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Review

Waste materials as potential catalysts for biodiesel production: Current state and future scope

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ABSTRACT

Recent studies on the exploration of eco-friendly approach by utilizing large-scale waste materials as potential catalyst in biodiesel production have attracted much attention. The development of heterogeneous catalysts especially from calcium has gained much awareness due to the large availability of calcium-rich waste materials and their corresponding high catalytic activity in the transesterification of oil. Most of the waste materials employed as heterogeneous catalysts have an abundance of natural Ca content and they have high catalyst activity and selectivity despite being environment-friendly and cost-effective. Heterogeneous catalysts with high activity can be produced from Ca based waste materials when calcined at high temperatures. This review gives a brief overview of the developments of various Ca based catalysts derived from waste materials as an efficient catalyst for biodiesel production with significant yield. Industrial wastes (red mud, slag, ash) and biological catalysts (chicken eggshells, mollusk shells, animal bones) possess enormous potential towards developing an economical catalyst and subsequently, low-cost biodiesel generation. However, future challenges await a better utilization of useless wastes into a useful resource to satisfy human needs.

1. Introduction

The continuous exigency for fossil fuels for industrial, transportation and domestic purposes has led to the exploration of alternative energy sources. Coal, oil, and gas are the main contributors in the energy sector. The literature studies reveal that oil, coal, and gas may last for a further 40, 200 and 70 years, respectively, as per the ongoing consumption of fossil fuel reserves [1]. Sky-high prices of gasoline and diesel have forced the researchers and scientists to develop liquid biofuels as alternative fuels [2]. Bio-diesel, a non-renewable and biodegradable fuel, is a suitable alternative fuel whose properties match the specifications of the ASTM and EN standards [3]. Transesterification process is a widely used method, which involves the conversion of triglycerides to methyl esters (with methanol) or ethyl esters (with ethanol) along with the use of a suitable catalyst. Fig. 1 depicts the transesterification mechanism for biodiesel production.

Homogeneous base catalysts (KOH and NaOH) are not capable to convert used cooking oils and inedible oils due to their high FFA content causing the formation of soaps in the product. Moreover, the separation of biodiesel from the solution is difficult and thus costly. Acid-catalyzed reactions for pre-esterification of high FFA are not suitable due to the corrosive nature of acid catalysts. Therefore, the studies on the development of solid heterogeneous catalysts have escalated [4,5]. The higher molar ratios, catalyst amount and reaction temperatures required for the heterogeneous catalysis when compared to homogeneous catalysis is a complication for production of low-cost biodiesel. Solid base heterogeneous catalysts relatively require lower reaction conditions when compared to those for solid acid catalysts. Waste materials derived from industries and surroundings can assist in the development of an economical solid base catalyst. Awareness towards an exploration of more waste materials can help in the development of catalysts promoting a sustainable and environment-friendly approach towards biodiesel production [6]. Rice husk as by-product constitutes about 20% in terms of weight of rice when milled. Around 151 million tonnes of rice husk was produced as reported in July 2017 [7].

Calcium oxide (CaO) is one of the most active catalysts in the category of solid base catalysts. Due to its low cost, easy availability and high regenerability. CaO is a widely used catalyst for transesterification of feedstocks. Also, various waste products contain Ca content in huge amounts and are easily available at low cost. CaO as catalyst support is ideal due to its high surface area and a large number of pores available on the surface. CaO is a non-toxic catalyst possessing high basicity and

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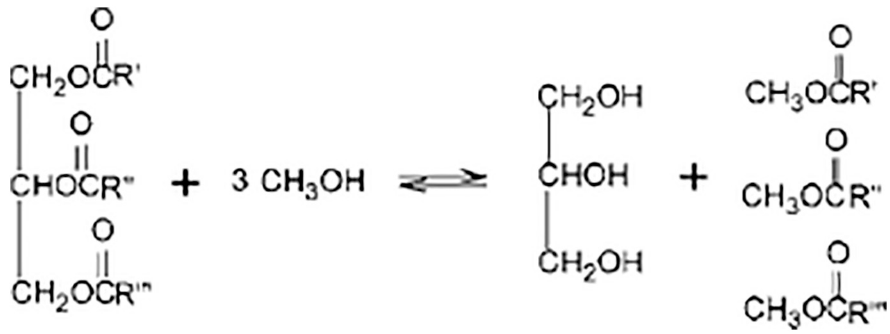

Fig. 1. Transesterification process mechanism [5].

promotes higher FAME yields [8,9].

Taking this in view, there is a need to explore waste-derived catalyst exhibiting high activities. Through this approach, the cost of biodiesel production will drop subsequently, taking in the view of industrial application. The objective of this review is to discuss the recent shift of heterogeneous catalysis towards more economical possibilities along with high activity and reusability. The calcination temperature for the activation of Ca-based catalyst is a crucial variable along with transesterification parameters: molar ratio, catalyst amount, reaction temperature and reaction time. This review focuses on the positive impacts of loading different metals over Ca based catalysts. The future challenges regarding the use of waste materials have also been presented. Table 1 [10–19] presents fuel properties as per the American and European Standards and Table 2 [7,20–23] shows the production rate of various waste products.

2. Industrial waste derived catalysts

Various mills, industries, and factories worldwide generate a large amount of superfluous waste every year. Among these industries, thermal power plants, steel industries, paper and pulp mills, sugar and fertilizer industries are major sources of waste generation.

2.1. Lime mud

Lime mud generated in pulp mills as a waste mainly composed of calcium carbonate with traces of magnesium carbonate and other minerals. The chemical components of lime mud have been depicted in Table 3 [24]. Calcination at high temperatures converts $CaCO_3$ into CaO. Hui et al. [25] used calcined lime mud as a catalyst and compared its activity with commercial CaO. XRD results (Fig. 2) showed that lime mud calcined at 800 °C was activated to form CaO. Fig. 3 displays that higher calcination temperatures resulted in the reduced conversion, probably due to sintering of catalyst. Molar ratio of 15:1, catalyst amount of 6 wt% and reaction temperature of 64 °C resulted in 94.4% yield in 3 h time. Catalytic reusability of lime mud, when tested for 5

Table 1
Fuel properties of diesel and biodiesel.

Fuel property	Unit	Biodiesel ASTM D 6751	Biodiesel EN 14214	Petroleum diesel
Kinematic viscosity at 40 °C	cSt	4–6	3.5–5.0	1.3–4.1
Density at 15 °C	kg/m^3	878.08	960–900	848.25
Flash point	°C	100–170	120 min.	60–80
Pour point	°C	−15 to 10	–	35 to −15
Cloud point	°C	−3 to 12	–	−15 to 5
Cetane number	–	48–65	51 min.	40–55
Sulphur	mg/kg	15 max.	10 max.	350 max.
Water	mg/kg	500 max.	500 max.	200 max.
Oxidative stability	h	3 min.	8 min.	–

Table 2
Large-scale wastes for use as catalysts.

Waste product	Reported production rate (annual basis)	Reference
Rice husk ash (worldwide)	151 million tonnes (in 2017)	[7]
Eggshells (Portugal)	10,678 tonnes (in 2016)	[20]
Fly ash	112 million tonnes	[21]
Red mud (India)	> 4 million tonnes	[22]
Iron and steel slag (U.S.)	16 million tonnes (in 2014)	[23]

Table 3
Chemical composition of waste materials.

Composition (wt %)	Lime mud	Carbide slag	Blast furnace slag	Red mud	Dolomite
CaO	72.5	54.2	32–45	35.09	30.24
SiO_2	–	9.46	32–42	18	0.18
Al_2O_3	0.2	2.93	7–16	6.31	0.25
Fe_2O_3	0.1	1.31	0.1–1.5	12.38	0.63
Na_2O	1.3	–	–	2.71	0.23
K_2O	0.1	–	–	0.45	0.03
MgO	0.5	1.01	1–2	1.13	21.33
TiO_2	–	–	–	3.3	–
SO_3	–	–	–	0.54	–
S	–	–	1–2	–	–
P_2O_5	0.9	–	–	–	–
V_2O_5	–	–	–	–	–
MnO	–	–	0.2–1.0	–	–
Cl^-	–	–	–	–	0.19
Moisture	34	–	–	–	–
Others	–	3.33	–	–	–
LOI	24.5	30.58	–	20.07	46.04
Reference	[24]	[34]	[35]	[31]	[36]

LOI = Loss on ignition.

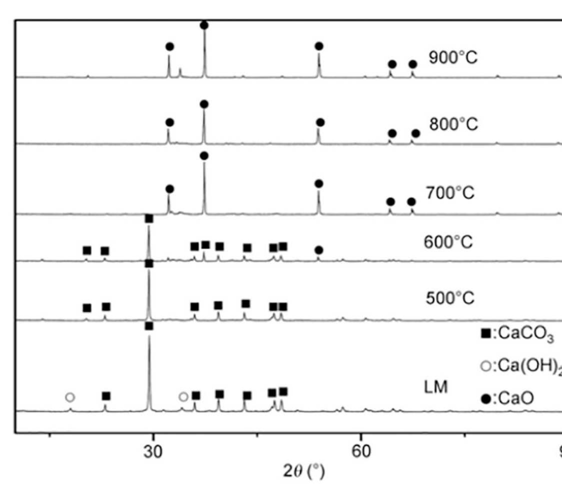

Fig. 2. XRD patterns of lime mud [25].