UTILIZATION OF WASTE PLANT DERIVED MATERIALS AS HETEROGENEOUS BASE CATALYST FOR BIODIESEL SYNTHESIS

A THESIS

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Summary and Conclusion

6.1 Summary

In this study, four different waste/post-harvest plants viz. *H. fragrans*, *M. champa* peduncle, *S. indicum* and *B. nigra* were employed for the preparation of heterogeneous base catalysts. Their catalytic efficacies were studied in biodiesel synthesis from various oil feedstocks. The catalysts were prepared by burning the dried waste materials followed by calcination and characterized by XRD, FT-IR, BET, SEM-EDX, XPS and HRTEM techniques including the determination of pH values and basic strength.

The elemental compositions obtained from EDX and XPS analyses of all the catalysts under study are summarized **Table 6.1** and **Table 6.2**. **Table 6.1** reveals that potassium is present as the dominating metal compared to other metals. The EDX analysis showed that the highest potassium content of 56.13% was found in the catalyst derived from *B. nigra* followed by *M. champa* peduncle (51.93%), *S. indicum* (29.64%) and *H. fragrans* (19.05%) (**Table 6.1**). However, the XPS analysis exhibited the highest potassium content in *M. champa* peduncle (18.78 atomic %) followed by 15.19 atomic % in *H. fragrans*, 15.13 atomic % in *B. nigra* and 6.13 atomic % in *S. indicum* (**Table 6.2**). The FTIR and powder XRD analyses confirmed that the catalysts are mainly composed of alkali and alkaline earth metal oxides and carbonates. The BET surface area, pore diameter, pore volume, pH value and basicity of the prepared catalysts determined were summarized in **Table 6.3**.

The morphological analysis of the catalysts using SEM technique demonstrated non-uniform shapes and sizes of the particles. The FESEM images of *H. fragrans* (**Fig. 2.5**) catalyst showed clusters of particles with spongy microstructure of burnt ash catalyst which on calcination changes to sheet like layered structure of non-uniform shape and size (**Fig. 2.5 C, E**). The FESEM images of *M. champa* peduncle burnt ash (**Fig. 3.5** A) catalyst depicted clusters of agglomerated particles and the morphology remained intake on calcination (**Fig. 3.5**). The SEM images of *S. indicum* (**Fig. 4.5 A–C**) catalyst portrayed the agglomeration of particle with layered like sheets of different size. The SEM images of *B. nigra* (**Fig. 5.5 A–C**) catalyst also indicated agglomeration of particles forming layered like spongy fibrous microstructures.

The HRTEM images of *H. fragrans* catalysts showed irregular shape and size in burnt ash which changes to needle-like shaped crystals on calcination at 550 ^{o}C that deformed to agglomerated particles on increasing the calcination temperature to 850 ^{o}C (**Fig. 2.8**). The

HRTEM images of *M. champa* peduncle (**Fig. 3.7**) catalyst calcined at 550 °C exhibited the porous crystalline structure with an irregular shape. The TEM images of *S. indicum* (**Fig. 4.7**) showed that the particles are in irregular shapes with cylindrical and hexagonal structures with well-ordered porous materials. The TEM images of *B. nigra* catalyst (**Fig. 5.8**) indicated that the particles are of irregular size and shape with hexagonal, cylindrical and spherical. Mixed polycrystalline nature of all the catalysts under study was noticed from the SAED patterns, which are in well agreement with the results of XRD studies of the catalysts depicting the presence of oxides and carbonates of various metals.

The catalytic efficacies of all the prepared catalysts in biodiesel synthesis at ORCs are summarized **Table 6.4**. It can be seen that all the prepared catalysts are showing excellent catalytic activities in biodiesel synthesis with high product yields. **Table 6.5** is showing the reusability studies of the catalysts in biodiesel production and demonstrating gradual decrease in the catalytic activities in each cycle of the reaction. The decrease of efficiency was due to leaching of potassium (**Table 6.2)** during separation and regeneration of the catalyst. This may also be due to morphological changes of the catalyst during recycling process and probable coating of glycerol and methyl esters molecules on the surface of the catalyst that blocks the active sites of the catalysts.

The kinetics study of *M. champa* peduncle catalyst depicted the pseudo-first order pathway of the transesterification reaction. The activation energies of *H. fragrans* (32.31 kJ mol^{-1}), *M. champa* peduncle (50.63 kJ mol^{-1}), *S. indicum* (27.45 kJ mol^{-1}) and *B. nigra* (27.87 kJ mol^{-1}) catalysts were found within the range of 21–84 kJ mol^{-1} specified for the transesterification of vegetable oil to biodiesel [204,211,256,257]. The study of thermodynamic parameters of *M. champa* peduncle resulted in positive value of ΔH and negative ΔS indicating endothermic reaction and positive ΔG representing the non-spontaneous and endergonic reaction. The fuel properties of the produced biodiesels under study are summarized in **Table 6.6** and are found within the limit prescribed by international standards ASTM D6751 and EN14214.

Table 6.1: Comparative elemental compositions of the prepared waste plant derived catalysts studied by EDX technique

Ash catalyst	**Calcinations condition**	**Composition (%)**														
		Na	**K**	**Ca**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Mn**	**Fe**	**Zn**	**Sr**	**C**	**O**
H. fragrans	Burnt ash	–	14.69	3.05	1.31	0.50	2.99	0.80	–	1.32	–	–	–	–	38.95	36.37
H. fragrans	550 ^{o}C, 2 h	–	19.05	5.13	0.86	0.44	8.51	0.64	–	1.92	–	–	–	–	16.71	46.74
H. fragrans	850 ^{o}C, 2h	0.44	19.27	5.44	2.13	0.40	12.51	2.27	0.72	2.17	–	–	–	–	9.90	44.75
M. champa peduncle	Burnt ash	–	31.88	2.65	0.70	–	4.36	–	–	0.71	–	–	–	–	14.90	44.81
M. champa peduncle	550 ^{o}C, 2h	–	51.93	4.72	1.83	–	3.60	1.53	–	3.52	–	–	–	–	2.48	30.38
Sesamum indicum	550 ^{o}C, 2 h	1.42	29.64	33.80	9.68	–	11.32	–	–	–	0.80	1.70	0.54	11.09	–	–
B. nigra	550 ^{o}C, 2 h	0.94	56.13	26.04	2.86	–	5.37	–	–	–	0.05	1.26	1.63	5.72	–	–

Table 6.2: Surface elemental composition of the prepared waste plant derived catalysts studied by XPS technique

Catalyst		**Elemental composition (Atomic %)**											
		C 1s	**O 1s**	**K 2p**	**Ca 2p**	**Si 2p**	**Sr 3d**	**Mn 2p**	**Fe 2p**	**Zn 2p**	**Na 1s**	**Mg 1s**	**Cl 2p**
H. fragrans	Burnt ash	46.46	25.12	9.02	5.15	10.59	0.83	0.65	0.29	0.46	0.00	0.42	1.01
	550 °C	36.66	31.63	15.19	0.59	11.48	0.94	0.55	0.63	0.28	0.15	1.21	0.70
	850 °C	39.59	23.47	15.71	5.88	11.00	0.78	0.09	0.45	0.46	0.63	0.13	1.80
M. champa peduncle	Burnt ash	63.97	22.56	6.80	0.04	4.83	0.45	0.27	0.39	0.32	0.15	0.04	0.18
	550 °C	50.63	23.01	18.78	0.05	5.71	0.50	0.18	0.03	0.29	0.05	0.17	0.66
	3rd recycle	34.14	32.11	7.05	3.52	19.33	1.68	0.25	0.28	0.24	0.09	1.26	0.04
S. indicum	550 °C	22.78	52.53	6.13	5.27	8.33	0.27	0.25	0.26	0.2	0.48	3.08	0.43
	3rd recycle	33.97	47.46	1.14	6.21	5.29	0.4	0.15	0.17	0.16	0.14	4.9	0.01
B. nigra	550 °C	29.91	41.26	15.13	4.03	3.02	0.25	0.37	0.42	0.15	0.29	0.85	4.32
	3rd recycle	27.71	38.81	10.19	9.13	7.92	0.76	0.30	0.52	0.41	0.63	3.24	0.38

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

Catalyst		**BET surface area (m^2 g^{-1})**	**Pore diameter (nm)**	**Pore volume (cm^3 g^{-1})**	**pH value (1:5 w/v)**	**Basicity (mmol g^{-1})**
H. fragrans	Burnt ash	57.77	10.6	0.14	11.54	0.298
	550 °C	27.50	1.677	0.04	12.89	0.423
	850 °C	78.45	3.57	0.22	12.18	0.303
M. champa peduncle	550 °C	8.57	3.71	0.034	13.4	1.65
S. indicum	550 °C	3.66	1.677	0.012	11.4	-
B. nigra	550 °C	7.308	1.67	0.011	11.91	-

Table 6.4: Performance of the prepared catalysts in biodiesel synthesis at optimum conditions

Biodiesel oil feedstock	**Catalyst source**	**Cal Temp (°C)**	**Surface area (m^2 g^{-1})**	**Optimum conditions**				**Yield (%)**
				MTOR	**Catalyst (wt.%)**	**Temp (°C)**	**Time (min)**	
Jatropha	*H. fragrans*	550	27.50	12:1	7	65	65	97.75
Jatropha	*H. fragrans*	850	78.45	12:1	7	65	115	96.58
Jatropha	*H. fragrans*	-	57.77	12:1	7	65	110	96.61
Jatropha	*M. champa* peduncle	550	8.57	12:1	7	65	6	98.23
Jatropha	*M. champa* peduncle	0	-	12:1	7	65	13	96.22
Sunflower	*S. indicum*	550	3.66	12:1	7	65	40	98.9
Soybean	*B. nigra*	550	7.308	12:1	7	65	25	98.79
Jatropha	*B. nigra*	550	7.308	12:1	7	65	30	98.26
Thevetia peruviana	*B. nigra*	550	7.308	12:1	7	65	25	97.78

Cal–calcination; wt. –weight; Temp–temperature; MTOR–methanol to oil ratio; min–minute

Table 6.5: Reusability of catalysts in biodiesel synthesis at optimum conditions

Catalyst	**Cycle of reaction**							
	Fresh catalyst		**1st cycle**		**2nd cycle**		**3rd cycle**	
	Time (min)	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**
H. fragrans	65	97.75	115	96.23	165	95.63	215	90.22
M. champa peduncle	6	98.23	53	95.06	105	92.22	195	90.03
S. indicum	40	98.9	85	97.1	125	96.1	165	94.1
B. nigra	25	98.79	55	97.0	105	96.6	135	96.0

Table 6.6: Properties of the produced biodiesels of this study

Properties	**ASTM D6751**	**EN 14214**	**Jatropha oil (*H. fragrans*)**	**Jatropha oil (*M. champa* peduncle)**	**Sunflower oil (*S. indicum*)**	**Soybean oil (*B. nigra*)**
Density (15 °C, g/cm^3)	NS	0.86-0.90	0.878	0.8906	0.859	0.8606
Specific gravity (20 °C g/cm^3)	0.86-0.90	0.85	-	-	0.854	0.8615
Kinematic viscosity (40 °C, mm^2/s)	1.9-6.0	3.5-5.0	3.624	5.580	3.11	3.76
Cetane number	47 (min)	51 (min)	55.5	49.4	53.95	56.67
Cetane index	NS	NS	59.23	55.58	-	56.13
Acid value (mg of KOH/g)	0.50 (max)	0.50 (max)	-	0.364	-	-
Pour point (°C)	NS	NS	-6	0	-6	-3
CFPP (°C)	NS	NS	-3	< 4	-3	0
Saponification number (mg KOH/g)	NS	NS	191.64	189.06	188.57	176.33
Iodine value (g I_2/100 g)	NS	120 (max)	69.11	87.03	-	121.91
API	36.95	NS	34.28	34.278	34.277	32.756
Diesel index	50.4	NS	68.37	70.043	50.82	55.309
Aniline index	331	NS	199.47	204.342	148.27	168.85
Total sulphur	15 (max)	-	-	-	3	2
HHV (MJ/kg)	NS	NS	40.53	41.226	39.79	40.37

CFPP–Cold filter plugging point; min–minimum; max–maximum; NS–not specified; API–American petroleum index; HHV–higher heating value (calorific value).

6.2 Conclusion

The present study successfully developed four different heterogeneous base catalyst from *H. fragrans*, *M. champa* peduncle, *S. indicum* and *B. nigra* wastes. Catalyst preparation involves drying of waste plants followed by burning to ash and calcination. Both the burnt ash and calcined materials were investigated as catalyst in biodiesel synthesis from different oil feedstocks. XRD and FT-IR analyses depicted the presence of oxides and carbonates of alkali and alkaline earth metals in the prepared catalysts. EDX and XPS techniques confirmed the presence of higher percentage of potassium compared to other metals, which is acting as the main active component in the catalysis of biodiesel synthesis. Higher potassium content in the catalyst resulted in higher pH value, high basicity and subsequently higher catalytic activity.

In this study, a highly efficient basic heterogeneous catalyst from *H. fragrans* could be developed for the effective synthesis of *J. curcas* biodiesel. The burnt ash catalyst (BHC) becomes more active for the reaction when it is activated at 550 ^{o}C, however, the catalytic activity was found to decrease when it is further calcined at 850 ^{o}C (CC-850). The catalyst CC-550 which exhibited better performance in catalysis yielded a maximum biodiesel yield of 97.75 % in 65 min with TOF of 35.55 min^{-1} under the ORCs of 12:1 MTOR and 7 wt.% of catalyst loading at 65 ^{o}C. The better catalytic activity of CC-550 catalyst was because of its higher basic character (pH value of 12.89 at 1:5 w/v and basicity of 0.423 mmol/g) due to its high K content (19.05 wt.% in EDX, 15.19 atomic % in XPS). The carbonate (CO_3^{2-}) concentration (K_2CO_3) in the catalyst on increasing the calcination temperature to 850 ^{o}C may decrease due to the partial conversion or decomposition of K_2CO_3 to K_2O at the higher temperature (850 ^{o}C). This may also be one of the reasons for displaying the lower catalytic activity of CC-850 catalyst compared to CC-550 catalyst.

In this study, the catalytic activities of all the four catalysts calcined at 550^{o}C are in the order of *M. champa* peduncle > *B. nigra* > *S. indicum* > *H. fragrans* under ORCs of 12:1 MTOR, 7 wt.% of catalyst loading and 65 ^{o}C of reaction temperature. A high biodiesel yield of 98.23 % was achieved in short reaction time of 6 min using *M. champa* peduncle catalyst. The excellent and superior catalytic activity of *M. champa* peduncle catalyst was due to the existence of the highest amount of K (51.93 wt. % in EDX, 18.78 atomic % in XPS) in the form of oxide and carbonate with the highest basicity of 1.65 mmol g^{-1} and pH value of 13.4 at 1:5 (w/v). Thus, in this study, the K as an active species in the form of K_2CO_3 and K_2O played the key role for the excellent efficiency in the catalysis of biodiesel production.

In this study, all the catalysts were effectively reused up to 3rd cycle (4th run) with good yield of biodiesel (90.03–96.0 %). *B. nigra* catalyst was found to have the higher reusability character, yielding 96.0 % of biodiesel in 135 min at 4th run of reaction. The better reusability of *B. nigra* catalyst was attributed due to the leaching of low amount of K compared to others catalysts, which was confirmed by EDX and XPS analyses.

The kinetics study of *M. champa* peduncle catalyst depicted the pseudo-first order pathway of the transesterification reaction. The activation energies of the reactions with *H. fragrans* (32.31 kJ mol^{-1}), *M. champa* peduncle (50.63 kJ mol^{-1}), *S. indicum* (27.45 kJ mol^{-1}) and *B. nigra* (27.87 kJ mol^{-1}) catalysts were found within the range of 21–84 kJ mol^{-1} specified for the transesterification of vegetable oil to biodiesel. The study of thermodynamic parameters of *M. champa* peduncle resulted in positive value of ΔH and negative ΔS indicating endothermic reaction and positive ΔG representing the non-spontaneous and endergonic reaction. The fuel properties of all the biodiesels produced in this study were found within the limits of ASTM D6751 and EN14214 standards.

The raw materials for the preparation of the catalysts in this study are readily available and the cost of catalyst depends mainly on the energy spent for their production which may be considered very nominal. Thus, the catalysts developed have the advantages for reducing the production cost of biodiesel. Since the catalysts were derived from biodegradable raw materials, these are non-corrosive, easy to handle and green catalysts. Besides, large scale disposal of these catalysts after use would not produce any potential harm to the environment and society as well. Moreover, utilization of these wastes in a convenient way to the benefit of mankind as a part of waste management is highly encouraged and thus the present catalysts which are highly efficient green catalyst can be recommended as a potential candidate for biodiesel production at industrial scale in a cost-effective manner.

6.3 Future work

In view of the outcome of the catalysts developed in the present study, the following points may be considered for future works.

(a) A number of waste plant sources are found to be utilized in the preparation of *Khardwi*, a traditional highly alkaline food additive. Thus, further investigation of other catalyst sources may give us more efficient catalyst for biodiesel synthesis.

(b) The present study was carried out in laboratory scale setup. Thus, a pilot study for biorefinery scale production of biodiesel utilizing these catalysts may be undertaken.

(c) Leaching of active components during recycling of catalyst was noticed leading to decrease in catalytic activity. Thus, research leading to low-cost modification of the catalyst to prevent leaching can be carried out.

(d) Magnetization of the catalysts for smooth separation by magnetic method may ease the catalyst regeneration simpler.

(e) The catalyst may also be tested for other organic reactions.