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# Conversion of glycerol to polyglycerol over waste duck-bones as a catalyst in solvent free etherification process

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**Abstract.** The alkaline catalyst derived from the duck-bones was used for conversion of glycerol to polyglycerol via solvent free etherification process. The physicochemical properties of prepared materials were duck-bones were systematically investigated as a catalyst by latest techniques of Thermo gravimetric analysis (TGA), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface properties. TGA showed different trends of duck-bones decomposition from room temperature to 1000C. XRD pattern showed a clear and sharp peaks of a crystalline phase of CaO. The activity of the catalysts was in line with the basic amount of the strong base sites, surface area, and crystalline phase in the catalysts. The prepared catalyst derived from duck-bones provided high activity (99 %) for glycerol conversion and around 68 % yield for polyglycerol production. These ample wastes of duck-bones have good potential to be used as polyglycerol production catalysts due to have high quantity of Ca compare to other types of bones like cow, chicken and fish bones.

## 1. Introduction

Energy demand and its resources are increasing day by day due to the rapid outgrowth of population and urbanization. Currently, fuel crisis has globally floundered the economy in every region, especially the oil consuming countries due to its rapidly decreasing available global stock. In view of this serious situation, biodiesel which comes from 100% renewable resources provides an alternative fuel option for future. Approximately 10 pounds of crude glycerol are created for every 100 pounds of biodiesel production [1,2]. A crude glycerol glut is created due to rapidly expanding biodiesel industry [3-5]. The production of biodiesel or value-added chemicals from biodiesel-derived glycerol requires new basic heterogeneous catalysts as well as optimization of the conventional catalyst materials. As mesoporous materials provide a combination of large specific surface area and a certain degree of pore size with shape selectivity, they have one of the greatest potential applications as a heterogeneous catalyst but limited for thermal stability or alkaline loading for basicity due to structure collapse [6,7].

The conversion of glycerol to polyglycerol was studied well and found the suitable reaction path that is etherification process [8]. Moreover, for etherification reaction these heterogeneous catalysts have limitation and sometime cause reactor corrosion, mixing problem, leaching and some are difficult



to recover, thus increases the overall polyglycerol production cost. The problems associated with the conventional catalysts can be resolved by using the heterogeneous catalysts in the biodiesel production technology [9]. Heterogeneous catalysts simplify the biodiesel production process; where they can be reused repeatedly without any major loss in their catalytic activity, making the process more economical [10,11]. The high cost of biodiesel is the key issue for a large scale application of biodiesel as compared to that of conventional petroleum based diesel [12]. It has been reported that approximately 70e 95% of the total biodiesel production cost is related to the cost of the raw materials [13,14]. In this context, low value byproduct glycerol is considered to be a promising for converging it to value able product as polyglycerol that ultimately reduce the biodiesel production cost [15]. Moreover, the production of polyglycerol from waste duck-bones will not only provide value able catalyst for glycerol conversion but will also solve the problems associated with restaurants and food related disposal [16]. Similarly, the cost of catalyst also contributes enough to the total biodiesel production cost via utilization of crude glycerol as a byproduct of this product into a highly demandable polyglycerol product. Several studies have been made to use waste materials for low cost catalyst preparation to develop sustainable biodiesel production process [17].

In the present study, duck-bones were used as waste solid catalyst for etherification of biodiesel derived glycerol to value able polyglycerol. This process help to reduce overall cost of biodiesel production by utilizing its value glycerol into value able polyglycerol via a catalyst prepared by waste bones of duck. First duck-bones were converted into CaO as a catalyst and well characterized by different latest techniques to show CaO presence, stability, basicity and other surface properties. The prepared duck-bones based catalyst was used for etherification of glycerol conversion into polyglycerols in solvent free reaction. High conversion of glycerol and high yield of polyglycerol was observed over this prepared duck-bones based catalyst.

## 2. Experimental

### 2.1. Materials and catalyst preparation

The duck-bones was obtained from a local restaurant, located in Bandar Sri Iskandar, Malaysia. Prior to use, the bones were repeatedly washed using tap water to remove dirt and other impurity material and then dried overnight at 100°C. The duck-bones were then crushed and calcined at 800°C for 2 h in a tubular furnace to convert material into CaO form. After the reaction is complete, nitrogen with a flow rate of 3 l/min was introduced to furnace to cool down the system and to prevent the air entering the system. Subsequently, the catalyst was removed from the furnace and kept in a desiccator to prevent contact with air. Glycerol was purchased from R & M Chemicals, Malaysia. The chemicals and other analytical reagents were purchased from Sigma-Aldrich, Malaysia and they were used any further purification.

### 2.2. Characterization

The prepared duck-bones catalyst was characterized using TGA for decomposition of material, XRD for confirmation of Ca presence in prepared material and BET surface area techniques for measuring active surface area and pore size of the prepared material as duck-bones catalyst. X-ray diffraction (XRD) patterns of the material was recorded using a Bruker D 8 Advance diffractometer with Cu K $\alpha$  radiation in the 2 $\theta$  range from 5 to 80°C at 40 kV and 40 mA. The Brunauer-Emmett-Teller (BET) surface area (surface analyser Micromeritics; ASAP 2020) was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The pore volume is important property to find out activity of the reaction on catalyst surface because selectivity of the product into polyglycerol totally depend upon pore volume and pore size of the prepared material. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. The thermo gravimetric analyses (TGA) of the surfactant-modified clay catalysts were conducted using a Perkin Elmer thermal

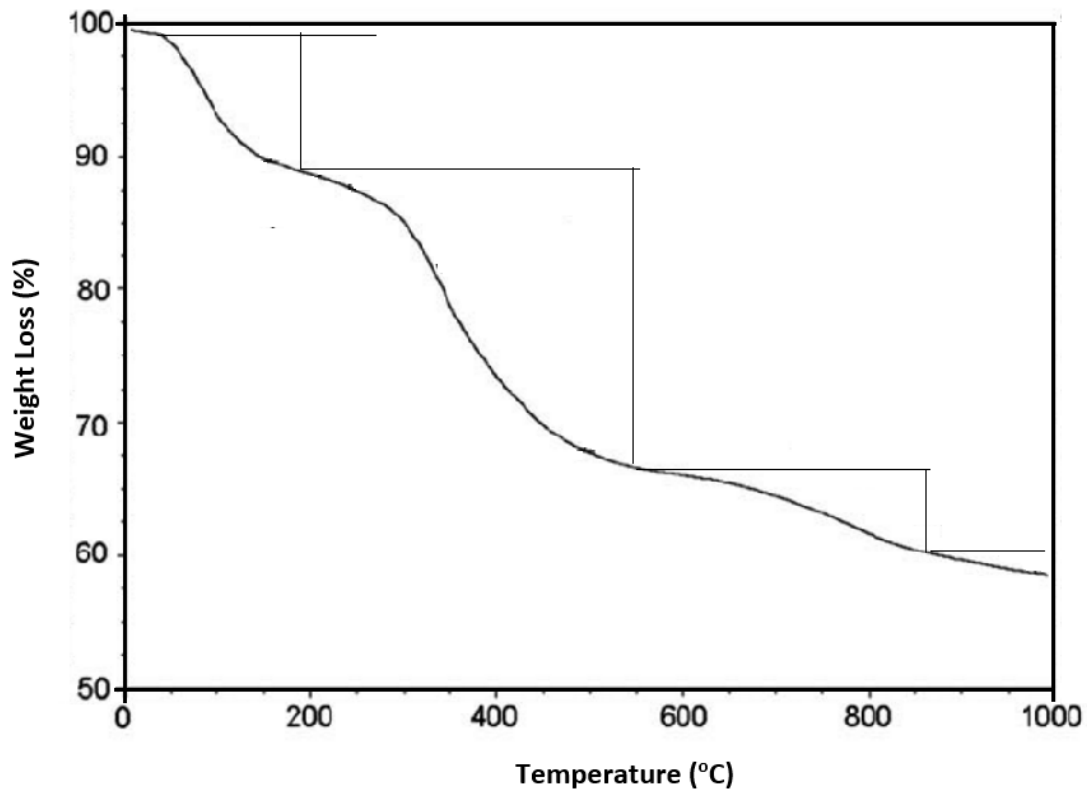
analyser (TGA7) under a high-purity nitrogen flow at a heating rate 20oC/min. Base strengths of the catalysts (H<sub>+</sub>) were determined using Hammett indicators.

### 2.3. Reaction procedure

The activity was identified by means of conversion of glycerol and the selectivity of these converted products to polyglycerol products (diglycerol, triglycerol and tetracyclol). The path of such etherification reaction through polymerization involves the conversion of glycerol to polyglycerol (diglycerol and triglycerol) by removing one or two water molecule. Glycerol etherification is carried out at 240 °C in a three neck glass reactor equipped with PID temperature controller and magnetic stirrer. This batch reactor was working at atmospheric pressure under inert media (N<sub>2</sub> gas) in the presence of 2wt% of catalyst; water being eliminated and collected using a Dean–Stark system. In a typical experiment, the reactor was charged with 50 g of anhydrous glycerol and 1.0 g of catalyst was added. The reactor was heated to the desired reaction temperature. After each 2 hours, withdraw the sample product for GC analysis.

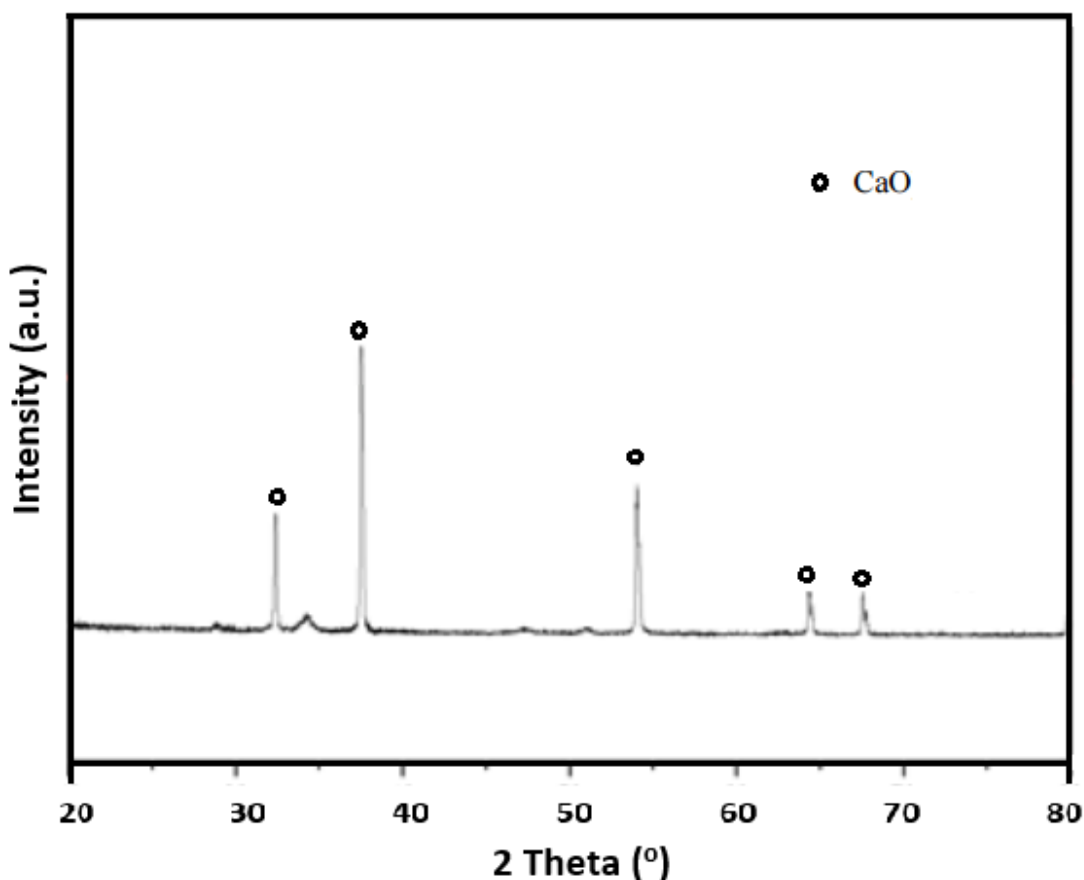
## 3. Results and Discussions

Thermal properties of the duck-bone catalyst was observed by using TGA as shown in Fig 1. In this thermo gravimetric analyser was analysed with the function of temperature. The weight loss of the material was calculated by TG curve. It was observed that under 100°C the weight loss was very low that was belong to water evaporation. After 100°C to 200°C the weight loss occurred 10% that was due to removal of any attached water molecule or any other contaminants. Further a big weight loss was found around 20% from 200°C to 575°C that might belong to the evaporation of CO<sub>2</sub> material or due to the evaporation of unreacted materials of the sample. Then the weight loss from 575°C to 800°C was found 7% might belong to complete conversion of material into CaO. Final weight loss was noted from 850°C to 1000°C that was very low might going to stable afterward. The total weight loss was calculated as around 40% from room temperature to 1000°C.



**Fig 1.** Thermo gravimetric analysis of prepared duck-bone catalyst

XRD patterns of the duck-bones catalysts calcined at 800°C temperature is shown in Fig. 2. It is clear from this figure that prepared material is stable at high calcination temperature and also clear that prepared catalyst has main peaks of CaO that supposed to be act as catalyst during reaction. As a result, the catalyst sample duck-bones showed clear and sharp peaks of a crystalline phase of CaO. This means that samples of duck bones material was sustained its structure successfully after calcined at 800°C.



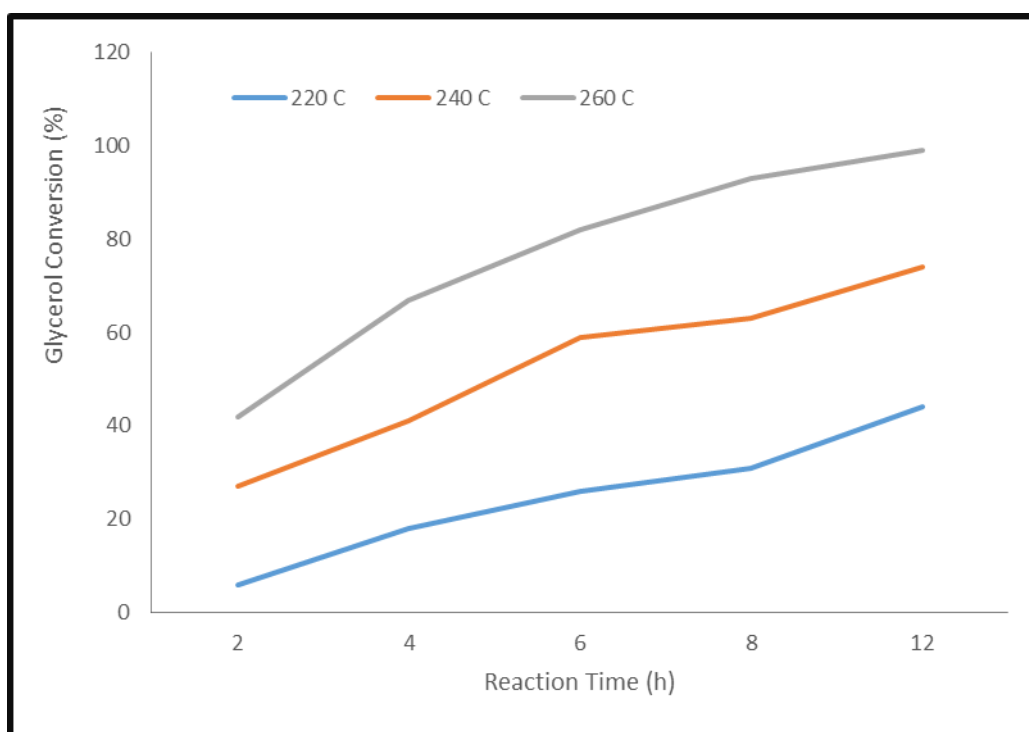
**Fig 2.** XRD pattern of prepared duck-bone catalyst

The surface properties of prepared duck bones catalyst was also observed and found some changes in surface area and pore size as shown in Table 1. In addition, the basic strength of prepared duck bones was also observed. Table 1 shows the basic strength, BET surface area and pore volume of duck bones catalyst after calcination at 800 °C. As clearly noted, the prepared duck bones catalyst have basic strength of a value  $7.2 < H_- < 9.3$ . The BET surface area and pore volume of prepared duck bones catalyst was recorded as  $123.70 \text{ m}^2 \text{ g}^{-1}$  and  $0.15 \text{ cm}^3/\text{g}$ , respectively. It is clear from this table that surface area and mesoporosity of prepared duck bones catalyst was not high. This might be due to preparation method and calcination at high temperature that might cause to reduce inside pores of prepared materials.

**Table-1.** The surface properties of prepared duck-bones

Properties	Duck bones catalyst
Surface Area ( $\text{m}^2/\text{g}$ )	123.70
Pore Volume ( $\text{cm}^3/\text{g}$ )	0.15
Pore Size ( $\text{\AA}$ )	31.80
Basic Strength ( $H_-$ )	$7.2 < H_- < 9.3$

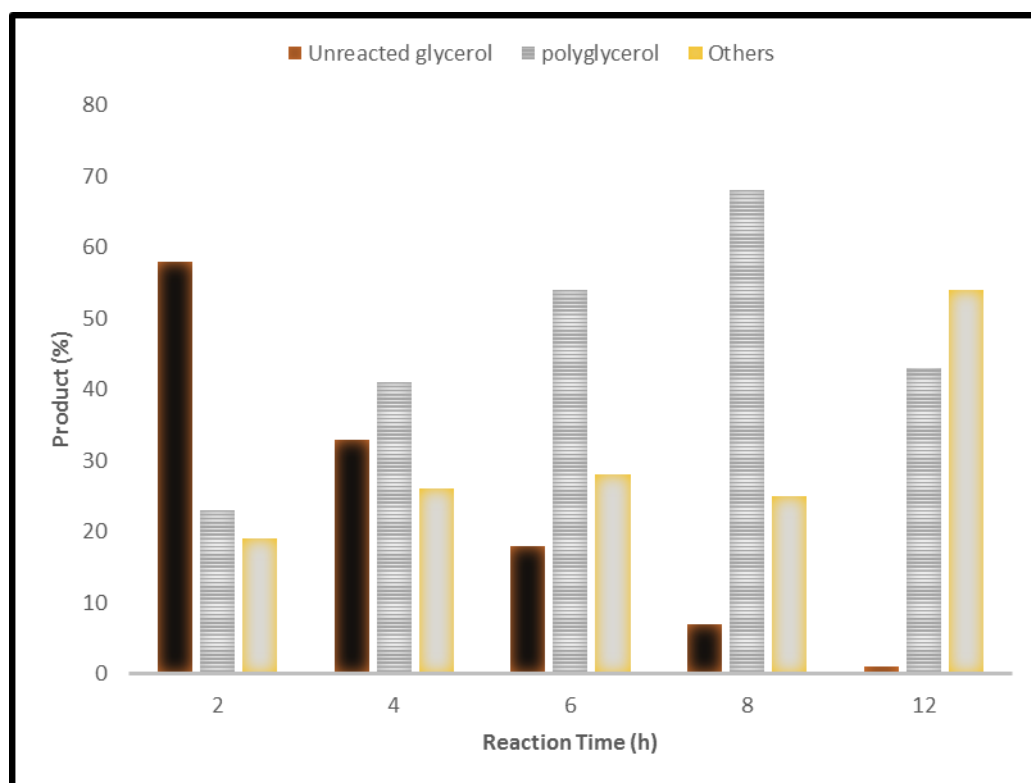
The influence of different reaction temperature over reaction time for glycerol conversion is shown in the Figure 3. The maximum conversion of glycerol 99% at 260°C was noted for 12 hours of reaction at the amount of 3 wt % of prepared duck bones catalyst. The conversion of glycerol was found to be increased with increasing time from 2 to 12 hours. Simultaneously, this conversion was also found to be increased with increasing reaction temperature from 220 to 260°C. Actually, with increasing reaction time, more glycerol molecules got to break up in the form of dehydration or any other form at given condition which cause increasing of glycerol conversion. The reaction was also conducted at temperature 280°C and glycerol conversion was found 100 % within 4 hours but all glycerol was converting in side product like soap formation and polyglycerol production was found very low. It may possible that at higher reaction temperature 280°C, the conversion of glycerol speedup in the presence of the strong alkali metal which may lead to the increase some by-product. This may cause to decrease the polyglycerol production by preceding some new reactions. This behaviour also studied by previous researcher and these results are in agreement with their results [18].



**Fig 3.** The influence of different reaction temperature over reaction time for glycerol conversion

The influence of different reaction temperature over reaction time for polyglycerol production is shown in the Figure 3. The maximum polyglycerol production was recorded 68% after 8 hours of reaction time at given 260°C with the amount of 3 wt % of prepared duck bones catalyst. The production was found to be increased with increasing time from 2 to 8 hours but after 8 hour of reaction time polyglycerol production started to decreased and reached 43% at 12 hours of reaction time. Actually, with increasing reaction time, more glycerol molecules got to break up in the form of dehydration or any other form at given condition which cause increasing of glycerol conversion. This may cause to decrease the polyglycerol production by preceding some new reactions. Therefore suitable reaction time might 8 hours at reaction temperature 260 C in the presence of 3 % prepared catalyst for maximum glycerol conversion to polyglycerol.





**Fig 4.** The glycerol conversion to polyglycerol at 260°C over reaction time

#### 4. Conclusion

The glycerol conversion to polyglycerol in solvent free heterogeneous etherification could be achieved by CaO catalysts derived duck bones. It was proved from characterization of prepared material that duck-bones as a catalyst was a stable material for etherification process and also found sharp peaks of a crystalline phase of CaO during XRD analysis. The highest catalytic activity for glycerol conversion was found 99 % at 12 h and 92 % at 8 h of reaction time. The maximum polyglycerol production yield was observed 68 % at 8 h over prepared duck bones-derived catalyst. These industrial wastes could stand for promising resources of low-cost catalysts to convert inexpensive biodiesel derived glycerol to value added polyglycerol that could bring down the overall biodiesel production cost.

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