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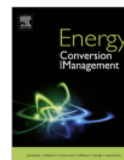
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ABSTRACT

For many years, the cost of production has been the main barrier in commercializing biodiesel, globally. It has been well researched and established in the literature that the cost of feedstock is the major contributor. Biodiesel producers are forced to choose between edible and non-edible feedstock. The use of edible feedstock sparks concern in terms of food security while the inedible feedstock needs additional pretreatment steps. On the other hand, the wide availability of edible feedstock guarantees the supply while the choice of non-edible results in a non-continuous or non-ready supply. With these complications in mind, this review attempts to identify possible solutions by exploring the potential of waste edible oils and waste catalysts in biodiesel preparation. Since edible oils are available and used abundantly, waste or used edible oils have the potential to provide plentiful feedstock for biodiesel. In addition, since traditional homogeneous catalysts are less competent in transesterifying waste/used oils, this review includes the possibility of heterogeneous catalysts from waste sources that are able to aid the transesterification reaction with success.

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1. Introduction

The European Union (EU-27) itself recorded over 22 million tonnes of biodiesel in 2011 (9.5 million tonnes in 2010) (European Biodiesel Board), while the US alone produced 1.1 billion gallons (approximately 3.7 million tonnes) of biodiesel in 2011. Whereas Europe uses rapeseed as a major biodiesel lipid feedstock, the US utilizes oil from soybean for this purpose. Notwithstanding these differences, it is certain that the production volume of biodiesel is in an increasing trend in both the EU as well as the US, thereby indicating the relevancy of biodiesel as one of the renewable fuels in the near future. Specifically, the trend also indicates the need for large amounts of vegetable oil supply and if the major portion of the oil comes from neat edible oil then the question of food starvation arises. The concern in respect of food starvation or food for fuel already constitutes a heated argument. With the increasing need for oil in the near future, it will definitely complicate the situation, as globally, we have a total of 925 million people undernourished; reported by the Food and

Agriculture Organization of the United Nations in 2011 [1]. To counter this state of affairs, one of the possible ways to lessen the impact is by exploring the use of waste/used edible oils to produce biodiesel.

The utilization of waste/used edible oils as a raw material is a relevant idea, and there are many advantages for using waste feedstock for biodiesel production: (i) abundant supply, (ii) relatively inexpensive, and (iii) environmental benefits. Waste oil in many countries is in abundance. It was reported that, annually, EU recorded 0.7–1.0 million tonnes of waste oil, Turkey 350,000 tonnes and Canada 120,000 tonnes, in addition to those uncollected oils, which goes to waste through sinks and garbage and eventually seeps into the soil and water sources [2]. Furthermore, it is generally accepted that reusing used cooking oil for human consumption is harmful to health [3].

The utilization of oil and catalyst from waste sources could also counter the environmental damage. Furthermore, within the last 5 years, many research works have focused on the exploitation of waste materials as catalysts for the production of biodiesel. They include shells, ashes, rock, and bone. Due to their abundance and low cost, the exploitation of such waste materials has become very attractive.

In view of this, a comprehensive report on the utilization of feedstock and catalysts from waste is presented in this review and tabulated, as shown in Table 1 [4–18] and Table 2 [19–42].

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Table 1
Comparison of reaction conditions and performance of various types of feedstock from waste sources in the production of biodiesel.

Feedstock from waste sources	Physical properties			Cat.	Reaction conditions			Conv. (C) or Yield (Y) (%)	Feedstock pretreatment	Ref.	
	WC	SV	AV		T (°C)	MeOH:Oil (mol:mol)	Cat. (wt%)				t (h)
<i>Homogeneous base catalyst</i>											
WSCO	0.42	188.20	–	KOH	87	90%	6	2	Y > 80	Heated at 122 °C	[4]
Mixtures	WFO = 0.05	–	–	WFO = 0.82	90	6:1	0.8	1	Y = 88	WFO = vacuum filtered, dehydrated with Na ₂ SO ₄ anhydrous.	[5]
WFO and PL	PL = 0.03	–	PL = 0.71	–	–	–	–	–	–	PL = heated at 100 °C	
Animal fat (PL, BT, CF)	–	–	–	NaOH	65	6:1	0.4	0.5	C (PL = 98.7%, BT = 98.8%, CF = 99.4%)	–	[6]
<i>Homogeneous acid catalyst</i>											
WCO	–	–	75.92	H ₂ SO ₄	95	20:1	4	10	C > 90	Filter	[7]
WCO	–	–	–	H ₂ SO ₄	80	162:1	1.9	4	Y = 98.9	–	[8]
WCO	–	–	–	–	70	245:1	3.8	4	Y = 99	–	
<i>Two-step: Acid-esterification (A) catalyst followed by base-transesterification (B) catalyst</i>											
WCO	–	–	75.92	Ferric sulfate Followed by KOH	95 (A) 65 (B)	10:1 (A) 6:1 (B)	2 (A) 1 (B)	4 (A) 1 (B)	C = 97.2	Filter	[7]
UFSO	–	–	–	H ₂ SO ₄ followed by NaOH	50 (A) 60 (B)	0.3:1 (A) (v/v)	0.75 (A) 1 (B)	1 (A) 4 (B)	Y = 97	2 L water added and heated over anhydrous Na ₂ SO ₄	[9]
<i>Heterogeneous base catalyst</i>											
WPFO	–	–	–	EFBA	60	18:1	5.35	0.5	Y = 71.7	Heated at 120 °C	[10]
WCO	0.65	223.6	7.70	K ₂ PO ₄	60	6:1	4	2	Y = 97.3	–	[11]
SBC	–	–	–	CaO	65	0.5:1 (wt/wt)	6	2.5	C = 98.6	–	[12]
WCO	0.00	–	5.08	Sr/ZrO ₂	115.5	29:1	2.7	2.8	Y = 79.7	–	[13]
<i>Heterogeneous acid catalyst</i>											
WCO	–	–	30	ZS/Si	200	18:1	3	10	Y = 98	–	[14]
WCO	1.9	207	3.6	TiO ₂ –MgO	160	50:1	10	6	Y = 92.3	Heated at 120 °C	[15]
<i>Enzymatic catalyst</i>											
WPFO	0.9	–	0.1	Novozym 435	40	4:1	4	12	Y = 88	–	[16]
WCO	–	191	54.3	Immobilized <i>Penicillium expansum</i>	35	1:1	Not clearly specified	7	Y = 92.8	–	[17]
WCO	–	299	143.6	Immobilized <i>Candida lipase</i>	45	1:1 (3 steps)	2.5	–	Y = 91.1	H ₂ PO ₄ was added	[18]

WC = Water content (wt%), SV = Saponification value (mg KOH g⁻¹), AV = Acid value (mg KOH g⁻¹), Cat. = Catalyst, T = Temperature, MeOH = Methanol, t = reaction time, Conv. = Conversion, Ref. = Reference, WSCO = Waste sunflower cooking oil, WFO = Waste frying oil, PL = Pork lard, BT = Beef tallow, CF = Chicken fat, WCO = Waste cooking oil, UFSO = Used frying soybean oil, WPFO = Waste palm cooking oil, SBC = Spent bleaching clay, EFBA = Empty fruit bunch ash.

Table 2
Summary of various types of waste catalysts in transesterification.

Waste sources	Catalyst	Preparation conditions			Reaction conditions			Conv. (C) or Yield (Y) (%)	Reusability C/Y (%)	Ref.
		Calcination temperature (°C)	Calcination duration (h)	T (°C)	MeOH:Oil (mol:mol)	Catalyst (wt.%)	Reaction duration (h)			
<i>Mollusc shells</i>										
Mud crab (<i>Scylla serrata</i>)	CaO	900	2	65	0.5:1 (wt/wt)	5	2.5	C = 98.8	15 (C = 94)	[19]
Cockle (<i>Anadara granosa</i>)	CaO	900	2	65	0.54:1 (wt/wt)	4.9	3	C = 99.4	3 (C > 96.5)	[20]
Biont (turtle)	KF-CaO	500	-	70	9:1	3	3	Y = 97.5	-	[21]
Shrimp	KF-CaO	450	-	65	9:1	2.5	3	C = 89.1	-	[22]
Oyster	CaO	700	3	65	6:1	25	5	C = 98.4	-	[23]
Freshwater mussel	CaO	900	4	70	12:1	5	1.5	Y = 96	7 (Y > 90)	[24]
Sea snail (<i>Turbonilla striatula</i>)	CaO	900	3	65	9:1	3	6	Y = 93.3	2 (Y > 80)	[25]
Exoskeleton (<i>Pila globosa</i>)	CaO	900	2.5	60	10:1	4	5	C = 97.8	-	[26]
Snail	CaO	900	3.5	60	6:1	2	8	C = 99.58	-	[27]
Golden apple snail and <i>Meretrix</i>	CaO	800	2-4	60	12:1	10	2	Y > 90	-	[28]
<i>venus</i>										
Clam (<i>Meretrix meretrix</i>)	CaO	900	3.5	60	6:1	3	3	C > 97	-	[29]
<i>Egg shells</i>										
Chicken	CaO	800	2-4	60	12:1	10	2	Y > 95	-	[28]
Chicken	CaO	1000	2	65	9:1	3	3	Y = 95	13	[30]
Chicken	CaO	900	2	60	9:1	3	3	Y = 96	14 (Y = 88)	[31]
Quail	CaO	800	-	65	12:1	0.03	2	C > 98	5 (C > 98)	[32]
<i>Aches</i>										
EFBA	K ₂ O	105	2	60	15:1	3	0.5	C = 90	-	[33]
EFBA	KOH	550	4	65	15:1	1.5	20	C = 98.54	5 (C = 97-85)	[34]
KOH/EFBA	KOH	550	4	65	15:1	0.75	15	C = 99.45	5 (C = 98-93)	[34]
Coal fly ash loaded with KNO ₃	K ₂ O	500	5	160	15:1	15	5	C = 86.13	3 (C = 47-24)	[35]
Coal fly ash loaded KNO ₃	K ₂ O	500	5	70	15:1	15	8	C = 87.5	-	[36]
Coal fly ash loaded egg shell	CaO-Al ₂ O ₃ and SiO ₂	1000	2	70	69:1	1	5	Y = 96.97	16	[37]
<i>Rocks</i>										
Alum	KAl(SO ₄) ₂	550	-	170	18:1	7.09	12	Y = 92.5	-	[38]
Dolomite	CaMg(CO ₃) ₂	850	2	67.5	6:1	3	3	Y = 91.8	5 (Y > 90-82)	[39]
Dolomite	CaMg(CO ₃) ₂	800	2	60	30:1	6	3	C = 98.6	7 (C > 90)	[40]
Calcite	CaCO ₃	800	2	60	30:1	6	3	C = 46.8	-	[40]
<i>Bones</i>										
Rohu fish (<i>Labeo rohita</i>) bone	β-Ca ₃ (PO ₄) ₂	997.42	2	70	6.27:1	1.01	5	Y = 97.7	6	[41]
Sheep bone	Hydroxyapatite	800	-	65	18:1	20	4	C = 96.78	5 (C = 83.7)	[42]
Cuttlebone	CaCO ₃	800	2	60	30:1	6	3	C = 24.1	-	[40]

T = Temperature, MeOH = Methanol, Conv. = Conversion, EFBA = Empty fruit bunch ash, Ref. = Reference.

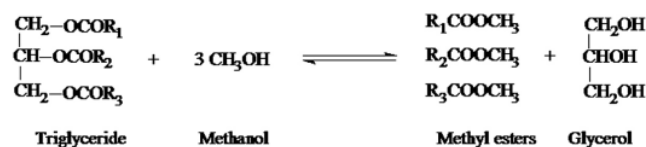


Fig. 1. General equation of transesterification.

Table 3

Average international price of virgin vegetable oil, waste grease and fat in 2007 [4].

Feedstock	Price (US\$/tonnes)
Crude palm oil	543
Rapeseed oil	824
Soybean oil	771
Refined cottonseed oil	782
Crude corn oil	802
Crude tea seed oil	514
Waste cooking oil	224
Yellow grease	374
Poultry fat	256

Transesterification is a catalytic process of alcohol displacement from an ester to another (Fig. 1). Although stoichiometrically, three moles of methanol are required, since transesterification is a reversible process, excess methanol is proposed to shift the reaction forward. Transesterification between triglyceride and alcohol is commonly known as alcoholysis, and, if methanol is used, then it is called methanolysis. The methanolysis of oil, together with a suitable catalyst, produces fatty acid methyl esters and glycerol. At the end of the reaction, the latter settles down to form the bottom layer. It is important to note that the main purpose of transesterification is to lower the viscosity and at the same time to increase the volatility of the oil. The overall transesterification process is normally a sequence of three consecutive steps, which are reversible reactions. From triglycerides, the first step is the formation of diglycerides, followed by the conversion of diglycerides to monoglycerides and finally from monoglycerides, the formation of 3 moles of methyl esters and a mole of glycerol.

2. Feedstock from waste sources

Currently, biodiesel seems more costly than petro-diesel, which is largely due to the high cost of the feedstock. The right selection of feedstock could counter this problem, to some extent, by lowering the overall production cost. As a solution, waste/used oil could be one of the best choices in order to produce biodiesel with a comparable cost to petro-diesel. Many studies have investigated the use of waste cooking oil (WCO); animal fats including chicken fats, pork, lard, tallow and grease, and spent bleaching clay (SBC).

Table 4

Fatty acids distribution of animal fats, greases and vegetable oils.

Product	Fatty acid distribution (%)								Σ	Ref.
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	Others		
Chicken fat	–	19.82	3.06	6.09	37.62	31.59	1.45	0.37	100	[48]
Tallow	3.10	23.80	4.70	12.70	47.20	2.60	0.80	5.10	100	[6]
Pork Lard	1.30	23.50	2.60	13.50	41.70	10.70	–	6.70	100	[6]
Rapeseed oil	–	3.49	–	0.85	64.40	22.30	8.23	0.73	100	[48]
Sunflower oil	–	5.40	0.10	2.90	18.70	72.90	–	0.00	100	[4]
Soybean oil	–	10.58	–	4.76	22.52	52.34	8.19	1.61	100	[48]
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67	5.62	100	[49]
Brown grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	4.48	100	[49]

2.1. Waste cooking oil

Waste cooking oil (WCO) is any vegetable oil that has been previously used for frying or cooking and which is deemed unhealthy to reuse [3]. As such, one of the ways to add value to WCO is by utilizing it as a feedstock in transesterification. Table 3 [4] depicts that WCO is the most inexpensive feedstock as it can be readily collected from households, hotels and restaurants. The price of these waste oils is two to three times cheaper than virgin vegetable oils.

However, the drawback of used/waste oil is the presence of high free fatty acids (FFA) and water content. The quality of this type of oil can be improved by several pretreatments, especially for waste oil and fat with FFA content over 2.5% [43] and moisture beyond 0.5% [44]. Excess FFA and moisture must be removed from the feedstock as they will affect the transesterification reaction through saponification reaction, and, eventually, decrease the yield and complicate the product separation.

Commonly, alkali catalysts can tolerate FFA up to 2.5 wt.%, however, feedstock with FFA over 2.5 wt.% needs a pretreatment to bring down the FFA prior to transesterification. Three main ways have been identified to remove water in the oil. Heating the oil is one of the preferred methods, where the waste oil is heated at 100 °C for 15 min with continuous stirring [45]. Chemical treatment is also an option where magnesium sulphate is used to absorb the water [46] and warm water or water vapour is also used to deal with the moisture in the waste oil [47].

2.2. Animal fats and grease

Animal fats and grease could be a suitably affordable feedstock for biodiesel (Table 3) [4]. The availability of a large quantity of animal fats and the ease of collecting them from slaughter houses or meat processing units make animal fats one of the desired choices. The fatty acid distribution of animal fats, greases and vegetable oils are presented in Table 4 [4,6,48–49], proving the very small differences in terms of the fatty acid distributions between these three sources.

In general, a major disadvantage of animal fats and grease utilized as feedstock in transesterification is that they provide products with poorer cold temperature properties than virgin vegetable oil and contain high FFA [6]. Improving the cold properties of biodiesel using white sesame oil was investigated in which the researcher used methyl stearate, isopropyl stearate, methyl

oleate and isopropyl oleate as pour point depressants [50]. The most effective results were shown by isopropyl oleate at 30 wt.%. The cloud and pour points decreased from 1 °C to –6.6 °C and 0 °C to –8 °C, respectively. In addition, another study to improve the cold flow properties by using surfactants and detergent fractionation was investigated by Wang et al. [51]. The effect of different surfactants was studied, including sugar esters, silicone oil, polyglycerol ester, and diesel conditioner. Another solution to improve the cold properties, involves blending biodiesel with poor cold properties with biodiesel with higher cold properties or using cold point depressants [52].

Nevertheless, for the case of high FFA, the feedstock can be treated via esterification to lower the FFA content. To deal with the high FFA in feedstock, the researchers carried out esterification as a pretreatment step to convert the FFA to ester. In a related study, esterification was carried out using acids (sulphuric, hydrochloric and sulphamic acids) to esterify chicken fat with 13.45% FFA. After pretreatment, the FFA level in the feedstock was reduced to less than 1%. The authors reported that sulphuric acid gave the best result among the three acid catalysts, in the following conditions: 20% sulphuric acid, methanol to oil molar ratio 40:1 at 60 °C for an 80 min reaction. Sulphamic acid did not have any significant effect in reducing the FFA [48].

2.3. Spent bleaching clay

Spent bleaching clay (SBC), which is a waste from edible oil refineries, could be an affordable feedstock similar to waste cooking oil, animal fats and grease. Bleaching clay is used to remove soap, metals, polymers and colouring substances in the palm oil refinery. SBC contains a high amount of oil, approximately 20–40% and the availability of SBC at refineries makes clay an attractive feedstock material for biodiesel [53]. Its benefits can be further harnessed by the construction of a sizeable biodiesel plant adjacent to oil refineries. Another advantage is that the adsorbed oil on the clay is comparatively better in quality compared to other waste feedstock. Annually, 600,000 metric tonnes or more SBC is used worldwide. In Malaysia alone, with a CPO production of 18.9 million tonnes in 2011 [54], it is estimated that about 190,000 tonnes of SBC is generated.

In situ biodiesel production from residual oil from SBC was investigated by Mat et al. [55]. The researchers compared two different catalysts to synthesize biodiesel from SBC oil. Sodium hydroxide (alkali) and sulphuric acid were used as catalysts, and hexane was used to extract the oil from the SBC. The yield of biodiesel resulting from the use of an alkali catalyst was higher than that from the acid catalyst, and the reaction time using the alkali catalyst is much shorter. In another related study, the transesterification of SBC using different solvents was explored [12]. The authors used different polar and non-polar solvents, such as methanol, ethanol, petroleum ether and hexane to convert the adsorbed oil on SBC to biodiesel. Among them, ethanol gave the highest extracts, which contains polar components and triglyceride. However, for the purpose of transesterification, triglyceride without other components is preferred. As such, the non-polar solvent, together with moderate extracts, provides the best extraction solvent, which extracts triglyceride (without polar components) from SBC with the least FFA content.

3. Catalyst from waste sources

3.1. Shells

3.1.1. Mollusc shells

Calcium oxide derived from mollusc shells has been proven to be a potential heterogeneous catalyst for biodiesel production.

Boey et al. investigated the use of waste mud crab shells (*Scylla serrata*) as a catalyst for the transesterification of palm olein and the report revealed that the calcined shell contains mainly CaO [19,56]. Under the optimal conditions of 0.5:1 (mass ratio of MeOH:oil); catalyst amount, 4–5 wt.% and reaction temperature 65 °C, the calcined catalyst could be reused several times without much reduction in its effectiveness. The performance of waste crab shells was comparable to the laboratory grade CaO. A similar observation was noticed for the catalyst from waste cockle shells (*Anadora granosa*), in which the calcined shell (900 °C, 2 h) could transesterify chicken fat [20]. Both of the waste catalysts recorded 98.2–99.0% methyl ester conversion in 3 h reaction time.

Xie et al. investigated the carbonization of biont shell (from turtle shells) [21]. The catalyst was prepared via a series of treatments; incomplete carbonization at 500 °C, followed by impregnation in KF, for 6 h at 25 wt.%, and, finally, thermal activation at 300 °C. The authors reported by observation at CO₂-TDP spectra that strong basicity sites were formed on the catalyst after the impregnation of KF. Chitin, the major constituent of the biont shell formed the active sites after reaction with KF. The report concluded that the heterogeneous catalyst from biont shell exhibited an excellent activity as well as stability under mild reaction conditions. Similar work has been reported using shrimp shells [22]. The catalyst was prepared in a similar manner as the biont shell, except for the carbonation temperature (450 °C) and activation temperature (250 °C). While using biont shell recorded a yield of 97.5% in 3 h (3% catalyst), this waste reported a conversion of 89.1% in 3 h (2.5% catalyst).

Nakatani et al. [23] investigated the use of waste oyster shells as a catalyst in the transesterification of soybean oil. In a 5 h reaction, a methyl ester content of 98.4% was achieved. Similar to mud crab and cockle shells, the main constituent of the calcined oyster shell is CaO. Sea snail shells (*Turbonilla striatula*) were also found to be a source of CaO in the investigation by Boro et al. [25]. The calcined (800 °C, 4 h) shell was able to transesterify mustard oil with a yield of 93.3 wt.%, in a 6 h reaction. In term of reusability, the catalyst was stable until the second cycle and exhibited a sharp reduction for the third and fourth cycles. However, the authors found that the used catalyst can be reactivated upon calcination at 900 °C for 3 h.

Another CaO source was derived from calcined waste freshwater mussel shells, from the work of Hu et al. [24]. The catalyst was prepared by calcination (900 °C, 4 h) then impregnation in deionized water before being thermally activated again (600 °C, 3 h). In this way, a 'honey-comb' catalyst structure was obtained, which recorded the highest surface area at 23.2 m² g⁻¹. The resultant catalyst was able to yield 90% methyl ester in 1.5 h of reaction time. Interestingly, the catalyst can be reused seven times before the yield dropped below 90%, maintaining 80% yield up to the twelfth cycle and 60% yield at the seventeenth reuse.

Calcium oxide can also be derived from waste egg shells, snails (golden apple), and clams (*Meretrix venus*) [28]. The calcined (800 °C, 2–4 h) shells were able to produce methyl ester content over 90%, in 2 h reaction time; egg shells and snail shells have higher initial activities.

3.1.2. Egg shell

Chicken and quail egg shells were found to be a reliable source of CaO, consisting of 85–95% of calcium carbonate and 15–5% other components (MgCO₃, phosphate, organic matter and a small amount of metal) in dry egg shells [57]. The catalytic performance was comparable to laboratory grade CaO in transesterification. In a 3 h reaction time, Wei et al. [30] achieved 95% biodiesel yield and reported that the catalyst can be reused 13 times without any significant loss of activity. Viriya-empikul et al. [28] also reported the good performance of egg shells in transesterification. Chicken egg

shell contains the highest calcium and has larger surface area as compared to golden apple snail and *Meretrix venus* shell. Recently Semwal et al. [58] prepared the metal oxide CaTiO_3 using egg shell by calcination at 1050 °C for 3.5 h; yielding over 95% methyl ester content. The metal oxide catalyst was stable for four reuse without any major structural changes as confirmed through XRD. It proves that regardless of the origin, CaO could catalyze the reaction with success. Calcium oxide from these waste sources compliments where they could be co-used with laboratory grade CaO.

3.2. Ashes

3.2.1. Empty palm fruit bunch-based boiler ash

Empty palm fruit bunch (EPFB) fibre (dry basis) consists mainly of glucan (42.85%), xylan (24.01%), lignin (11.70%) and other components. As for oxides, EPFB contains potassium oxide as the major constituent, followed by silica, calcium oxide and others [59]. The ash was successfully utilized by Boey et al. [33] as a catalyst in the transesterification of palm olein. With oven drying (105 °C, 2 h), 3 wt.% ash was capable of transesterifying palm olein at 90% conversion in a 0.5 h reaction time. However, since the ash acts as pseudo-homogeneous, it is intolerant to the presence of moisture and FFA at 1 wt.% in the feedstock.

The transesterification reaction of palm oil with methanol using a methanolic extract of empty fruit bunch ash (EFBA) as a homogeneous catalyst was reported by Imaduddin et al. [60]. In contrast, Yaakob et al. [34] used EFBA as a heterogeneous catalyst. They made a comparison between EFBA and the EFBA doped with 20 wt.% KOH and used *Jatropha curcas* oil for the transesterification. Optimum conditions for the EFBA-catalyzed reaction were 20 wt.% EFBA; MeOH/oil molar ratio 15:1 at 65 °C, for 90 min; a maximum oil conversion of 98.54% was achieved and the report showed that the KOH/EFBA catalyst reaction has better activity than the EFBA alone; 99.45% conversion in the much shorter reaction time of 45 min at 15 wt.%. The reusability study of the catalyst indicated that KOH/EFBA is a better catalyst for repeated use. After five cycles, the conversion of both catalysts was more than 85%. The decreased activity of the catalyst after the fifth run was confirmed by XRF analysis due to the absence of metals like K and Ca, which indicates leaching of the active ingredients.

3.2.2. Fly ash

Fly ash as an inorganic waste generated from coal combustion processes has a typical chemical composition (on dry basis), of around 55% SiO_2 , 30% Al_2O_3 and other oxides [61]. It is obvious that the oxides of both silica and alumina could work excellently as a catalyst support. Consequently, researchers have used thermally activated fly ash as a support for loading CaO for chemical production. This supported catalyst gave higher conversions of up to three cycles and the catalyst was able to be reused without much loss in the activity. The presence of the high amount of SiO_2 and Al_2O_3 prompts its potential applicability as a low-cost catalyst support. In a recent work, fly ash supported CaO has been employed as a recyclable solid base catalyst [62]. Fly ash supported heterogeneous CaO catalyst from egg shells have been investigated to transesterify soybean oil [37]. Fly ash supported a CaO catalyst prepared by wet impregnation method, with 30 wt.% CaO loading and followed by calcination at 1000 °C for 2 h. A maximum FAME yield of 96.97% was achieved with 6.9:1 methanol/oilmolar ratio. The study of the reusability of catalyst showed higher catalytic activity in which the catalyst showed remarkable repeated usability of 16 times without major loss in activity; indicating a high degree of catalyst stability. However, the catalyst became completely deactivated after being used more than 18 times. Fly ash-based base catalyst was investigated by Kotwal et al. [36], in the transesterification reaction of sunflower oil. The catalyst was pre-

pared by the conventional wet impregnation method using KNO_3 . In the work, fly ash loaded with 5 wt.% KNO_3 , followed by calcination at 500 °C was able to convert the oil at 87.5% in 8 h reaction time. However, the catalyst suffered from being reused, probably due to the leaching of active species. Similarly, Babajide et al. [35], reported that fly ash loaded with 5 wt.% KNO_3 could transesterify sunflower oil to about 86% but at an elevated reaction temperature of 160 °C. Similar to the previous study, the catalyst also suffers with respect to its reusability.

3.3. Rocks

Alum ($\text{KAl}(\text{SO}_4)_2$) has a traditional role in water treatment and potential as a catalyst in the transesterification of palm oil. Ademiri and Hameed reported the preparation of alum as a catalyst in the transesterification of palm oil [38]. The alum successfully transesterified the oil to 92.5%, with 7.09 wt.% catalyst and MeOH/oil molar ratio of 18:1 in 12 h reaction time at an elevated temperature of 170 °C. Another potential catalyst with high carbonate content originating naturally are dolomite ($\text{CaMg}(\text{CO}_3)_2$) and calcite (CaCO_3). At present, the low cost of dolomite is the main reason of major domestic usage in cement manufacturing and landfill. While dolomite consists of 23.5% Ca, 12.1% Mg, 63% CO_3 and 1.4% other components (Fe, SiO_2 , PO_2 , SO_4) [39], calcite contains high purity of CaCO_3 (over 91 wt.%) [40]. Both dolomite and calcite could be easily transformed to CaO and MgO by thermal activation. Comparison of dolomite and calcite has been reported by Ngamcharussrivichai et al. [40], in the transesterification reaction of palm kernel oil (PKO). In their study, the dolomite successfully transesterified the PKO, over 98% methyl ester, under the reaction conditions of: 6 wt.% catalyst, MeOH/oil molar ratio 30:1 in 3 h reaction at 60 °C. Meanwhile, calcite performed at 46.8% methyl ester under the same reaction conditions. The calcined dolomite at 800 °C for 2 h could be reused up to seven cycles without much loss in the activity.

3.4. Bones

Bone from waste Rohu fish (*Labeo rohita*) has been reported as another low-cost heterogeneous catalyst for the synthesis of biodiesel from soybean oil [41]. The analysis of TGA and XRD revealed that a significant portion of the main component of fish scale, hydroxyapatite, could be transformed into β -tri-calcium phosphate when calcined above 900 °C for 2 h, with optimal conditions of MeOH/oil molar ratio, 6.27:1, catalyst at 1.01 wt.% for 5 h. This compound was able to yield 97.73% of methyl ester. The reusability of the catalyst shows that it could be reemployed up to six times. Similar work has been reported using sheep bone [42]; the calcined bone at 800 °C, transformed calcium phosphate of the bone into hydroxyapatite with an increase in surface area. In a 4 h reaction, methyl ester content of 96.78% was obtained under the reaction conditions of: methanol to oil 18:1 (molar ratio) and 20% catalyst at 65 °C. The catalyst was stable for five cycles at 83.7% conversion. On the other hand, cuttle bone (calcined at 800 °C for 2 h) could also catalyze transesterification of PKO but with much lower conversion (24%) although the bone contains over 91 wt.% CaCO_3 [40]. Increasing the calcination temperature of the bone to above 800 °C may increase the methyl ester conversion.

4. The future trend

Exploration of feedstock and catalysts from waste sources/materials should be intensified in order to make the process more affordable and sustainable as well as countering the environmental complications. Along the way, research needs to be expedited to

enhance the existing performance of such materials. Awareness should be created so that any material that is deemed to be waste is considered for usage in some other applications. As such, more waste can be collected and the mass could be easily used for human betterment over a prolonged period.

In addition, the efforts to employ waste need to receive the support of governments, for instance, in terms of tax relief/reduction. Most importantly, the government can play a serious role in introducing regulations to enforce the use of waste substances. In this way it is no longer a choice but a must to include the ingredients from waste products in many more processes.

By comprehending the fact that humans are trustees of the resources and not the mere users, more and more processes could be modified to become green and sustainable.

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