Review

Waste Animal Bones as Catalysts for Biodiesel Production; A Mini Review

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Abstract: Slaughterhouse waste is considered to be an emerging issue because of its disposal cost. As an alternative, it would be a great prospect for the bioeconomy society to explore new usages of these leftover materials. As per food safety rules mentioned by EU legislation, all bone waste generated by slaughterhouses ought to be disposed of by rendering. The huge quantity of worldwide bone waste generation (130 billion kilograms per annum) is an environmental burden if not properly managed. The waste animal bones can be efficiently employed as a heterogeneous catalyst to produce biodiesel. This mini review summarized the recent literature reported for biodiesel generation using waste animal bones derived heterogeneous catalyst. It discusses the sources of bone waste, catalyst preparation methods, particularly calcination and its effects, and important characteristics of bones derived catalyst. It suggests that catalysts extracted from waste animal bones have suitable catalytic activity in transesterification of different oil sources to generate a good quality biodiesel.

Keywords: waste animal bones; heterogeneous catalyst; calcination; biodiesel; catalytic activity

1. Introduction

The enormous consumption of conventional fuels and the rising concerns of greenhouse gas emissions have shifted the trend of scientific community towards the exploitation of renewable energy sources [1]. It has become crucial and demanding to replace fossil fuels with comparable renewable fuels to avoid environmental anomalies which may become severe if exploration of alternate energy sources are ignored [2]. The global inclination toward the utilization of biofuels has gained great popularity in recent decades. Among biofuels, biodiesel is viewed as a main substitute for mineral diesel in many countries, as it is considered to be renewable, sustainable, and non-toxic in nature [3,4].

In general, biodiesel production is performed through the transesterification of oils, fats, or greases with low carbon alcohols, with the assistance of homogeneous basic or acidic catalysts [5]. The homogeneous base catalysts hold high catalytic effectiveness under mild conditions and, hence, are more frequently utilized as compared to acid catalysts [6]. Although, these homogeneous acidic or basic catalysts are very favorable in terms of biodiesel yield, but the complications associated with their corrosive nature for the reactors and their separation from the mixture advert the negative side of these catalysts. Moreover, water washing and purifications steps to attain the stipulated quality of fuel eventually lead to rather high production cost [7]. On the contrary, the usage of heterogeneous catalysts for biodiesel manufacturing emerges out to be more effective and feasible owing to their easy separation, and non-corrosive and eco-friendly nature [8]. The literature reports the application of acid and base heterogeneous catalyst displaying varying traits, respectively. The base catalyzed transesterification process is considered to be more striking owing to the concerns of extended reaction times and high reaction temperature involved in acid catalyzed transesterification [9,10]. Therefore, the process of exploring numerous categories of heterogeneous base catalysts have been carried out in the recent past, such as metal oxides, calcined hydrotalcite, supported alkali metals, and anion exchange resins [11–14]

Among base heterogeneous catalysts, calcium oxide (CaO) captures a great deal of admiration as a result of depicting properties such as high basicity, mild reaction conditions, cheap, higher biodiesel yield along with least solubility in fuel [15,16]. In the recent past, a number of investigators have shifted their focus to design and develop catalytic materials from cheap and waste renewable sources for improving the general sustenance of the process [16]. Waste materials containing calcium are extensively available in the world [16,17]. Furthermore, transforming waste into valuable materials is the best practice for managing waste [18–20]. These calcium rich waste materials involved waste animal bones, mollusk and eggshells, industry wastes, and furthermore based on their origin which can be potentially used as catalysts for biodiesel production [21]. In addition, Boro et al. [22] reviewed the waste shell extracted solid oxide as heterogeneous catalysts for biodiesel production. The application of previously mentioned Ca rich wastes as a heterogeneous catalyst possesses a substantial potential for biodiesel production: the synthesis of catalysts from these waste materials may avoid ecological damage and disposal issues, the Ca- based waste has moderate catalytic activity in transesterification, these waste-based catalysts can be synthesized at lower costs and hence, made the process more competitive.

The most effective method for controlling waste is to transform it into useful and valuable substances through ecofriendly processes [18–20]. Waste animal bones which cause land pollution can be effectively transformed into valuable materials, such as catalysts. These bones generally contain an alkaline metal oxides and other non-metals [12,23,24]. The major ingredients in bones are calcium and phosphorous which can be transformed into hydroxyapatite and beta tri calcium phosphate upon thermal calcination, indicating considerable catalytic activity [12]. In the past decade, the number of investigators catalysts derived from waste animal bones being effectively utilized in various applications [16,25]. Waste bones derived catalysts and their modified versions are being used for many reactions including synthesis of bioactive compounds, hydrogen and biodiesel production, organic synthesis, organic reduction reactions, oxidation of organic compounds, and treatment of environmental pollutants. Moreover, bone derived HAp could be used for oximes formation in an economical way [26]. In addition to the calcium and phosphorous majorly present in bone powder, it also contains other elements, such as Mg, Fe, B, Mn, Zn, Cu, K, Al, Sr, Na, etc. These ingredients serve as catalytic, structural, and electrochemical components in numerous applications. Furthermore, bones are utilized in food and biomedical sector due to their rich component. Waste bone derived HAp has further usage in drug delivery agents, adsorbents, chemical sensors, bio-ceramics, chromatographic lighting materials, and powder carriers [27].

The purpose of this study is to point up the waste generation particularly bone waste that could possibly be transformed into valued catalysts for biodiesel generation based on

the literature reported for waste bones involved catalysts to produce biodiesel. This mini review summarizes the recent literature reported for biodiesel production using a waste animal bones derived heterogeneous catalyst. It explores the sources of bone waste, catalyst preparation methods, recent literature reported for bone-based catalyst to produce biodiesel and some characteristics of waste animal bones derived catalysts. In addition, reaction mechanism and heterogeneously catalyzed process technology is also briefly discussed.

2. Sources of Bone Waste

With the rise of worldwide population, the fresh meat consumption has been increasing correspondingly each year. Therefore, the slaughterhouses and meat processing plants generate huge quantity of poultry, beef, goat, fish, and pork bones as a waste material which could be a bigger environmental challenge if not properly disposed. Approximately, 130 billion kg of waste animal bones have been generated each year by the slaughter industry, can be considered as an alarming environmental burden. More than 10% of this waste is merely produced by the European countries. The slaughtering of one animal generates 18% weight of waste bones in its total live weight. This generated waste is generally treated as slaughterhouse waste and is disposed in landfills and rendering plants which otherwise can be used commercially for useful purposes [28].

As per food safety rules mentioned by EU legislation [29], all bone waste generated by slaughterhouses ought to be disposed of by rendering. Although, the existing commercial rendering technique has three important effects for farming industries, slaughterhouses, and food production which are directly associated with high costs, raw material loss, and unsustainability of processes. Commercial scale rendering plants charge service dues for animal waste disposal and impose an additional cost for the slaughter industry. In Finland, meat producers paid at least 0.18 €/kg for bone waste disposal in 2017.

The portion of waste residue is again utilized as bone meal for animal feed, fertilizers, and animal food ingredients after rendering. Even though, the disposal charges for bones embody a major expenditure for the slaughtering, meat and fish processing industries [28].

3. Catalyst Preparation

There are different unit operations involved in catalyst synthesis, such as calcination, precipitation, forming operation, gelation, hydrothermal transformation, decantation, impregnation, crushing, filtration, and grinding washing, mixing, drying, activation [30–32]. The most prominent and simple method that has been utilized in biomass derived heterogeneous catalyst is calcination. It is basically a heat treatment of material without air in order to decompose a compound into smaller components. Calcination phase of material involves various processes such as elimination of chemically bonded H_2O or CO_2, texture alteration through sintering, active phase generation, structure modification, and stabilization of mechanical properties [30].

Calcination is performed within broad temperature range for instance, from 300 to 1000 °C, depending on the feedstock nature and type. At higher temperatures, carbonates in the organic compound will decompose into their oxides with the release of CO_2. Figure 1 demonstrates the generic method for the manufacturing of CaO/HAp-derived catalyst and supported catalyst extracted from waste animal bones [33].

The three-step procedure may be applied for the synthesis of supported heterogeneous base catalyst which involved calcination followed by wet impregnation and then activation, as indicated in Figure 1. First step involved the calcination process of material at a specific temperature. In the second step, wet impregnation is carried out using active metal precursor blend with the heat-treated specimen in an aqueous solution to yield supported catalyst. Generally, high basic strength metal salts and oxides are utilized in wet impregnation. Upon impregnation, the metal salt will begin to disperse in the pores of the catalyst support. Subsequently, the impregnated specimen would then thermally be activated to eliminate moisture and volatile matter along with the deposition of metal salt on the catalytic surface. This modified catalyst possesses high catalytic activity owing

to the improvement in its basic strength [33]. Moreover, transformation of waste animal bones into bone ash via thermal calcination is shown in Figure 2.
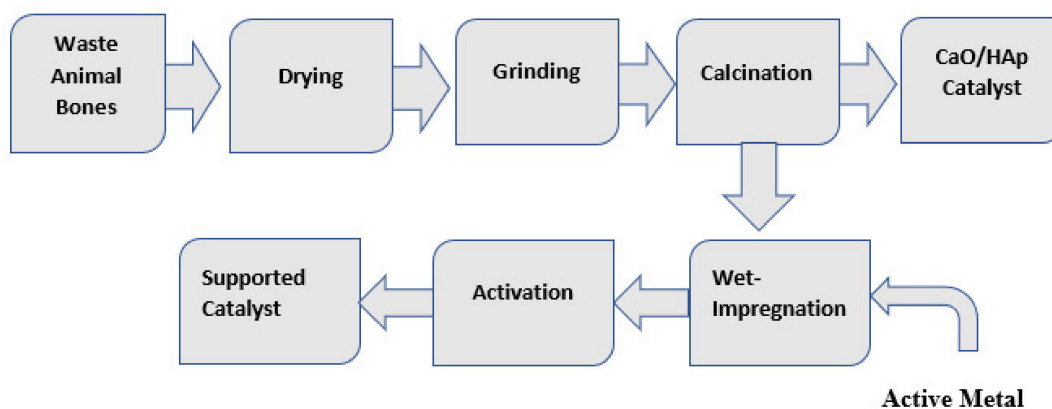
Figure 1. The generic practice for the manufacturing of CaO/HAp-derived catalyst/Supported catalyst.
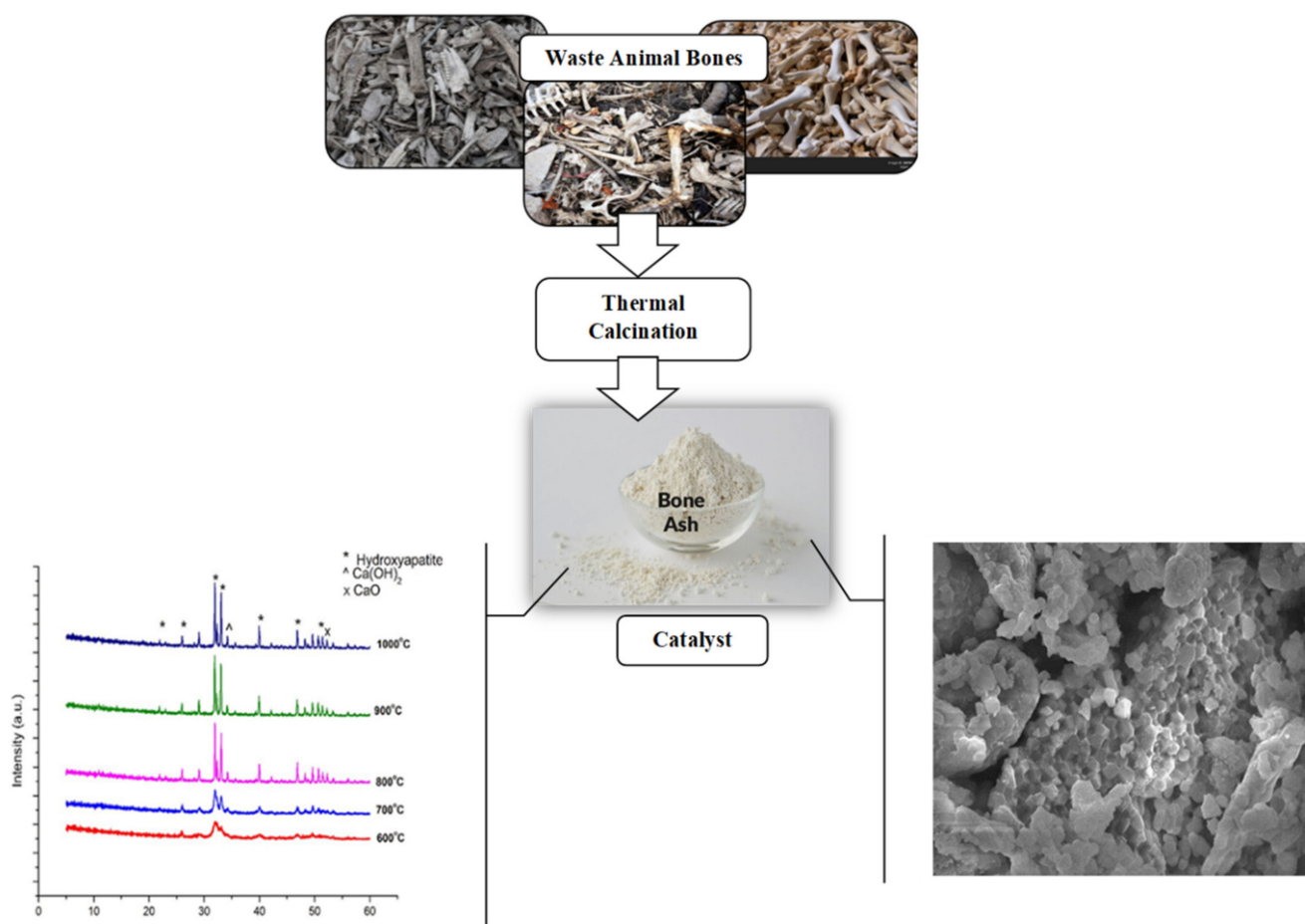
Figure 2. Conversion of waste animal bones into catalyst.

3.1. Effect of Calcination Temperature on Bones Derived Catalysts

The formation of CaO/HAp/beta tri-calcium phosphate and growth of surface structure of catalyst is predominantly associated with temperature at which sample is calcined. The total surface area of synthesized catalyst is reflected by the size of developed particles owing to the non-porous nature of bones. Therefore, the calcination temperature strongly affects the catalytic activity which is associated with the active site density [33].

Obadiah et al. [34] revealed the influence of different calcination temperature of sheep bone derived HAp catalyst for biodiesel production. As per their investigation, higher calcination temperatures are favorable with respect to catalytic activity and biodiesel yield, owing to the desorption of CO_2 within bone sample generating more basic sites. The highest FAME yield of 96.78% was achieved at the calcination temperature of 800 °C.

The effect of different calcination temperatures of bovine bone waste derived catalyst have been stated by Smith et al. [35]. It was analyzed that calcined bone samples within temperature range of 350–550 °C did not indicate any positive effect on biodiesel yield, suggesting the mentioned temperature range may not possess enough energy for the conversion of carbonates into their respective oxides. Higher calcination temperatures within the range of 650 to 950 °C assured the CaO existence in the bone specimen which led to the increment in biodiesel yield. In addition, higher calcination temperatures below 950 °C generated additional voids on the catalyst surface led to rise in the total pore diameter and volume of catalyst along with yield improvement. Although, drastic reduction in catalytic activity was observed with the additional rise of calcination temperature above 950 °C which might be owing to low pore volume and existence of micro pores. It may lessen the approachability of reactants to the active sites on the catalyst surface.

Nisar et al. [15] reported the influence of calcination temperature on KOH modified animal bones were calcined within a wide range of temperature (200–1000 °C). Above 600 °C, no significant change in catalytic activity was observed. The highest biodiesel yield was attained at the calcination temperature of 900 °C. It could be due to the increase in crystallinity and active site density of the catalyst with the rise in calcination temperature. Moreover, further rise in calcination temperature up to 1000 °C put down the catalytic activity due to high sintering rate. Therefore, the higher calcination temperatures lead to collapsing of structure and generation of new inactive phases in catalyst that extremely affect the catalytic activity.

Furthermore, the calcination holding time also has substantial influence on metal oxide surface development in case of bone derived heterogeneous catalyst. The short holding time may not be effective because of underdeveloped metal oxide surface resulted in lowering the catalytic activity. Therefore, longer holding time is needed to confirm the entire transformation of $CaCO_3$ into its oxide. On the other side, the extended calcination process may cause sintering of the particles that activate contraction of the catalyst grains [36].

3.2. Effect of Calcination Temperature on Surface Area of Bones Derived Catalysts

The catalytic surface area is a substantial role-playing factor in catalytic activity of any catalyst. The effect of calcination temperature on the surface area of catalyst is strongly dependent on waste source. For example, Farooq et al. [37] conveyed that the surface area of uncalcined chicken bones was 5.25 m^2/g. Upon calcination, the surface area of chicken bones derived catalyst began to rise. The highest surface area of 120.02 m^2/g was observed at the calcination temperature of 1000 °C. On the contrary, the calcination of bovine bones derived heterogeneous catalyst above 650 °C did not indicate the significant improvement in catalytic surface area. That was merely 2–3 m^2/g showing loss of pore volume and crystallite sintering [35]. In another study, Li doped chicken bones-based catalysts indicated reduction in surface area from 8.62 to 2.58 m^2/g on the increment of calcination temperature from 750 to 900 °C. The reduction in surface area might be because of the sintering process and changing in phase crystallization [38]. In case of calcined sheep bones derived heterogeneous catalyst, substantial increase in surface area (from 6.8 to 885 m^2/g) was observed with an increment in calcination temperature [34]. This variable trend of surface area with the calcination temperature may be due to the different methodologies bone preparation prior to calcination.

3.3. Effect of Calcination Temperature on Total Basicity of Bones Derived Catalysts

The calcination temperature also strongly influences the total basicity of catalyst [39]. Chen et al. [40] reported that the total basicity of potassium doped calcined pig bones (30 K/HAp) started to rise from 10.8 to 13.2 mmol/g with the rise in calcination temperature from 500 to 600 °C and then reduced from 13.2 to 9.8 mmol/g with the further increment in calcination temperature at 750 °C. In another investigation, chicken bones derived heterogeneous catalyst showed the maximum basicity at the calcination temperature of 900 °C in comparison with catalysts synthesized at 800 and 900 °C [37]. It suggests that the maximum value of total basicity would be achieved at the optimum calcination temperature depending upon the bone source.

4. Diverse Animal Sourced Bone-Based Catalysts and Their Biodiesel Yields

The numerous authors have reported the effective catalysts derived from different animal bones including sheep, chicken, goat, pig, bovine, fish, ostrich, guinea fowl, and fusion of bones for biodiesel generation as indicated in Table 1. For instance, the HAp derived from sheep bones at the calcination temperature of 800 °C displayed 96.78% yield for palm oil based biodiesel at the reaction temperature of 65 °C [34]. Similarly, in another study, sheep bone derived catalyst at the calcination temperature of 600 °C (calcined for 8 h) depicted more than 95% yield for canola oil based biodiesel at the reaction temperature of 60 °C [41]. In another similar investigation, bovine bone derived catalyst upon calcination at 750 °C for 6 h showed 97% yield for soybean oil based biodiesel at the reaction temperature of 65 °C [35]. The previously mentioned investigations present that bone derived catalysts, upon calcination, may provide significant biodiesel yields from different oil sources and hence, assures the suitability of waste bones-based catalysts for energy generation. In addition, the reaction time for biodiesel production can be substantially reduced upon utilizing microwave and ultrasonic assisted technologies using bones-based catalysts as reported in literature. For instance, pork bone derived catalyst offered 94% yield within 5 min in microwave assisted transesterification for Jatropha Cucras oil based biodiesel [42]. Similarly, in another place, ultra-sonic assisted transesterification yielded more than 95% biodiesel within 32.08 min (reaction time) in the presence of chicken bone derived catalyst [43]. Moreover, biodiesel yield can be further enhanced along with the reduction in reaction time by modifying the bone derived catalyst through wet impregnation or loading with active metals which may increase the effectiveness of catalyst. For example, pig bone derived catalyst loaded with K depicted greater than 96% biodiesel yield within 90 min of reaction time [40]. Similarly, catalysts derived from fusion of bones have also been reported in the literature [44]. In another study, waste animal bone derived novel layered heterogeneous catalyst has been synthesized in two step process involving calcination followed by hydrothermal reaction for getting better biodiesel yields [45].

Table 1. Various animal sourced bone-based catalysts and their biodiesel yields.

Animal bone	Catalyst Synthesis	Catalyst	Feedstock	Reaction Conditions (M/O, Catalyst wt%, Time, Temperature)	Yield	References
Waste animal bone	Calcined at 900 °C and soaked in KOH solution	HAp/KCaPO$_4$	Jatropha oil	9, 6, 180, 70 ± 3	96.1	[15]
Sheep bone	Calcined at 800 °C	HAp	Palm oil	18, 20, 240, 65	Y = 96.78	[34]
Chicken bone	Calcined at 900 °C for 4 h	β-Ca$_3$(PO$_4$)$_2$	Low FFA WCO	15, 5 g, 240, 65	Y = 89.33	[37]
Pig bone	Calcined at 900 °C for 4 h, 30 wt.% K$_2$CO$_3$ loaded, and calcined at 600 °C	K/HAp	Palm oil	9, 8, 90, 65	Y = 96.4	[40]
Bovine bone	Calcined at 750 °C for 6 h	CaO	Soybean oil	6, 8, 180, 65	Y = 97	[35]
Fish bone	Calcined at 900 °C for 2 h	H$_2$SO$_4$, β-Ca$_3$(PO$_4$)$_2$	WFO	6.5, 1.5, 120, 55	Y > 96	[46]
Fish bone	Calcined at 997.42 C for 2 h	β-Ca$_3$(PO$_4$)$_2$	Soybean oil	6.27, 1.01, 300, 70	Y = 97.73	[47]
Fish bone	50 wt.% Cu(NO$_3$)25H$_2$O impregnated, 90 °C freeze drying temperature, and calcined at 500 °C for 4 h	Cu/HAp	Oleic acid	/,/, 60, 70	C = 91.86	[48]
Goat bone	Calcined at 800 °C soaked in KOH	K/CaO	WCO	9, 6, 300, 65	Y = 84	[49]
Ostrich bone	Calcined at 900 °C for 4 h	HAp	WCO	15, 5, 240, 60	Y = 90.56	[50]
Waste animal bone	Calcined at 900 °C for 2 h	HAp	Peanut oil Rapeseed oil	20, 18, 240, 60	Y = 94 Y = 96	[51]
Chicken bone	Calcined at 800 °C for 4 h	β-Ca$_3$(PO$_4$)$_2$	E. compressa algal oil	9, 5, 180, 65	Y = 94	[52]
Pork bone	Calcined at 900 °C for 2 h	β-Ca$_3$(PO$_4$)$_2$	Jatropha Curcas oil	18, 4, 5, 800 W	Y = 94	[42]
Sheep bone	10 mass% of calcined animal bone powder loaded catalyst on fly ash through wet impregnation and calcined at 900 °C for 2 h	β-Ca$_3$(PO$_4$)$_2$	Mustard oil	5.5, 10, 360, 65	Y = 90.4 o	[53]
Chicken bones	Li/Zn loaded chicken bones and calcined at 850 °C for 4 h	Li/Zn-chicken bones	Waste canola oil	18, 4, 210, 60	Y = 98	[54]
Fish bone	NaOH loaded over bone calcined by a hydrothermal process at 200 °C for 12 h.	Na/HAp	Waste palm oil	9, 2.5, 90, 65	Y = 98	[55]
Cow bone	Calcined at 800 °C	HAp	Soybean oil	9, 15, 180, 55	Y = 92.2	[56]
Guinea fowl bone	Calcined at 900 °C for 5 h	β-Ca$_3$(PO$_4$)$_2$	Annona squamosa L. seed oil	18, 4, 20, 65, 800 W	Y = 95.82	[57]
Cow bone	Calcined cow bones (900 °C for 5 h) and impregnated with sodium nitrate by wetness impregnation method	Sodium-supported nHAP	Schizochytrium oil	12, 9.5, 121,/	Y = 96	[58]

Table 1. *Cont.*

Animal bone	Catalyst Synthesis	Catalyst	Feedstock	Reaction Conditions (M/O, Catalyst wt%, Time, Temperature)	Yield	References
Fish bone	Calcined at 900 °C for 4 h and supported on polyvinyl alcohol (PVA)	CaO/PVA	Palm oil	20, 10, 180, 65	Y = 80.4	[59]
Sheep bone	Calcined at 600 °C for 8 h	CaO/HAp	Canola oil	12, 5, 300, 60	C = 95.18	[41]
Turkey bone	Calcined at 909.4 °C for 4 h	β -Ca$_3$(PO$_4$)$_2$	Mustard oil	9.9, 4.97,/, 65	Y = 91.2	[60]
Chicken bone	Calcined at 800 °C for 3 h	Ca-Fe$_2$O$_3$	WCO	6, 3, 180, 65	Y = 22	[61]
Waste bovine bone	Calcined at 750 °C for 4 h		WCO	15.49, 6.42, 128.67,/	Y = 97.59	[62]
Pig bone	Calcined at 1000 °C for 4 h and CaO-CeO$_2$/HAp catalysts were prepared using wet impregnation technique	30%CaO-CeO$_2$/HAp−650	Palm oil	9, 11, 180, 65	Y = 91.84	[63]
Fusion of chicken and fish bone	Calcined for 4 h in air environment to 1000 °C at a heating rate of 3 °C/min	CaO/HAp	UCO	10, 1.98 w/v, 92.4, 65	Y = 89.5	[44]
Cow bone	Calcined at 800 °C for 4 h for FFA esterification reaction	HAp	WFO	12, 10, 240, 70	C = 96	[18]
Chicken bone	Calcined at 900 °C for 4 h	HAp	Celtis australis L. oil	10.45, 5.69, 32.08,/(Ultrasonic)	Y = 95.1	[43]
Goat bone	Calcined at 900 °C for 3 h	CaO	Algae oil	11, 2, 180, 60	Y = 92	[64]
Goat bone	Calcined at 800 °C for 2 hand refluxed in distilled water for 24 h and recalcined at 900 °C for 2 h	CaO	Mixed Elengi and Pongamia Oil	60 mL/200, 0.5, 240,/	Y = 82.3	[65]
Bovine bone	Loadings of 12-tungstophosphoric acid (TPA) were varied 117 (0–30 wt.%), with the specimen gained in each case subjected to calcination at 750 °C for 6 h	Tungsten/HAp	WCO	6, 8, 300, 100	Y = 98.9	[66]

Note: M/O: methanol/oil, Catalyst (wt%), Time (min), Temperature (°C).

4.1. Reaction Parameters Study

The biodiesel yield in transesterification reaction is strongly altered by reaction parameters, such as methanol to oil ratio, catalyst weightage, and temperature of the reaction mixture. The transesterification reaction is reversible in nature; therefore, excess amount of methanol is needed to drive the reaction equilibrium forwardly and biodiesel yield would be increased [40]. The generation of methoxy species on the catalyst surface is promoted in the presence of excess methanol and hence, biodiesel is enhanced [34]. If amount of methanol beyond the optimum value is employed in reaction that will not enhance the conversion rather add cost for excess methanol recovery. This might be due to the reason figure that the excessive methanol beyond the optimum value would begin to dissolve in glycerol generated during reaction which may hinder the methanol reaction to the oil and catalyst [67]. Similarly, biodiesel yield is also affected by the catalyst loading. The biodiesel yield is increased with the enhancement in the amount of catalyst. This suggests that more catalyst amount may provide more active sites for the reaction which is directly associated with the conversion [68]. However, further increment in catalyst quantity beyond a certain optimum value would rather reduce the FAME yield. Excessive catalyst amount may enhance the viscosity of reaction mixture and some catalyst quantity may not be properly utilized because of mass transfer resistance, therefore, lowering the biodiesel yield [69]. The third dominant factor that influences the biodiesel yield is the reaction temperature. The optimum reaction temperature is essential to knock over the diffusion resistance created between three phases of heterogeneously catalyzed system to achieve good conversion [37]. In general, biodiesel yield enhances with the increase in temperature due to endothermic nature of reaction. High temperature promotes the collisions between the reactant molecules thereby increases the mass transfer and miscibility [70,71]. Instead, high temperature beyond the optimum value may lower the biodiesel yield owing to the vaporization of methanol [72,73]. In the previous section, the optimum reaction conditions with maximum biodiesel yield reported in literature using bones derived heterogeneous catalysts are presented in Table 1.

### 4.2. Elemental Composition of Waste Animal Bones

Bones majorly contain calcium and phosphorous components that can be transformed into calcium oxide, hydroxyapatite, and beta-tricalcium phosphate upon calcination which are catalytically active and can be employed as catalyst to generate biodiesel. The nature of bone source strongly affects the catalytic properties as different bone sources may display different elemental composition with respect to the major and minor elements (Table 2). As reported in the literature, some biotic influences, such as breeding and nutrition, substantially affect the elemental composition of bones [74]. For instance, the composition of fish bone calcined at 900 °C varied significantly from that of chicken bones at the same calcination temperature, as indicated in Table 2. Similarly, elemental composition of natural HAp obtained from pig and bovine bones has been reported differently by Haberko et al. [75]. Besides, varied composition of pork bone-derived HAp with respect to major and minor elements, has been reported by Buasri et al. [42]. Hence, the natural source derived HAp may possess varied elemental composition which may alter the catalytic properties such as basicity, surface area, etc. It can be deduced that the biodiesel yield using bones extracted heterogeneous catalyst could be varied depending upon the nature of bone source.

Table 2. Elemental composition of various animal source bone derived catalysts

Elements	Calcined Fish Bone (Salmo salar) [76]	Calcined Cow Bone [77]	Calcined Chicken Bone [78]	Calcined Bovine Bone [79]	Calcined Ostrich Bone [50]	Calcined Sheep Bone [53]
	(900 °C)	(950 °C)	(900 °C)	(800 °C)	(900 °C)	(900 °C)
Ca	38.43	27.71	53.58	64.92	60.0	29.79
P	19.08	16.39	40.99	31.53	12.8	9.2
Mg	0.43	0.31	0.813	1.36	0.8	0.48
Na	0.30	0.31	0.196	1.91	0.4	-
K	0.08	0.04	0.028	0.091	0.01	5.22
Sr	0.08	0.02	0.053	0.086	0.1	-

4.3. XRD Analysis of Bones Derived Catalysts

As mentioned earlier, the major components present in the calcined bone samples are CaO, hydroxyapatite, $Ca(OH)_2$, and β-$Ca_3(PO_4)_2$. The XRD analysis of fusion of calcined chicken and fish bones have been indicated in Figure 3 [44]. The major characteristic peaks of CaO were observed in the samples calcined from 800 to 1000 °C. Similarly, the other peaks of hydroxyapatite and $Ca(OH)_2$ have also been appeared in the calcined samples of chicken-fish bone fusion (Figure 3). Similarly, in another study, the major peaks of hydroxyapatite have been appeared in the calcined samples of ostrich bones derived catalyst along with the peaks of CaO and $Ca(OH)_2$ [50]. The appearance of calcium hydroxide may be owing to the hygroscopic nature of CaO. In addition, it has been reported that HAp present in calcined bones may potentially transform into beta tricalcium phosphate which acts as an active catalyst in transesterification reaction [37].
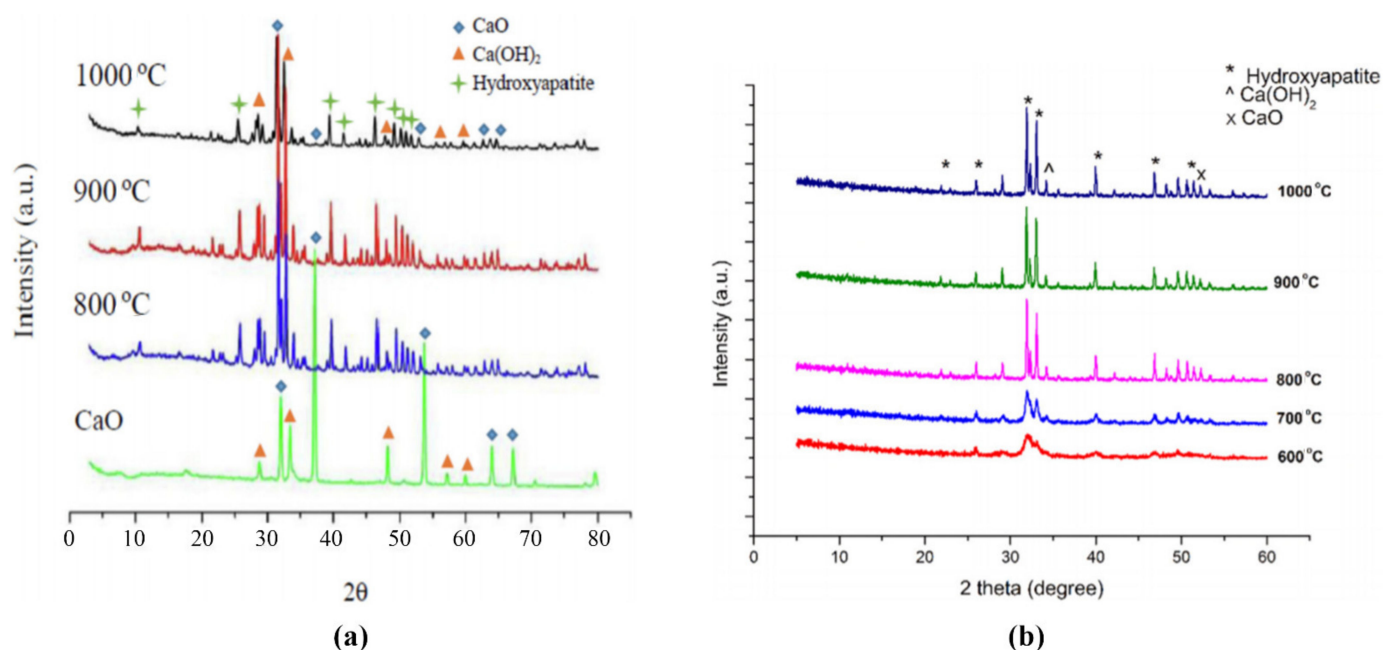
Figure 3. XRD analysis (**a**) fusion of chicken and fish bone, (**b**) ostrich bone.

4.4. Reaction Mechanism

The transesterification reaction arises on the surface of the active components of the catalyst, such as HAp/β-$Ca_3(PO_4)_2$/CaO. In the first step, methanol dissociates, and formation of methoxide anion takes place. In the second step, the carbonyl carbon of oil attracts the methoxide anion attached to the surface of catalyst to form tetrahedral intermediate [80]. Afterward, the tetrahedral intermediate reorders itself to form FAME and

diglyceride anion. In the last step, a hydrogen ion attached with the catalyst surface attacks oxygen of the diglyceride anion to generate diglyceride molecule along with regeneration of catalyst. The previous reaction stages are then repeated with diglyceride to generate monoglyceride and another mole of biodiesel. Lastly, monoglyceride reacts with another surface methoxide in the same way as described earlier to generate a total three moles of biodiesel and one mole of glycerol.

4.5. Bones Derived Catalyst Reusability

Bones derived heterogeneous catalysts are considered to be reusable for multiple runs in transesterification. Numerous researchers have reported the excellent reusability of bones-based catalysts up to five to six consecutive runs. For instance, Farooq et al. [37] reported the excellent reusability of chicken bones derived catalyst for four consecutive runs. Similarly, Obadiah et al. [34] reported the waste animal bone derived catalyst reusability up to five consecutive runs with more than 80% of biodiesel yield. On the other side, bone fusion-based catalyst has been outlined as reusable up to four consecutive runs in transesterification without any major yield loss [44]. The good reusability of waste bone derived catalysts favor the commercial suitability of bone waste as a catalyst for biodiesel production.

4.6. Heterogeneously Catalyzed Technology in Biodiesel Production

Up to the present time, most of the commercial biodiesel production involves homogeneous catalyzed process technology. However, trend of heterogeneous catalyzed process technology has been evolving by the several leading technology companies. For instance, novel heterogeneous catalyst-based biodiesel refinery has been developed by Benefuel, Inc. in Seymour, U.S [81]. Biodiesel plant having capacity of 160,000 tons per year is located in Sete, France, which is based on the heterogeneous catalyzed process technology. Similarly, 8000 MT per year capacity biodiesel plant has been developed in Malaysia by Biofuel, Ltd. cooperated with Incbio [82]. Due to the benefits associated with heterogeneously catalyzed technology, there is a need to promote its commercial development and suitability. It would be greatly beneficial if a heterogeneous catalyst, synthesized from waste sources such as waste animal bones, is abundantly available each year.

5. Conclusions

Each year, billions of kilograms of animal bone waste is generated that is either rendered or disposed to avoid environmental concerns. This bone waste can be potentially employed as a catalyst for energy production in a sustainable way. This mini review aimed to highlight the suitability of waste animal bones as an effective heterogeneous catalyst for biodiesel generation. Numerous researchers have investigated the catalytic activity of different waste animal bones such as chicken, goat, cow, pig, fish, ostrich, and even a fusion of bones for biodiesel production. It suggests that calcination is the most suitable method for transforming bone waste into a valuable catalyst. HAp/β -$Ca_3(PO_4)_2/CaO$ components present in the calcined bones serve as a catalyst. The parametric optimization is required to maximize the biodiesel yield using waste bone derived catalysts. In addition, some investigators modified the catalysts through metal impregnation methods to advance the overall effectiveness of catalysts. It concludes that all types of waste animal bones can be efficiently utilized as a heterogeneous catalyst for biodiesel production. The need of the hour is to evaluate commercial suitability of biodiesel generation employing waste animal bones derived heterogeneous catalysts as that would be a renewable energy source possessing additional benefit of environmental protection.

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