

## Effects of Milling Duration on Malaysian Dolomite to Enhance Hydrogen Production via Gasification of Oil Palm Fronds

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**Abstract.** The purpose of this work is to investigate the effect of mechanochemical treatment on Malaysian dolomite towards the enhancement of hydrogen production from gasification reaction of oil palm fronds (OPF). To accomplish the objective, Malaysian dolomite was subjected to high energy planetary ball mill for 1, 2 and 4 h in ethanol. The milling process reduced the particle size of the catalysts and consequently increased their surface area. The catalytic activity was investigated through temperature programmed gasification (TPG). The catalyst premixed with the biomass in a ratio of 1:1 and undergone TPG under partial oxygen environment (5% O<sub>2</sub> in He) tested from ambient temperature up to 900°C with heating rate 10°C/min. All the gases produced were detected by online mass spectrometer. The milled catalysts prominently showed the increasing of H<sub>2</sub> production together with the reduction of CO<sub>2</sub> produced due to the dual function of catalysts which acted as tar reduction and CO<sub>2</sub> sorbent.

**Keywords:** Dolomite, Hydrogen production, CaO, Oil palm fronds, Mechanochemical treatment.

### 1. Introduction

The increasing of fossil fuel burning on the daily basis for the energy demand had rose a huge concerned for the effect on the global warming. This due to the green house gases emitted from the fossil fuels combustion. Hence, there is a growing interest in the usage of H<sub>2</sub> as a replacement for the fossil fuels. Instead of contained high calorific value, the combustion and burning of H<sub>2</sub> produced no other than water. Moreover, the potential benefits of H<sub>2</sub> include [1]: (i) reductions on green house gases emissions; (ii) reduction on urban air pollutants; (iii) enhanced energy security; and (iv) increased energy efficiency. Hydrogen derived from biomass especially from agricultural waste had attracted so much attention because of the abundant availability. This source of energy is the most renewable and sustainable which played the main role attributed to the long-lived dependent on H<sub>2</sub> energy [2]. Oil palm tree which the main agricultural plantation industry in the tropical country like Malaysia has attributed enormous of waste [3]. Oil palm yielded more syngas, energy than any other type of biomasses like maize, mangrove wood and food waste [4]. Most of oil palm parts can be utilized to produce syngas [5].

There are several methods that can be used to produce hydrogen from biomass and each of it will differ on the gas composition and the quality of gas produced. The most effective ways by employed thermochemical process where consists of supercritical water gasification [6], pyrolysis [7], steam gasification [8-10] and gasification [11-14]. In order to obtain high production of syngas, gasification suits this requirement. The exact gas composition strongly depends on the process conditions especially temperature, the gasification agent, feedstock composition and the gasification technologies [15]. The main obstacle performing gasification is the formation of tar which only decomposed at high temperature

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(>1000°C) [15,16]. In this matter, the introduction of catalyst into the system plays a vital role in reduction of tar formation.

Dolomite is a magnesium ore which has chemical formula of  $\text{CaMg}(\text{CO}_3)_2$  can be found abundantly in the country like Malaysia. Dolomite attracted so much attention due to the ability for tar reduction [11,17,18] and  $\text{CO}_2$  sorbent [16,19,20]. In this work, the evaluation of mechanochemical treatment on Malaysian dolomite towards the hydrogen production via gasification of oil palm fronds (OPF) is studied. By employing milling process to the dolomite catalysts, the particle size of catalysts reduced consequently increased the surface area. However, milling media is the major factor affected the effectiveness of the milling process [21]. The use of ethanol as a media is believed to exhibit the dual role of solvent and reducing agent [22]. Hence, the benefits from the increased of surface area can be utilized during the gasification reaction whereby larger surface area can be provided for the reactant to undergo catalytic processes.

## 2. Experimental Materials and Method

Dried oil palm fronds (OPF) was initially ground and sieved to smaller particle size. The ultimate analysis is given in Table 1. On the other hand, Malaysian dolomite was obtained from Perlis and composed of 39.79%  $\text{MgO}$ ; 38.97%  $\text{CaO}$ ; 0.16%  $\text{Al}_2\text{O}_3$ ; 0.098%  $\text{SiO}_2$ ; and 0.08%  $\text{Fe}_2\text{O}_3$ . Natural dolomite was first been calcined at 900°C in static furnace under air environment for 8 h before undergoes milling process.

Table 1: Ultimate analysis of OPF

Ultimate analysis	wt %
C	38.16
H	7.14
N	0.37
S	0.74
O	49.57

The mechanochemical treatment was carried out by using planetary ball mill (model Pulverisette 4 from Fritsch) with an agate ball having 250 ml volume together with fifty 10 mm diameter agate balls. 5 g of natural Perlis dolomite and ethanol were put together inside the bowl. The bowl spins around its own axis and around second axis outside its centre at 1000 rpm for 1, 2, and 4 h. The milled dolomites were then been calcined at 900°C for 4 h. The unmilled dolomite was denoted as CD while the milled calcined dolomites were denoted by CDE1, CDE2 and CDE4 indicated to duration of milling which were 1, 2 and 4 h, respectively. Catalysts were then characterized using Brunauer-Emmer-Teller (B.E.T) surface area analysis model Thermo Finnigan Sorptomatic 1900 series. The morphology of catalysts was determined by X-ray diffraction patterns obtained from XRD-6000 Diffractometer and field emission scanning electron microscopy (JEOL JSM-7600F FESEM) was used to observed the 3 dimensional shape of catalysts.

Table 2: Reaction equations involved

Reaction equations	$\Delta H_{298}^\circ$ (kJ mol <sup>-1</sup> )	Equations
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$	- 96.6	1
$\text{C}_n\text{H}_m\text{O}_p + (2n-p) \text{H}_2\text{O} \rightarrow n\text{CO}_2 + (m/2 + 2n - p)\text{H}_2$	endothermic	2
$\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$	94.6	3
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$	- 41.5	4
$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$	- 178.2	5
$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	117.0	6
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	170.5	7
Biomass + oxidant ( $\text{O}_2$ , $\text{H}_2\text{O}$ ) $\rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{Tar} + \text{Ash} + \text{Char}$	endothermic	8

Approximate weight of catalysts (unmilled and milled dolomite) and OPF were premixed followed the ratio of 1:1. Temperature programmed gasification (TPG) was performed by using a ThermoFinnigan TPDRO 1110 instrument online with mass spectrometer (Pfeiffer Omnistar) which measured multiple masses continuously to detect the product gas composition. The gas mixture of 5%  $\text{O}_2$  in He was using during gasification process with flow rate of 10 ml/min. Gasification of the mixture sample was done at

temperature from ambient temperature till 900°C at the heating rate of 10°C/min and was held for 1 h at final temperature. The syngas produced was detected by mass spectrometer. All the reaction occurred in this study as shown in the Table 2.

### 3. Results and Discussion

#### 3.1. XRD Analysis

Figure 1 shows the unmilled and milled catalysts for OPF gasification in these studies. The main peaks which at angle of diffraction,  $2\theta = 32^\circ, 37^\circ, 54^\circ, 64^\circ$  and  $67^\circ$  referred to CaO phase where  $2\theta = 43^\circ$  and  $62^\circ$  represented to MgO phase. This approved it was a dolomite which mainly decomposed by CaO and MgO phase [9]. Remarkably on the calcined dolomite phase after undergone milling process,  $\text{Ca(OH)}_2$  phase appeared at diffraction angle  $2\theta = 34^\circ, 47^\circ$  and  $50^\circ$ . This may due to the reaction between dolomite and water molecule during the milling process (Eq. 1). The milling process attributes to the changes of the xrd patterns where the peaks widened compared to the unmilled dolomite indicating the reduction of particle size [23] leading to the increment of catalyst surface area.

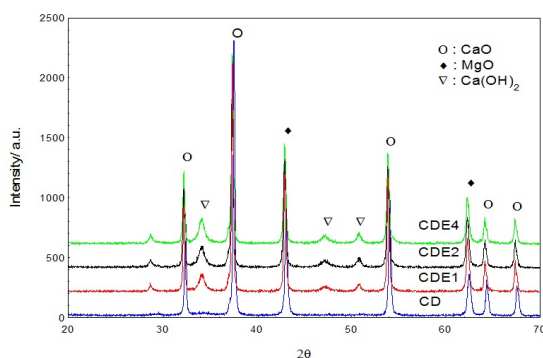


Fig. 1: XRD diffraction of unmilled and milled dolomite catalysts

#### 3.2. BET Surface Area

Table 3 showed the increment of milled catalysts surface area over time of milling process compared to unmilled ones. This depicted the abatement of particle size of catalysts. The surface area for 1 h milled catalysts increased from 13 m<sup>2</sup>/g (unmilled dolomite) to 17 m<sup>2</sup>/g and then further increased to 19 m<sup>2</sup>/g and 21 m<sup>2</sup>/g for 2 and 4 h milling process, respectively. The milling process caused repeated fracture of the solid particles at first, followed by diminished particle size and consequently increases surface area of the catalysts [21].

Table 3: BET surface area of unmilled and milled dolomite catalysts

Catalysts	Surface Area (m <sup>2</sup> /g)
CD	13
CDE1	17
CDE2	19
CDE4	21

#### 3.3. OPF Gasification

In the gasification reaction, the equations involved during the reaction as aforementioned in Table 2. The overall gasification reaction generally represented as Eq. 8 in which the addition of oxidant may contributes to the product-end composition. Fig. 2 and 3 showed the evolution of the product gas spectra during the gasification. F was referred to the oil palm fronds undergone gasification without the presence of the catalyst. Apparently, the onset temperature was at high of about 450°C. Interestingly, the presence of the catalysts has reduced the onset temperature of gasification reaction down to 300°C. This may due to the catalytic cracking of the volatile compounds [16] generally represented by the Eq. 2. The similar trend was showed by each reaction in the presence of milled dolomite catalysts. The high catalytic activity clearly showed from the spectra especially in the range of 500 – 750°C. It is believed that water gas shift reaction (WGSR) played a vital role in the system during that time of period. The reaction equation as described by Eq. 4. Although

during the experiment set up, there is no H<sub>2</sub>O been supplied into the system, that H<sub>2</sub>O molecule is believed derived the biomass content as well as Ca(OH)<sub>2</sub> phase. Ca(OH)<sub>2</sub> will released H<sub>2</sub>O molecule at starting temperature around 400°C. The reaction equation represented in Eq. 3. However, at temperature from 700-900°C, the catalytic activity has reduced. This may due to the surface of CaO has been covered by CO<sub>2</sub> as described in Eq. 5. Hu [9] noted that the activity of calcined dolomite almost completely lost when the CO<sub>2</sub> partial pressures were higher than the equilibrium decomposition pressure of CaCO<sub>3</sub>. Moreover, at holding temperature, there is a catalytic activity for milled dolomite catalysts compared to unmilled ones. This may due to the catalytic cracking of tar. Temperature played imperatively very crucial role in decomposing tar. Conversion of tars increases when the temperature is raised from 800-900°C [24]. Referring to the Fig. 5, the milling process on the catalysts renders the increment in H<sub>2</sub> production where CDE1 showed superior in the production of the gas.

Fig. 3 showed the evolution of CO<sub>2</sub> spectra from gasification reaction. It clearly showed that onset temperature of CO<sub>2</sub> produced was at early 300°C. Interestingly, the presence of catalysts attributed to higher onset which at 380°C. As the temperature increased, CO<sub>2</sub> produced alleviated by the absorption on CaO phase as referred to Eq. 5. Meanwhile, MgO effectively inert with respect of CO<sub>2</sub> captured. MgCO<sub>3</sub> decomposed at lower temperature than CaCO<sub>3</sub> which higher enthalpy energy required for it to decompose (refer to equation 6 and 7 respectively). Hence, MgO phase stabilized the dolomite particle structure thus providing additional void space [19] and continuous free passage [16] for CO<sub>2</sub> diffusion to the interior dolomite catalysts. Significant increased of CO<sub>2</sub> production started at temperature 830°C may due to the catalysts surface has been covered by CO<sub>2</sub> molecules. Based on Fig.5, the production of CO<sub>2</sub> gas was higher in the presence of catalysts due to the effectiveness in hydrocarbon cracking performed by catalysts. However, the production of CO<sub>2</sub> remarkably decreased when milled dolomite catalysts been employed in the system due to the high surface area provided by the catalysts to absorb more CO<sub>2</sub> gases. Nevertheless, all milled catalysts produced about an equal CO<sub>2</sub> gas from the OPF gasification.

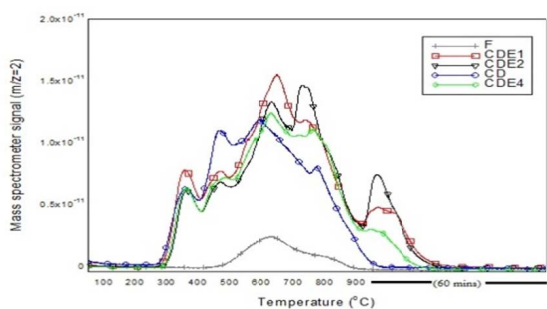


Fig. 2: TPG profile of H<sub>2</sub> production with unmilled and milled with catalysts

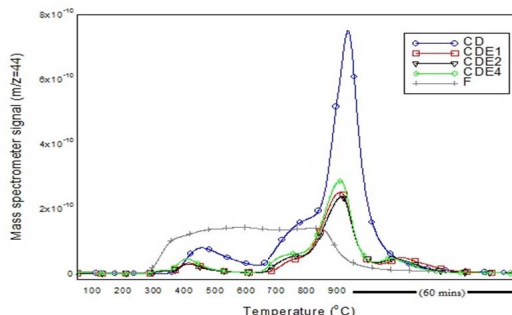


Fig. 3: TPG profile of CO<sub>2</sub> production unmilled and milled catalysts

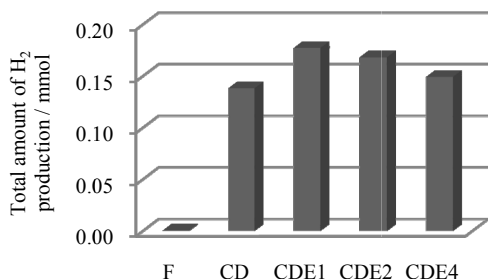


Fig. 4: Cumulative of H<sub>2</sub> production

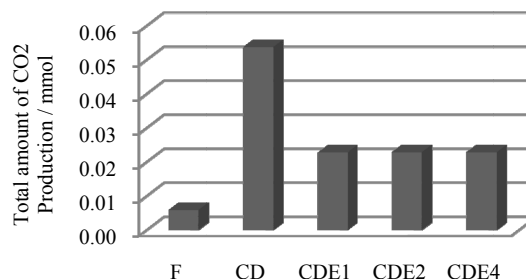


Fig. 5: Cumulative of CO<sub>2</sub> production

#### 4. Acknowledgements

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## 5. Conclusions

OPF gasification was successfully been evaluated in term of hydrogen production as well as catalytic activity. Apparently, higher catalytic activity and H<sub>2</sub> production attained in the presence of dolomite catalysts. Increased in catalytic activity and H<sub>2</sub> production showed when milled catalysts been employed in the system. Superior in H<sub>2</sub> showed by CDE1 depicted the optimum duration for milling process was 1 h. Moreover, remarkably decrement of CO<sub>2</sub> production showed by milled catalysts.

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