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Preparation of heterogeneous catalyst derived from natural resources for the transesterification of biofuel

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Abstract-*The main aim of this research is to develop environmentally and economically heterogeneous catalyst derived from waste mud crab shell and waste fish bones for the bio-diesel production via transesterification of waste fried soyabean oil. The effect of methanol to oil ratio on the reaction was studied. The physicochemical properties of the resultant catalysts were characterized by Energy-dispersive X-ray spectroscopy (EDX), Scanning electron microscopy (SEM), and X-ray diffraction (XRD). The waste material calcined at 900˚C in muffle furnace to give the highest bio-diesel yield. The optimal condition at 300 rpm, reaction time 4 h for fish bones was found at methanol to oil ratio 15:1 (methanol/oil), a reaction temperature of 65˚C and the catalyst loading 6 wt % (based on oil weight) of oil giving the highest bio-diesel yield up to 84 %. For the crab shell the optimal condition was found at 600 rpm, reaction time 2 h methanol to oil ratio 15:1 (methanol/oil), and the catalyst loading 3 wt % (based on oil weight) percent giving the highest bio-diesel yield 78.84%. On mixing of crab shell and fish bones catalyst the maximum yield of bio-diesel was found to be 70.24% at 750 rpm, methanol to oil ratio 12:1 (methanol/oil) for reaction time 2 h and the catalyst loading 4 wt % (based on oil weight). These waste showed good potential to be used as bio-diesel production catalyst.*

Key Words: Heterogeneous catalyst, Crab Shell, Fish Bones, Transesterification, Calcination, Biofuel, SEM, XRD, EDX.

1. Introduction

The worldwide energy consumption is increasing due to rapid population growth and industrial development that causes the price of crude petroleum to rise. The conventional energies such as petroleum-derived fuels, coal and natural gas will be exhausted in the near future and greenhouse gas emission by the usage of fossil fuels is also becoming a greater concern. An effective way to reduce the cost of bio-diesel production is to use non edible oil, animal fats, fish oil, and waste frying oil as raw material. Bio-diesel has been chosen as one of the interesting alternative fuels as it is renewable, biodegradable, non-toxic and environment-friendly fuel. [1-4]

Bio-diesel is produced from any fat or oil through a process called transesterification. In the production of bio-diesel, the triglycerides present in various sources viz. edible oil, non-edible oil, animal fats, waste oil and oil from algae are transesterified with methanol in presence of a catalyst (acid, base or bio-catalyst) to give fatty acid methyl esters (FAME) and glycerol as a by product. [5-20] The transesterification reaction for bio-diesel production can be carried out using both homogeneous (acid or basic) and heterogeneous (acid, basic or enzymatic) catalysts. The base-catalyzed transesterification of oils proceeds faster and give very high yields in short reaction times than that catalyzed by the same amount of an acidic catalyst. Enzyme-catalyzed transesterification is carried out at moderate temperatures with high yields, but this cannot be used for bio-diesel production due to high enzyme costs.[21]Homogeneous base-catalyzed transesterification generates a certain amount of water even if a water-free vegetable oil and methanol is used due to the reaction of hydroxide with methanol. The presence of water leads to the hydrolysis of the esters, and as a result, soap is formed. The formation of soap not only reduces the bio-diesel yield but also causes significant difficulty in the separation of ester and glycerol. [22-27] Moreover, in this conventional homogeneous method, the removal of catalysts after reaction is technically difficult and a large amount of waste-water is produced to separate the catalyst and clean the products. Therefore, heterogeneous catalysts are very important for bio-diesel synthesis as these catalysts have many advantages over homogeneous catalysts. They are noncorrosive, environmentally benign and present fewer disposal problems. Besides, the use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization or triglyceride saponification. They are also much easier to separate from liquid products, reusable and they can be designed to give higher activity, selectivity and longer catalyst lifetimes.[28-33]

The use of a heterogeneous catalyst is promising to reduce the present high production cost of bio-diesel making it competitive with petroleum-based diesel fuels. Therefore, research is being directed towards the development of environment friendly and cost-effective heterogeneous catalyst for bio-diesel production. Recently, various heterogeneous catalysts derived from renewable materials (natural resources) have been reported in various literature for conversion of oils to bio-diesel and these are *Musa balbisiana* Colla [34], waste shell of *T. Striatula*[35], waste freshwater mussel shell[36], turtle shell [37], waste eggshell [38], waste cockle shell [39], waste shells of mollusk and egg [40], waste fish scale [41], waste mud crab shell [42], chicken eggshells [43], snail shell [44], industrial waste shells of egg [45], golden apple snail and meretrix venus[46], waste animal bone [47], shrimp shell [48], clamshell (*M.meretrix*) [49], *Pomacea sp*. Shell[50], and oyster shell [51]. Most of these waste material derived catalysts are cheap resources of CaO for application as low-cost heterogeneous catalyst for bio-diesel synthesis.

In the present work, we attempt to develop novel, low cost and highly efficient catalysts derived from the two waste materials of waste mud crab shell and fish bones for the transesterification of soyabean oil. Calcination of powdered crab shell and fish bone at 900˚C for 2 h would result into formation of CaO catalyst.

Till today,to the best of our knowledge ,no investigation is related to mixing of these two catalysts in different ratio to study effect on yield of bio-diesel.The physicochemical properties of the prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive x-ray spectroscopy (EDX). Also the effect of methanol to oil ratio were carefully studied.

2. Experimental

2.1 Material

Crab shell and fish bones were collected from a nearby market Itwari,Nagpur, India. Waste frying oil was procured from the Priyadarshini Canteen.Methanol (analytical grade, Aldrich) was used for bio-diesel synthesis.

2.2 Catalyst preparation and characterization

The crab shell and fish bones were washed by hot water and then by distilled water in order to remove dust and impurity. Then, the fish bones and crab shell dried in oven at 70˚C and 105˚C for 24 h in the dry oven. The fish bones and crab shell were crushed and sieved until it become into powder form, and then calcined at 900˚C in muffle furnace for 3 h to generate CO_2.[52]

The crystalline phases of calcined catalyst were analyzed by X-ray diffraction (XPERT-PRO) with Cu Kα radiation (λ=0.154nm), operated at 45 kV and 40 mA.

The elemental chemical composition of the crab shell and fish shell were analyzed by EDX (JEOL 6308A) for precise measurement of both heavy and light elements.

Morphology of the calcined and uncalcined catalyst were investigated by SEM (JEOL 6308A) which was operated at the acceleration voltage of 10kV for uncalcined, 5kV for calcined sample with filament current of 50mA.

2.3 Transesterification process

The transesterification reaction were carried out in a 500 ml three necked round bottom flask. The middle neck was used to insert mechanical stirrer, one of the side neck was fitted with a water cooled condenser, and the other neck was fitted with temperature indicator. The transesterification reaction were performed with a stirring speed of 600 rpm for crab shell, 300 rpm for fish bones and 750 rpm for mixture of fish bone and crab shell.[36,41.47] The 3 weight % of crab shell catalyst for different methanol to oil ratio was introduced to round bottom flask which is at 65˚C or 2 h at 600 rpm. The 6 weight % of fish bone catalyst for different methanol to oil ratio was introduced to round bottom flask which is at 65˚C for 4 h at 300 rpm.[41] The 4 weight % of mixture of crab shell and fish bone catalyst for different methanol to oil ratio was introduced to round bottom flask which is at 65˚C for 2 h at 750 rpm.[52]

After the transesterification reaction, the catalyst was removed from the mixture and filtered by the whitmann filter paper. The filtrate was kept in a separating funnel for 24 h for clear separation of bio-diesel and glycerol.

The yield of bio-diesel was then calculated by using following formula:

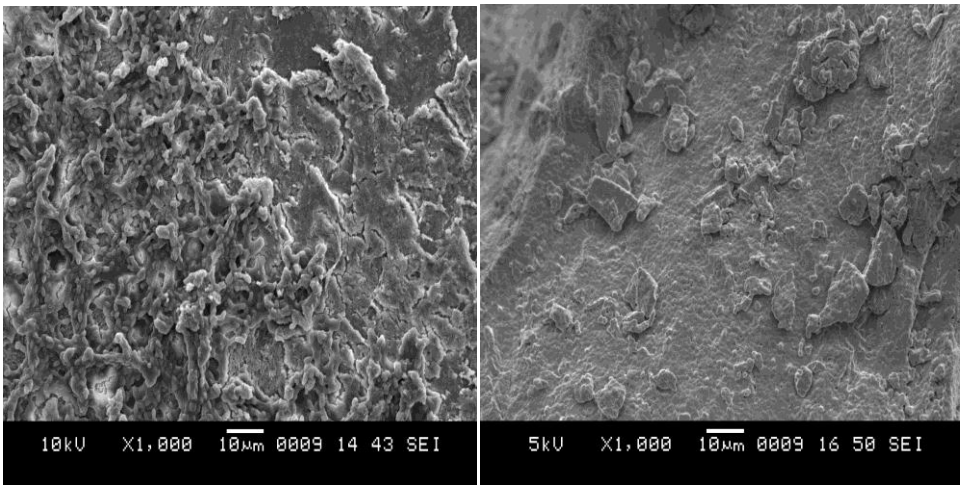
Yield (%) = (weight of bio-diesel / weight of oil)*100

3. Result and discussion:

3.1 Catalyst characterization

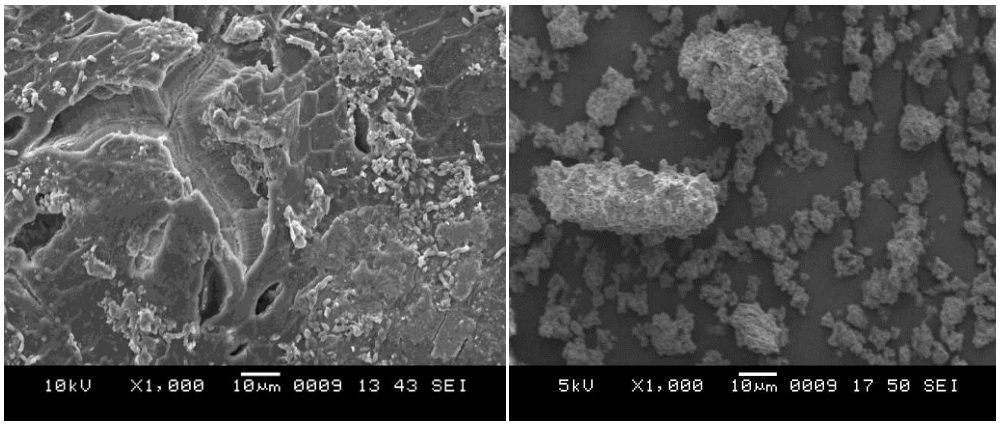
3.1.1 SEM analysis

Fish bones and crab shell catalyst before and after calcinations were tested using scanning electron microscope. The sample were analyzed on its structure and catalyst morphology. The SEM observation is as shown in fig 1



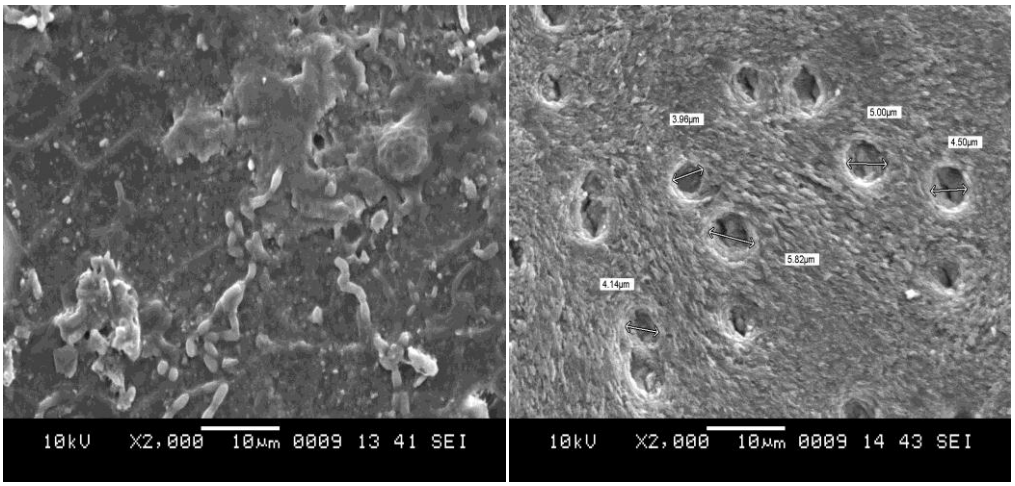
(a) (b)

Fig-1: SEM image for (a) uncalcined fish bones and (b) for calcined fish bones



(a) (b)

Fig-2: SEM image for (a) uncalcined crab shell and (b) for calcined crab shell



(a) (b)

Fig-3: SEM image for Mixture of both catalyst crab shell and fish bone

It showed that there is difference between before and after calcinations with equal magnification 1000x. In fig1 uncalcined fish bone showed irregular structure and some of them bonded together as aggregates. Whereas the calcined fish bone showed angular structure. The surface area of uncalcined fish bone is bigger compared to calcined fish bones .

In fig2 the uncalcined crab shell was angular in shape however in case of calcined crab shell the structure like aggregate obtained with size ranging from 1 to 10um.

In fig3 (a) the mixture of crab shell and fish bone catalyst was fibrous in shape and in fig3 (b) spherical in shape.

3.1.2 XRD analysis

Fish bones and crab shell were tested using XRD after calcinations process. XRD patterns of the shell derived catalyst sample calcined at 900^0C for 2hr are shown in fig3 .The catalyst sample of fish bones and crab shell showed clear and sharp peaks, identical for all sample. This peaks match a crystalline phase of cao. This result confirmed that the condition to synthesize cao from the shell was acceptable.

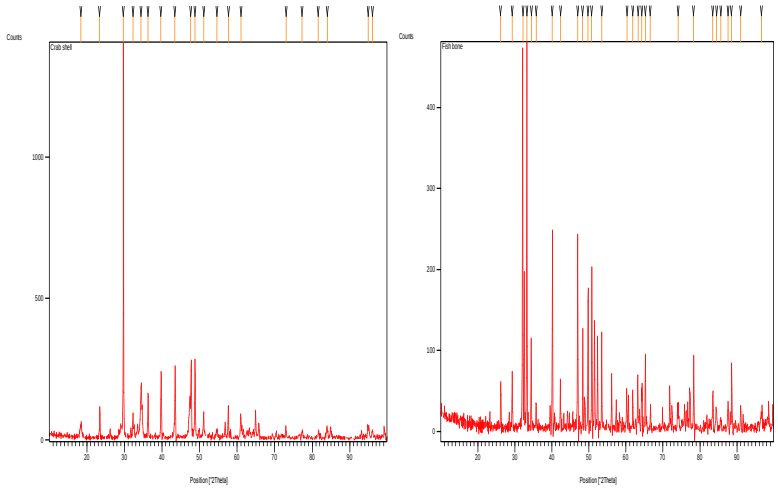


Fig-4: XRD for calcined crab shell

Fig-5: XRD for calcined fish bone

XRD spectra of calcined crab shell and fish bone were obtained with Cu Kα radiation (λ=1.54nm) at 45kV, 40mA. For the calcined crab shell the main peak was observed at 2θ=29.7147. this peak were characteristics of calcium oxide. Whereas for calcined fish bone the main peak was observed at 2θ =33.2196 which were characteristic of calcium oxide.

The particle size of the crystalline catalyst was also calculated from the XRD data using Scherrer's formula

$$D=\frac{0.89*\lambda}{\beta\ cos\theta}$$

The particle size for calcined crab shell and fish bone catalyst was calculated and was found to be 0.410 nm and 0.357 nm respectively.

3.1.3 EDX analysis

For the determination of element present in the catalyst were analysed by edx. The EDX curves of the uncalcined fish bone and crab shell catalyst were also acquired and several typical points on the surface of samples were selected in order to determine the elemental contents of Ca, and O.

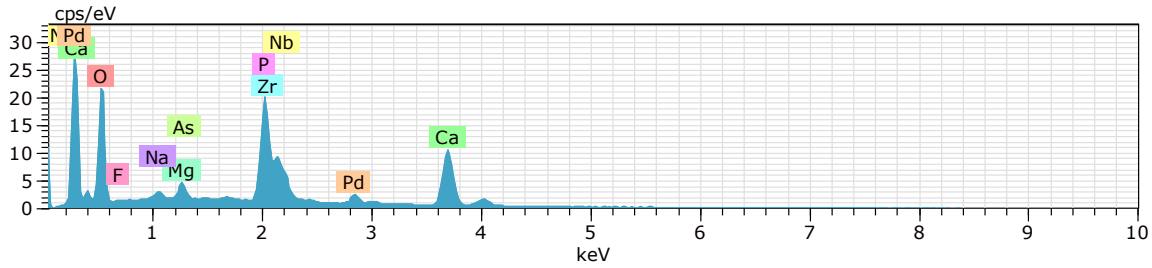


Fig-6: Elemental composition of fish bone

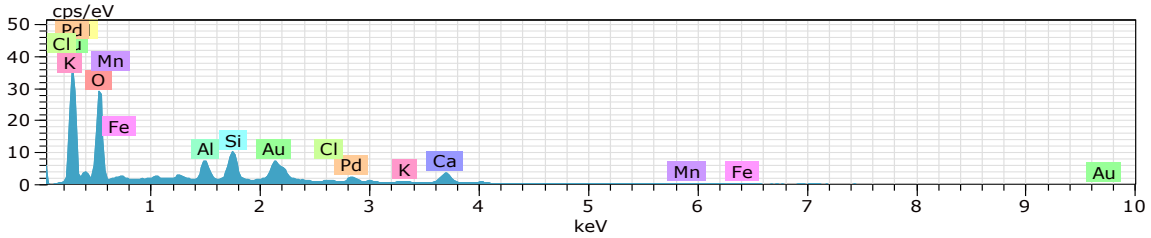


Fig-7: elemental composition of crab shell

Compositions	Elements contents (wt%)										
Crab Shell	Ca	Si	O	Au	Fe	N	Pd	Al	Mn	K	Cl
	10.78	9.28	33.43	18.99	7.15	5.49	5.43	4.26	3.84	0.81	0.43
Fish Bone	Ca	C	O	Zr	P	Nb	Pd	Mg	Na	F	As
	23.65	14.09	28.99	11.43	8.27	8.04	3.48	1.00	0.49	0.41	0.13

Table-1: Elemental composition of crab shell and fish bone

The result were shown in table1. It was observed that on the surface of fish bone sample the primary element were Ca And O. The calcium and oxygen content was found to be 28.99% to 23.65%. apart from ca and O, several metal namely carbon (C), zirconium (Zr),phosphorus (P), niobium (Nb) ,magnesium (Mg), sodium (Na) were also observed.

For the crab shell the result shown in table1. It was observed that on the surface of crab shell sample the primary element were O,Au and Ca. The Ca and O content ranged from 33.43 to 10.78 also the Au element as a major component also present. Apart from ca and O others metal namely silicon (si), iron (fe) ,nitrogen (N), palladium (Pd), manganese (Mn) , potassium (K) chlorine ,(Cl) also observed.

3.2 Effect of reaction parameter

3.2.1 Effect of the molar ratio of Methanol to oil

The transestrification activity also depends on the molar concentration of methanol to oil. Large excess of methanol is required to shift the equilibrium favourably during transestrification for better biodiesel yield. Chart 1 shows the experimental condition and obtained results. In case of fish bones it was observed that with an increase in the molar ratio from 6:1 to 12:1 biodiesel yield decreases from 78% to 70% and further increases to 84% at 15:1 molar ratio. However at highest molar ratio 18:1 the yield again decreases to 77%. In case of crab shell it was observed that with an increase in the molar ratio from 6:1 to 12:1 biodiesel yield decreases to 52.76% and the maximum yield of biodiesel 76% found at 15:1 methanol to oil ratio. Also for the mixed catalyst the maximum biodiesel yield is 70.24%.

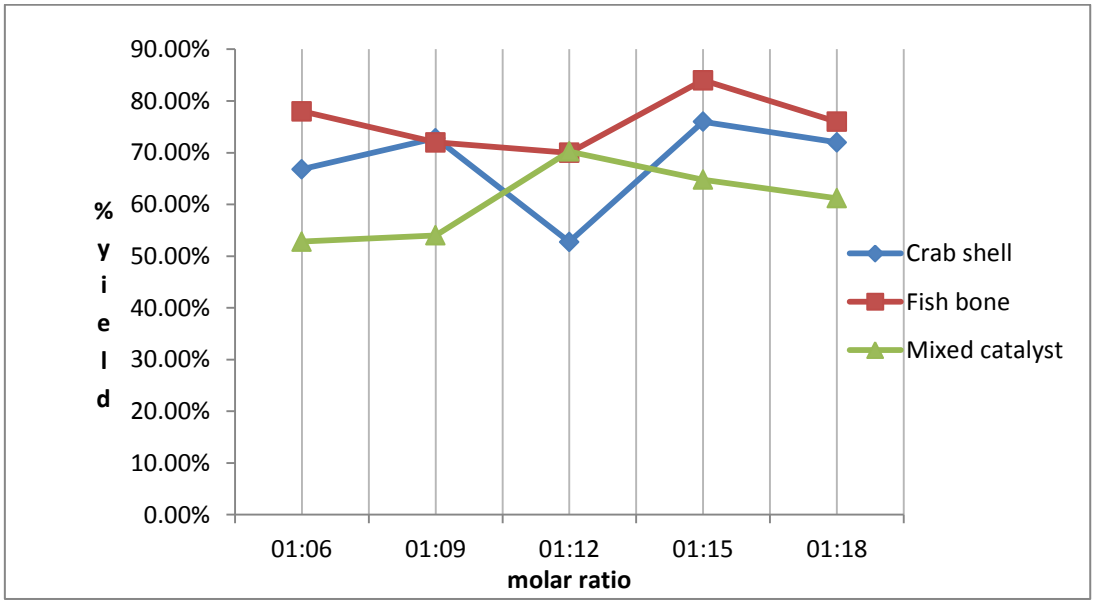


Chart-1: Effect of methanol to oil ratio on % yield of methyl ester for crab, fish and mixed catalyst

4. Conclusion

CaO Catalyst derived from waste mud crab shell and fish bone.Transesterification of soyabean oil was carried out by using CaO catalyst and shown effective conversion of waste soyabean oil to biodiesel. The reaction performed at different methanol to oil ratio ranging from (6:1 to 18:1) with constant temp 65^0C.The maximum biodiesel yield for the fish bones catalyst 84%, crab shell 76% and mixing of fish bones and crab shell 70.24% is found at 15:1 and 12:1 methanol to oil ratio .The optimum calcinations temperature and time were 900^0C and 2hr. The study revealed that the waste crab shell and fish bones as a source of catalyst for biodiesel production could be effectively utilized in developing highly efficient cost effective and environmental friendly heterogeneous catalyst for biodiesel synthesis.

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