isotherm with H3 hysteresis loop. The determination of surface area, pore diameter, pore volume, pH, basicity and soluble alkalinity of the catalysts are summarized in **Table 6.3.**

From the summarized catalytic activity studies presented in **Table 6.4**, it can be observed that the calcined catalysts performed better than the burnt ash material in terms of catalytic activity and biodiesel yield %. Whereas, calcined sugarcane bagasse has very low catalytic activity. The reusability performance of *M. paradisiaca* trunk, CMCP-550, CBS- 550 and

SBCC are summarized in **Table 6.5**. The conducted reusability test interprets that the catalyst loses its activity after every cycle of the reactions. It is mainly due to the leaching of some active components of the regenerated catalyst. The confirmation of leaching was found by the EDX study (**Table 6.1**). When the regenerated catalysts were employed again, the production percentage of biodiesel steadily decreased.

The obtained activation energies of *Musa paradisiaca* peel, trunk and rhizome catalysts are 48.68, 47.56 and 48.93 kJ mol^{-1} respectively (**Chapter 2, Page no. 71**). In **Chapter 3** (**Page no. 128**), the calculated activation energies of CMCP-550, CMCS-550 and CMCR-550 catalysts are found to be 54.256, 63.150 and 61.677 kJ mol^{-1} respectively. The activation energy of SBCC was found to be 22.12 kJ mol^{-1} (**Chapter 4, Page no. 162**) and the activation energies of CBP-550, CBS-550 and CBR-550 catalysts are 48.56, 44.36 and 49.26 kJ mol^{-1} respectively (**Chapter 5, Page no. 203**). The overall obtained activation energies of all the calcined catalysts are within the range of 21–84 kJ mol^{-1} (Nath et al., 2019; Kaur and Ali, 2015). The investigated thermodynamic parameters of the reaction catalyzed by SBCC (**Chapter 4, Page no. 165-166**) and CBP-550, CBS-550 and CBR-550 (**Chapter 5, Page no. 208**) revealed that the value of ΔH^o is positive and ΔS^o is negative, which implies that the reaction follows an endothermic pathway. The ΔG^o values of the transesterification processes were also found positive values, reflecting that the reaction is non-spontaneous and endergonic. The transesterification reactions catalyzed by the present catalysts follow the pseudo-first order kinetic model. In the present study, the transformation of biodiesel by employing the calcined *M. paradisiaca, M. champa,* sugarcane bagasse and *Musa* AAA catalysts was confirmed by FT-IR, NMR and GC-MS study. Moreover, the fuel properties of the synthesized biodiesel were investigated and the results are summarized in **Table 6.6**. It is found that the fuel properties of biodiesel in present studies are within the specified range of EN14214 and ASTM D6751 international standards.

Table 6.1: Comparison of elemental compositions of solid catalysts derived from waste biomasses.

Catalysts of the present study	**Calcination condition**	**Composition (%)**												
		C	**O**	**K**	**Ca**	**Mg**	**Si**	**P**	**S**	**Cl**	**Al**	**Fe**	**Na**	**Mn**
Musa paradisiaca peel	550 °C, 2 h	24.02	33.34	29.25	4.01	1.08	3.81	1.06	0.43	3.01	-	-	-	-
Musa paradisiaca trunk	550 °C, 2 h	13.22	37.87	36.31	2.21	3.08	2.84	1.12	-	2.13	0.63	0.59	-	-
Musa paradisiaca trunk	3^{rd} recycled catalyst	20.57	39.20	13.79	9.44	2.11	8.12	5.30	0.53	-	0.26	0.30	-	-
Musa paradisiaca rhizome	550 °C, 2 h	18.43	43.27	30.06	3.06	0.69	1.67	1.00	-	1.83	-	-	-	-
BMCP	Burnt ash	14.17	48.68	27.88		4.38	2.09	0.74	-	0.96	0.56	0.51	-	-
BMCS	Burnt ash	29.78	44.48	19.55	1.45	0.94	1.82	0.48	-	1.46	-	-	-	-
BMCR	Burnt ash	16.80	43.76	23.62	6.17	1.83	2.38	1.25	-	4.15	-	-	-	-
CMCP-550	550 °C, 2 h	6.78	37.55	47.49	2.40	1.01	2.05	-	1.63	1.09	-	-	-	-
CMCP-550	3^{rd} recycled catalyst	18.94	44.22	11.37	4.83	5.90	10.88	2.50	1.00	0.33	-	-	-	-
CMCS-550	550 °C, 2 h	4.94	41.07	24.09	21.88	1.86	0.93	1.44	-	3.79	-	-	-	-
CMCR-550	550 °C, 2 h	0.70	36.22	40.94	4.14	6.26	2.84	2.72	0.84	4.04	1.28	-	-	-
SBCC	550 °C, 2 h	5.89	50.22	12.07	2.43	1.12	24.11	2.14	0.94	-	0.24	0.25	0.60	-
BBP	Burnt ash	21.26	33.83	32.83	1.16	0.82	1.81	1.70	0.18	6.42	-	-	-	-
BBS	Burnt ash	19.68	25.73	36.53	1.22	0.91	2.15	-	-	13.75	-	-	-	-

BBR	Burnt ash	17.83	41.37	30.80	3.66	1.02	1.91	0.48	-	2.87	-	-	-	-
CBP-550	550 ºC, 2 h	4.67	39.86	44.88	3.40	1.92	2.28	-	-	3.00	-	-	-	-
CBS-550	550 ºC, 2 h	6.46	38.96	46.88	1.15	1.53	2.49	1.00	-	1.52	-	-	-	-
CBS-550	3rd recycled catalyst	24.63	45.29	13.06	8.18	2.29	3.50	1.76	-	1.06				0.19
CBR-550	550 ºC, 2 h	4.55	44.52	39.33	2.01	1.45	2.16	2.42	-	3.55	-	-	-	-

BMCP- burnt *Musa champa* peel, BMCS- burnt *Musa champa* stem, BMCR- burnt *Musa champa* rhizome, CMCP-550- calcined *Musa champa* peel, CMCS-550- calcined *Musa champa* stem, CMCR-550- calcined *Musa champa* rhizome, SBCC- sugarcane bagasse calcined catalyst, BBP-Burnt Bharatmoni peel, BBS- Burnt Bharatmoni stem, BBR- Burnt Bharatmoni rhizome, CBP-550- Calcined Bharatmoni peel, CBS-550- Calcined Bharatmoni stem, CBR-550- Calcined Bharatmoni rhizome.

Table 6.2: XPS analysis of the prepared waste plant derived catalysts.

Source of catalyst	**Calcination condition**	**Composition (Atomic %)**												
		C1s	**O1s**	**K2p**	**Si2p**	**Cl2p**	**Mg1s**	**Ca2p**	**Na1s**	**Fe2p**	**Mn2p**	**Sr3d**	**Zn2p**	**N1s**
Musa paradisiaca peel	550 ºC, 2 h	48.92	29.25	14.15	3.50	2.38	0.60	0.34	0.27	0.26	0.23	0.10	-	-
Musa paradisiaca trunk	550 ºC, 2 h	50.75	19.43	20.32	5.69	2.09	0.13	0.21	0.06	0.26	0.31	0.54	0.21	-
Musa paradisiaca rhizome	550 ºC, 2 h	37.29	27.74	15.50	16.2	0.88	0.59	0.29	0.28	0.30	0.34	0.26	0.33	-
BMCP	Burnt ash	54.71	28.27	10.39	1.90	1.54	0.73	1.46	0.09	0.18	0.20	0.40	0.14	-

BMCS	Burnt ash	42.71	30.93	7.65	10.83	1.58	1.44	2.66	0.16	0.23	0.34	1.22	0.27	-
BMCR	Burnt ash	47.61	41.35	7.98	-	0.85	0.17	0.85	0.07	0.19	0.35	0.31	0.23	-
CMCP-550	550 ºC, 2 h	46.03	24.11	18.09	8.37	0.62	0.82	0.23	0.07	0.62	0.25	0.51	0.30	-
CMCP-550	3rd recycled catalyst	19.31	54.1	5.5	7.71	0.14	3.6	6.3	-	0.22	0.51	2.35	0.26	-
CMCS-550	550 ºC, 2 h	49.91	21.83	17.31	8.44	0.85	0.12	0.22	0.09	0.15	0.33	0.57	0.16	-
CMCR-550	550 ºC, 2 h	53.53	21.06	17.68	5.56	0.56	0.03	0.18	-	0.37	0.33	0.53	0.18	-
SBCC	550 ºC, 2 h	19.78	25.12	9.49	38.19	0.31	0.41	4.22	0.40	0.21	0.32	1.19	0.36	-
BBP	Burnt ash	58.2	24.91	11.41	1.45	1.15	0.31	0.79	-	0.26	0.49	0.98	0.05	-
BBS	Burnt ash	60.36	23.05	11.48	-	0.63	0.12	0.33	-	0.38	0.09	0.4	0.18	2.39
BBR	Burnt ash	46.97	36.1	10.23	3.3	1.03	0.18	0.05	-	0.86	0.35	0.35	0.37	-
CBP-550	550 ºC, 2 h	51.72	19.38	18.45	6.13	2.9	0.06	0.23	0.12	0.24	0.34	0.27	0.17	-
CBS-550	550 ºC, 2 h	50.72	21.26	19.44	4.17	2.33	0.25	0.09	0.08	0.4	0.28	0.63	0.33	-
CBS-550	3rd recycled catalyst	27.42	50.26	5.81	5.42	0.61	2.55	5.41	0.09	0.33	0.34	1.26	0.51	-
CBR-550	550 ºC, 2 h	50.48	20.59	17.57	7.43	1.65	0.13	0.11	0.38	0.42	0.14	0.66	0.44	-

BMCP- burnt *Musa champa* peel, BMCS- burnt *Musa champa* stem, BMCR- burnt *Musa champa* rhizome, CMCP-550- calcined *Musa champa* peel, CMCS-550- calcined *Musa champa* stem, CMCR-550- calcined *Musa champa* rhizome, SBCC- sugarcane bagasse calcined catalyst, BBP- Burnt Bharatmoni peel, BBS- Burnt Bharatmoni stem, BBR- Burnt Bharatmoni rhizome, CBP-550- Calcined Bharatmoni peel, CBS-550- Calcined Bharatmoni stem, CBR-550- Calcined Bharatmoni rhizome.

Table 6.3: BET surface area, pore diameter, pore volume, type of isotherm, porous type, pH value and basicity of catalysts.

Catalyst	**Surface area (m^2 g^{-1})**	**Pore diameter (nm)**	**Pore volume (cm^3 g^{-1})**	**Type of isotherm**	**Porous type**	**pH value (1:5 w/v)**	**Basicity (mmol g^{-1})**
M. paradisiaca peel	4.1	2.1	0.010	Type IV	Micro-mesoporous	13.39	1.43
M. paradisiaca trunk	6.4	2.6	0.014	Type IV	Micro-mesoporous	13.56	1.59
M. paradisiaca rhizome	7.0	2.1	0.006	Type IV	Micro-mesoporous	13.34	1.39
CMCP-550	6.848	2.327	0.018	Type IV	Micro-mesoporous	12.7	1.25
CMCS-550	1.388	2.246	0.004	Type IV	Micro-mesoporous	11.9	0.42
CMCR-550	0.876	2.587	0.003	Type IV	Micro-mesoporous	12.4	0.91
SBCC	7.66	2.479	0.014	Type IV	Micro-mesoporous	12.10	0.0891
CBP-550	2.061	4.059	0.008	Type IV	Mesoporous	13.17	1.36
CBS-550	0.730	3.459	0.002	Type IV	Mesoporous	13.56	1.45
CBR-550	0.857	2.976	0.002	Type IV	Mesoporous	12.87	1.26

Table 6.4: Comparison of catalytic activity of ash-based catalysts from agricultural waste in biodiesel synthesis.

Biodiesel feedstock	**Catalyst source (Ash)**	**Cal Temp (^oC)**	**Surface area ($m^2 g^{-1}$)**	**Parameters**				**Biodiesel, Y or C (%)**
				MTOMR	**Catalyst (wt. %)**	**Temp (^oC)**	**Time (min)**	
J. curcas oil	*M. paradisiaca* peel	550, 2 h	4.1	9:1	5	65	12	97.56 (Y)
J. curcas oil	*M. paradisiaca* trunk	550, 2 h	6.4	9:1	5	65	9	97.65 (Y)
J. curcas oil	*M. paradisiaca* rhizome	550, 2 h	7.0	9:1	5	65	14	95.67 (Y)
J. curcas oil	*M. paradisiaca* peel	Burnt	-	9:1	5	65	60	94.89 (Y)
J. curcas oil	*M. paradisiaca* trunk	Burnt	-	9:1	5	65	50	95.47 (Y)
J. curcas oil	*M. paradisiaca* rhizome	Burnt	-	9:1	5	65	60	94.57 (Y)
J. curcas oil	*M. champa* peel	550, 2 h	6.848	9:1	5	65	10	98.27 (Y)
J. curcas oil	*M. champa* stem	550, 2 h	1.388	9:1	5	65	60	97.78 (Y)
J. curcas oil	*M. champa* rhizome	550, 2 h	0.876	9:1	5	65	14	97.89 (Y)
J. curcas oil	*M. champa* peel	Burnt	-	9:1	5	65	45	96.70 (Y)
J. curcas oil	*M. champa* stem	Burnt	-	9:1	5	65	80	95.68 (Y)
J. curcas oil	*M. champa* rhizome	Burnt	-	9:1	5	65	50	96.20 (Y)
J. curcas oil	Sugarcane bagasse	550, 2 h	7.66	9:1	10	65	285	92.84 (Y)
J. curcas oil	Bharatmoni peel	550, 2 h	2.061	9:1	5	65	16	96.89 (Y)
J. curcas oil	Bharatmoni trunk	550, 2 h	0.730	9:1	5	65	12	96.97 (Y)

J. curcas oil	Bharatmoni rhizome	550, 2 h	0.857	9:1	5	65	18	96.53 (Y)
J. curcas oil	Bharatmoni peel	Burnt	-	9:1	5	65	30	96.19 (Y)
J. curcas oil	Bharatmoni trunk	Burnt	-	9:1	5	65	25	96.67 (Y)
J. curcas oil	Bharatmoni rhizome	Burnt	-	9:1	5	65	45	95.73 (Y)

Cal–calcination; MTOMR–methanol to oil ratio; wt–weight; min–minute; Temp–temperature; h–hour; C–conversion; Y–yield; MBUS–*Musa balbisiana* underground stem; MB–*Musa balbisiana*; MA–*Musa acuminata.*

Table 6.5: Catalysts reusability in biodiesel synthesis under optimal circumstances.

Catalyst	**Cycle of reaction**							
	Fresh catalyst		**1st cycle**		**2nd cycle**		**3rd cycle**	
	Time (min)	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**
M. paradisiaca trunk	9	97.65	45	95.53	85	93.97	115	91.23
M. champa peel	10	98.27	50	96.57	180	95.35	310	93.79
Sugarcane bagasse	285	92.84	475	89.76	690	83.65	-	-
Bharatmoni trunk	12	96.97	45	95.67	105	94.43	150	93.20

Table 6.6: Physicochemical properties of *J. curcas* biodiesel of this study.

Properties	**ASTM D6751**	**EN 14214**	***J. curcas* oil (*M. paradisiaca*)**	***J. curcas* oil (*M. champa*)**	***J. curcas* oil (Sugarcane bagasse)**	***J. curcas* oil (*Musa* AAA)**
Density at 15 ºC (g/cm^3)	NS	0.86–0.90	0.866	0.877	0.874	0.8757
Specific gravity	0.86–0.90	-	-	0.8797	0.854	-
Kinematic viscosity at 40 ºC (mm^2/s)	1.9–6.0	3.5–5.0	3.799	4.136	5.659	4.027
Cetane number	47 (min)	51 (min)	55.2	48.1		50.3
Cetane index	NS	NS	61.48	54.234	58.95	57.58
Pour point (ºC)	NS	NS	-6	0		0
CFPP (ºC)	NS	NS	-3	<4	-	<4
SN (mg KOH/g)	NS	NS	192.03	191.39	191.84	191.28
Iodine value (g I_2/100 g)	NS	120 (max)	58.87	73.70	70.24	76.70
API	36.95	NS	34.28	34.27	34.28	34.28
Diesel index	50.4	NS	71.50	66.99	67.98	66.08
Aniline point (ºF)	331	-	208.58	195.44	198.33	192.77
HHV (MJ/kg)	NS	NS	40.67	40.47	40.51	40.44

WCO–Waste cooking oil; NS–Not specified; max– maximum; min– minimum; CFPP–Cold filter plugging point; SN–Saponification number; API–American petroleum index; HHV–Higher heating value.

6.2 Conclusion

This research has demonstrated the preparation and utilization of the catalysts from post-harvest agricultural materials. This study has successfully established the production of biodiesel from *J. curcas* oil via transesterification reaction using the catalysts developed from *Musa paradisiaca*, *Musa champa*, sugarcane bagasse and Bharatmoni banana (*Musa* AAA) plants. The synthesized catalysts from different parts (fruit's peel, stem or trunk and rhizome) of the three banana species mentioned in this study are proven to be highly basic materials. The investigation achieved that the calcined (550 ºC) catalysts are found with more amount of potassium than the burnt ash material. The elemental composition analysis of this study has also proven that catalysts obtained from banana plants have more potassium concentration than the sugarcane bagasse catalyst. Based on the EDX, XPS, XRD and FT-IR characterization of the catalyst, it is clear that potassium in the form of oxides and carbonates plays a significant role in catalyzing the transesterification reaction in the production of biodiesel. According to this investigation, the optimum reaction conditions achieved are methanol to oil molar ratio of 9:1, catalyst loading of 5 wt. %, and a reaction temperature of 65 °C. Under optimum reaction conditions, among all the catalysts in this study, *Musa paradisiaca* trunk showed the best activity yielding 97.65 % of biodiesel in 9 min. Comparatively, the catalytic activities of calcined catalysts derived from the three banana species mentioned in this study do not show much difference. However, sugarcane bagasse catalyst showed the lowest activity, yielding 92.84 % in 285 min. The reactions catalyzed by sugarcane bagasse and a variety of mentioned catalysts prepared from the three banana species revealed the large difference in the rate of reaction because the sugarcane bagasse catalyst has a very low concentration of potassium in the form of carbonates and oxides (12.07 wt. % in EDX, 9.49 atomic % in XPS). In this investigation, the reusability of *M. paradisiaca* trunk and CMCP-550, CBS- 550 catalysts are found to be effective up to 3rd recycled with gradual decline of the biodiesel yield. The fuel specifications of the biodiesel produced in the present study are within the limits prescribed by international EN14214 and ASTM D6751 standards. Finally, the present study established that the heterogeneous solid base catalyst derived from agricultural post-harvest, specifically banana plants are the most appropriate raw material for catalysis to produce biodiesel. The present catalysts not only address the concerns associated with the use of homogenous basic or acid catalyst for the synthesis of biodiesel, but this study also discovered such a catalyst which is cost effective, possessing high catalytic activity, environmentally benign, non-toxic, easy to handle and use, and can be prepared in a relatively simple method.

6.3 Future scope of the work

(a) Current catalysts have been found to be effective in producing biodiesel on a laboratory scale. Therefore, using these catalysts, a study may be conducted to synthesize biodiesel for biorefinery scale production.

(b) In accordance with the characterization of the catalysts found in this work, research on the application of these catalysts in other organic synthesis can be done.

(c) The utilisation of current catalysts for the removal of organic dye may be investigated.

(d) This study suggests to explore other source or material from agricultural waste that occurs with high concentration of potassium carbonate and potassium oxide for the preparation of such a catalyst that can enhance the conversion rate of triglyceride into biodiesel.

(e) The investigation is required to be performed to avoid the deactivation of the catalyst by means of physical or chemical change.