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Biofuel production from waste cooking oil by catalytic reaction over Thai dolomite under atmospheric pressure: Effect of calcination temperatures

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Abstract

This study represented the catalytic pyrolysis of waste cooking oil (WCO) to produce biofuel via continuous reaction by using a pelleted Thai dolomite catalyst. The effect of calcination temperatures on catalyst synthesis was also examined in varying from 600 to 900°C for 2 h. Calcined Thai dolomite (CTD) samples were characterized by X-ray fluorescence spectrometer (XRF), thermo-gravimetric analysis (TGA) and differential-thermal analysis (DTA), X-ray diffractometer (XRD), N_2 adsorption-desorption apparatus, and scanning electron microscope (SEM). In the catalytic pyrolysis process, the CTD catalysts were taken place in a packed bed pyrolysis reactor under atmospheric pressure for biofuel production in different reaction temperatures (450 to 550°C), and WHSV was about 0.5 h^{-1}. The results were found that the effect of calcination temperature significantly altered the physicochemical properties of catalyst as well as the catalytic performance. The specific surface area and pore volume decreased with increasing the calcination temperatures. Besides, $CaCO_3$ was transformed entirely into CaO at 900°C. For the catalytic pyrolysis process, the results were found that the highest pyrolytic yield was obtained at 500°C of reaction temperature using catalyst calcined at 700°C. Additionally, the results also expressed that the calcined temperature was significant in the quality of biofuel products. Moreover, the biofuel products can be separated into biogasoline, biokerosene, and biodiesel. The kinetic viscosity and heating value were satisfied following the standard values except for the acid value of all biofuel products. However, the acid value decreased when the CDT calcined at the highest temperature due to the obvious presenting of the CaO phase.

Keywords: CaMgO, Packed bed reactor, Bio-oil, Continuous reactor, Used cooking oil

1. Introduction

About 14,000 million tons of oil equivalent (Mtoe), it is the amount of energy consumption around the world annually in 2018 [1]. There is a troubling shortage of fossil fuel due to its massive usage around the world [2]. Not only is it a lack of petroleum resources, but also its prices increase continually over the world. There are many renewable resources, including solar, geothermal, hydro, wind, fresh water, fresh air, biomass and biofuel. Additionally, they are used for substituting fossil fuels (coal, fuel oil or natural gas). Ethanol, biodiesel and Bio-jet fuels are types of biofuel, and interestingly, most of them can be produced from vegetable oil [3] or WCO [4] via transesterification. Nowadays, oil is used a lot in cooking, particularly in the household and industrial sections. After cooking, it is usually released into a drainage pipe and causes many water pollutions or even sewerage problems.

In this study, we are interested in altering WCO to biofuel products since WCO appears as an attractive feedstock because of utilizing waste. WCO contains high fatty acid concentrations affecting the transesterification reaction, so it significantly causes soap production during the reaction. Some of the researchers reported that WCO contains high fatty acid; however, this high fatty acid value can be reduced by using a homogeneous acid catalyst in an esterification reaction together with a transesterification reaction using an alkaline catalyst [5]. The later researcher used a solid catalyst prepared by sulfonating pyrolyzed rice husk with sulfuric acid and subjected to esterification and transesterification reactions to produce biodiesel from WCO [6]. Unfortunately, the product from the combined reactions was only biodiesel. Besides, these methods are quite complicated compared to pyrolysis. The advantage of pyrolysis is to produce many products such as biogasoline, biokerosene, and biodiesel [7]. As known from many research, biofuel can be produced via the pyrolysis process by using many kinds of catalysts, e.g., activated carbons, alumina, H-ZSM-5, MgO, and dolomite; even raw material has high fatty acid concentrations such as WCO and free fatty acid. For instance, Hafriz et al. [8] used Malaysian dolomite as a catalyst for biofuel production via the pyrolysis of WCO. The catalyst expressed

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very high activity because of the decomposition of $CaMg(CO_3)_2$ phase and the formation of the MgO-CaO phase. It is well known that dolomite compositions are $CaCO_3$ and $MgCO_3$, and after calcination, $CaCO_3$ and $MgCO_3$ can turn into CaO and MgO, respectively [9].

Moreover, several researchers studied the pyrolysis process by using alkaline dolomite as a catalyst taken place in a batch reactor. The results were found that adding hydrogen during the pyrolysis process caused decarboxylation over CaO and MgO catalyst in dolomite, which can be able to reduce acidity in biofuel products [10]. Also, they studied the effect of calcination temperatures at 800 to 1,000°C of dolomite-powder and found that high calcination temperature significantly decreased the acidity of the products. Hafriz et al. [8] calcined Malaysian dolomite powder at 900°C for 4 h and used it as a catalyst for biofuel production in the pyrolytic batch process. The result showed a high liquid product (21%wt), which consisted of gasoline (48%wt), kerosene (35%wt), and diesel (26%wt). Moreover, the hydrocarbon compound highly produced about 76.51% and its acid value was about 33 mgKOH/g. Additionally, Ajala et al. [11] used dolomite catalysts that were calcined at 800 and 900°C for 2 h. The result showed that the calcination temperature affected the efficiency of dolomite catalysts. CaO and MgO phases appeared when dolomite samples were calcined at 800 or 900°C for Nigeria dolomite [11], while CaO and MgO phase existed at 589 and 490°C, respectively for Malaysian dolomite [8]. Besides, some of the batch reactors showed low productivity and unstable quality. Incidentally, using dolomite powder as a catalyst in a continuous reactor causes high-pressure drop because the reactant flowed through the catalyst layer difficultly, and the catalyst was agglomerated at the high reaction temperature. According to previous studies, there is no research on using pelleted dolomite in continuous reaction for biofuel production and no research about focusing the effect of calcination temperature using Thai dolomite for biofuel production. Thus, the optimal calcination temperature of Thai dolomite for biofuel production via pyrolysis is interesting.

This work aimed to study the effect of different catalyst calcination temperatures (600 to 900°C) for biofuel production via a packed bed reactor. The physical and chemical properties of the catalysts were characterized by using many techniques such as X-ray fluorescence spectrometer (XRF), thermogravimetric analysis (TGA) and differential thermal analysis (DTA), X-ray diffractometer (XRD), N_2 adsorption-desorption apparatus, and scanning electron microscope (SEM). The reaction was conducted at WHSV of about 0.5 h^{-1} and different reaction temperatures (450 to 550°C). After that, the products were distilled following ASTM D86. Kinetic viscosity, heating value, and acid value of the products after distillation were measured following ASTM D445, ASTM D240, and Shao & Agblevor report [12], respectively.

2. Materials and methods

2.1 Chemicals

WCO was obtained from Khon Kaen Municipality, Thailand. Dolomite was purchased from Agricultural Technology Club in Khon Kaen, Thailand. Phenolphthalein ($C_{20}H_{14}O_4$, Riedel-de Haën), potassium hydroxide (85% KOH, RCI Labscan Ltd.), and acetone (99.5% C_3H_6O, RCI Labscan Ltd.) were used for acidity measurement by titration method.

2.2 Catalyst synthesis and characterizations

Dolomite was ground thoroughly by a ball mill about 6 h before pelletizing. Then, dolomite was pelleted in cylindrical shape about 1.0 to 1.5 cm in length by using a hydraulic press machine. After that, pelleted catalysts were calcined at designed calcination temperatures (600, 700, 800, and 900°C) for 2 h in a muffle furnace (Electric service device Co., Ltd.), namely calcined Thai dolomite (CTD). After calcination, dolomite pellets turned to be brick red. The physical and chemical properties of CTD were examined by many characterization techniques. The chemical compositions were analyzed by X-ray fluorescence spectrometer (XRF, model XGT-5200, HORIBA Scientific, Japan). Thermal stability and thermal behavior of catalysts were measured by the thermogravimetric analyzer (TGA-50, Shimadzu, Japan) and differential thermal analyzer (DTG-60/60H TG/DTA, Shimadzu, Japan) heated up 5°C/min under air zero until 1,000°C. The crystallinity and phase compositions were analyzed by X-ray diffractometer (XRD, Empyrean, Malvern Panalytical, UK) from 20 to 80° under 40 kA and 40 kV, with step increasing about 0.02°. The specific surface area and pore size distribution of the catalysts were computed by applying the Brunauer-Emmett-Teller (BET) and Barrett Joyner and Halenda (BJH) methods, respectively. The nitrogen gas (N_2) was used as the adsorbate and operated at 77 K by using the N_2 adsorption-desorption apparatus (ASAP2460, Micromeritics, USA). The morphologies of the catalysts were investigated by using the scanning electron microscope (SEM, S-3000N, Hitachi, Japan).

2.3 Biofuel production

In typically, 250 g of the CTD catalysts was compacted in a packed bed reactor. Then, the raw bio-oil (WCO) was fed to the evaporator through a peristaltic pump. After that, the WCO was heated to 500°C in order to evaporate to the vapor which called the primary pyrolytic cracking process. Next, WCO vapor was passed through the reactor for a secondary catalytic cracking process. The pyrolytic catalysis process was conducted under atmospheric pressure, WHSV of 0.5 h^{-1}, and different reaction temperatures (450, 500, and 550°C) without feed any gases. After the pyrolytic catalysis process, the product was cooled by using a heat exchanger and condenser, respectively. The liquid product was collected at the bottom of the separator, and the vapor product was left to the environment via flare. The water and organic phase were separated by using a separating funnel. The organic product of 100 mL was distilled by petroleum product distillation tester (SYD-6536, China) following ASTM D86 standard. Biogasoline, biokerosene, and biodiesel were obtained at different distillation temperatures as following biogasoline (75 to 150°C), biokerosene (150 to 250°C), and biodiesel (250 to 330°C). During distillation, the temperature was noted every 10 mL, and the distilled product container was changed at different temperatures of each type of biofuels. After distillation, kinetic viscosity, heating value (Auto bomb calorimeter, Automatic adiabatic, Gallenkamp, Thailand), and an acid value of products were measured following ASTM D445, ASTM D240, and Shao & Agblevor report [12], respectively.

3. Results and discussion

3.1 Catalyst characterizations

Uncalcined Thai dolomite catalyst was characterized by XRF. It was found that there were many oxide forms such as CaO (41.4 wt%), Fe_2O_3 (30.9 wt%), SiO_2 (18.6 wt%), and a small amount of MgO. According to the XRF result, CaO represented the highest content in the catalyst, which is similar to other dolomite samples [13]. CaO can reduce the acidity of pyrolytic products, as reported in the previous study [7]. However, the ferric content still showed higher content than dolomite from other counties. Besides, uncalcined Thai dolomite was also characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), as shown in Figure 1. For the TGA curve, 3% weight loss around 100 to 120°C can be attributed to the chemical bond of water [14]. Accordingly, there was an endothermic reaction at about 100°C.

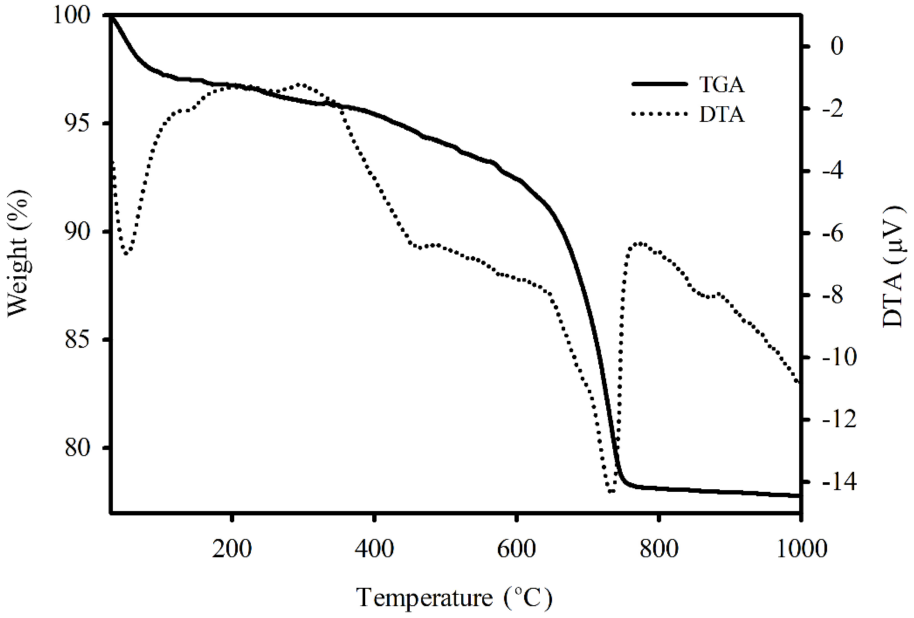

Figure 1 TGA and DTA curves of uncalcined dolomite

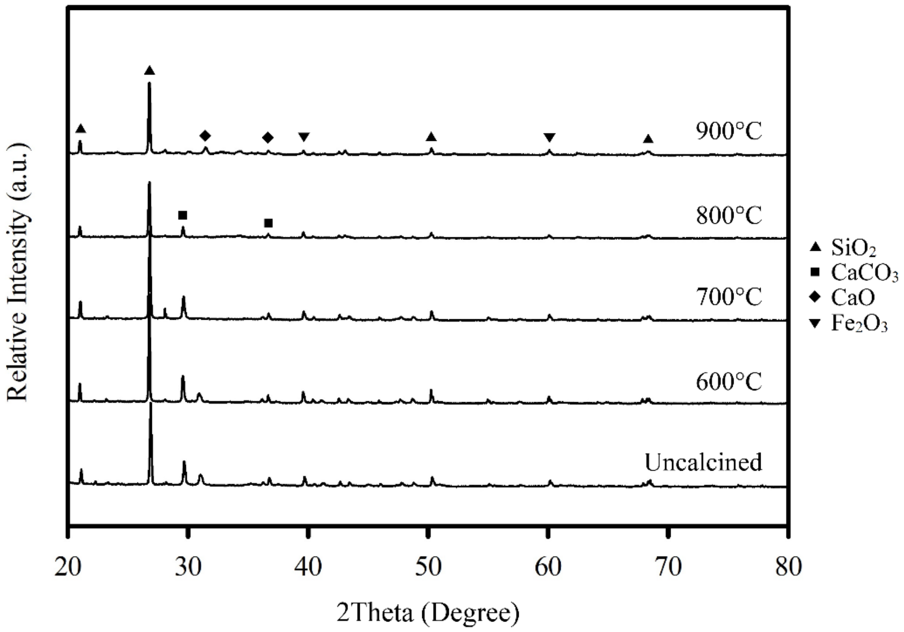

Figure 2 XRD diffractogram of uncalcined and calcined dolomite samples

The total weight loss was about 22%, from 100 to 750°C. In terms of DTA, there was an endothermic reaction at 750°C due to carbonate decomposition in the dolomite. After that, it turned into an oxide form at 800°C, paralleling previous research [15]. This occurrence can be explained by the following Equations (1) and (2):

$$CaMg(CO_3)_2 \rightarrow MgO + CaCO_3 + CO_2 \quad (1)$$

$$MgO + CaCO_3 \rightarrow MgO + CaO + CO_2 \quad (2)$$

Consequently, according to the results, the calcination temperatures were chosen at 600 to 900°C and 2 h.

The phase transformation was described by XRD, as presented in Figure 2. For uncalcined dolomite, the presence of peaks at 2θ = 21.2, 26.8, 50.6, and 68.5° was confirmed as SiO_2, and $CaCO_3$ and Fe_2O_3 were also apparent. After calcination, CTD samples depicted peaks belonging to $CaCO_3$ in the samples calcined at 600, 700, and 800°C, in which peaks at 2θ = 29.7 and 36.8°. For the sample calcined at 900°C, $CaCO_3$ was completely transformed to CaO, which can be seen from the peaks at 2θ = 32.3 and 37.2° [16], relating to the result of thermal behavior as depicted in Figure 1. However, Fe_2O_3 was still displayed in all samples at 2θ = 39.8 and 60.3° [17], which corresponded to the results of XRF.

Regarding the N_2 adsorption-desorption isotherm and pore size distribution analysis of catalyst as demonstrated in Figures 3(a) and (b), N_2 adsorption-desorption method using BET and BJH techniques was considered. The results showed that the hysteresis loop of the samples calcined at 600, 700, and 800°C appeared as adsorption isotherm IUPAC type IV. However, which in the graph slope tended to be sharply at high pressures because absorbent came in and accumulated in the pore of the sorbents (capillary condensation) [18]. Additionally, the hysteresis loop was decreased with increasing calcination temperature due to the annealing of capillary pores. Until calcined at 900°C, the hysteresis loop almost disappeared, which can be confirmed as isotherm type I.

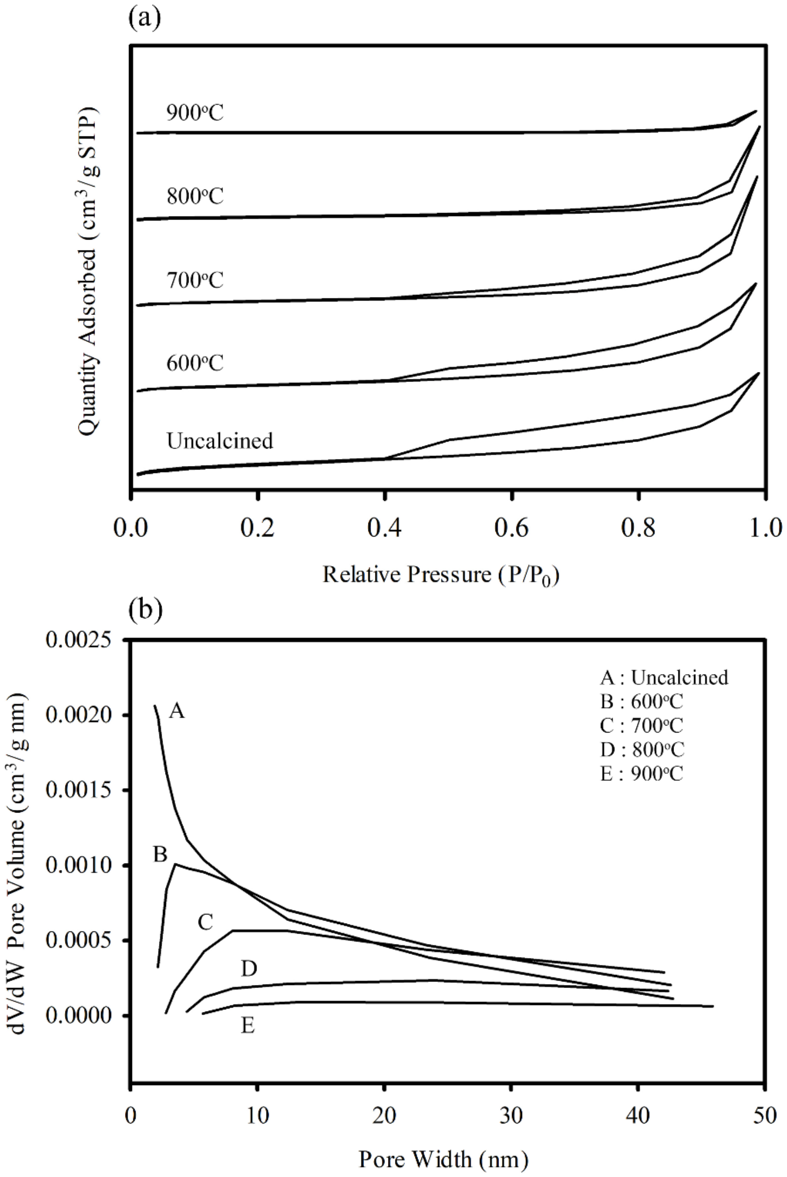

Figure 3 N_2 adsorption-desorption isotherm (a) and pore size distributions of dolomite calcined at different temperatures (b)

Moreover, according to the phenomena, the pore sizes can be classified as mesoporous materials (2 to 50 nm) for the uncalcined sample and samples calcined at 600 to 800°C and then may trend to no pore for 900°C, as can be seen in the broad pore size distribution (Figure 3(b)). Furthermore, it can result in a smaller specific surface area when calcined at higher temperatures. The pore volume and specific surface area values of the dolomite samples calcined at 600, 700, 800, and 900°C were 0.027, 0.024, 0.012, and 0.0036 cm^3/g and 12.0, 8.3, 4.6 and 1.1 m^2/g, respectively. The results were consistent with Ngamcharussrivichai et al. [19], in which the authors reported that the carbonate group could decompose to oxide form at high calcination temperature, and the increase of temperature can force the changing specific surface area and pore size of the sample.

The typical SEM images of all samples are collected in Figure 4. It can be seen that the calcined dolomite catalysts at every calcination temperature illustrated a rough surface because of the cracking of uncalcined dolomite and releasing of CO_2 from carbonate [20], which these phenomena can affect the pore size of the catalysts [21, 22]. Moreover, the characteristic surface of the calcined dolomite sample, particularly at 900°C, was quite different from the uncalcined dolomite. As seen in the images, the morphology of the uncalcined sample showed plate-like (Figure 4(e)), while the calcined samples formed to spherical shape when increased calcination temperatures (Figure 4(a) to (d)). It might be due to a force out of CO_2 from the lattice, resulting in more basic sites were formed in the residual materials [20]. Additionally, in which it appeared to have more spherical particles of CTD when calcined at higher temperatures, compared with uncalcined dolomite. This phenomenon might be caused by $CaCO_3$ in the samples was destroyed and transformed into CaO phases at high calcination temperature (800 and 900ºC), as approved by XRD results and previous research [23, 24].

3.2 Effect of calcined catalysts on WCO in pyrolysis

The parameters of WCO raw material, collected in the Khon Kaen Municipality, such as acid value following Shao & Agblevor report [12], kinematic viscosity following ASTM D445 were analyzed. The results showed that acid value was about 7.0 mg KOH/g and kinematic viscosity was 31.3 cSt. Interestingly, the analyzed parameters of the WCO in this work showed lower kinematic viscosity and higher acid value from the previous report. For instance, Wu et al. study [25], the acid value and kinematic viscosity of WCO were about 2.5 mg KOH/g and 44.7 cSt, respectively.

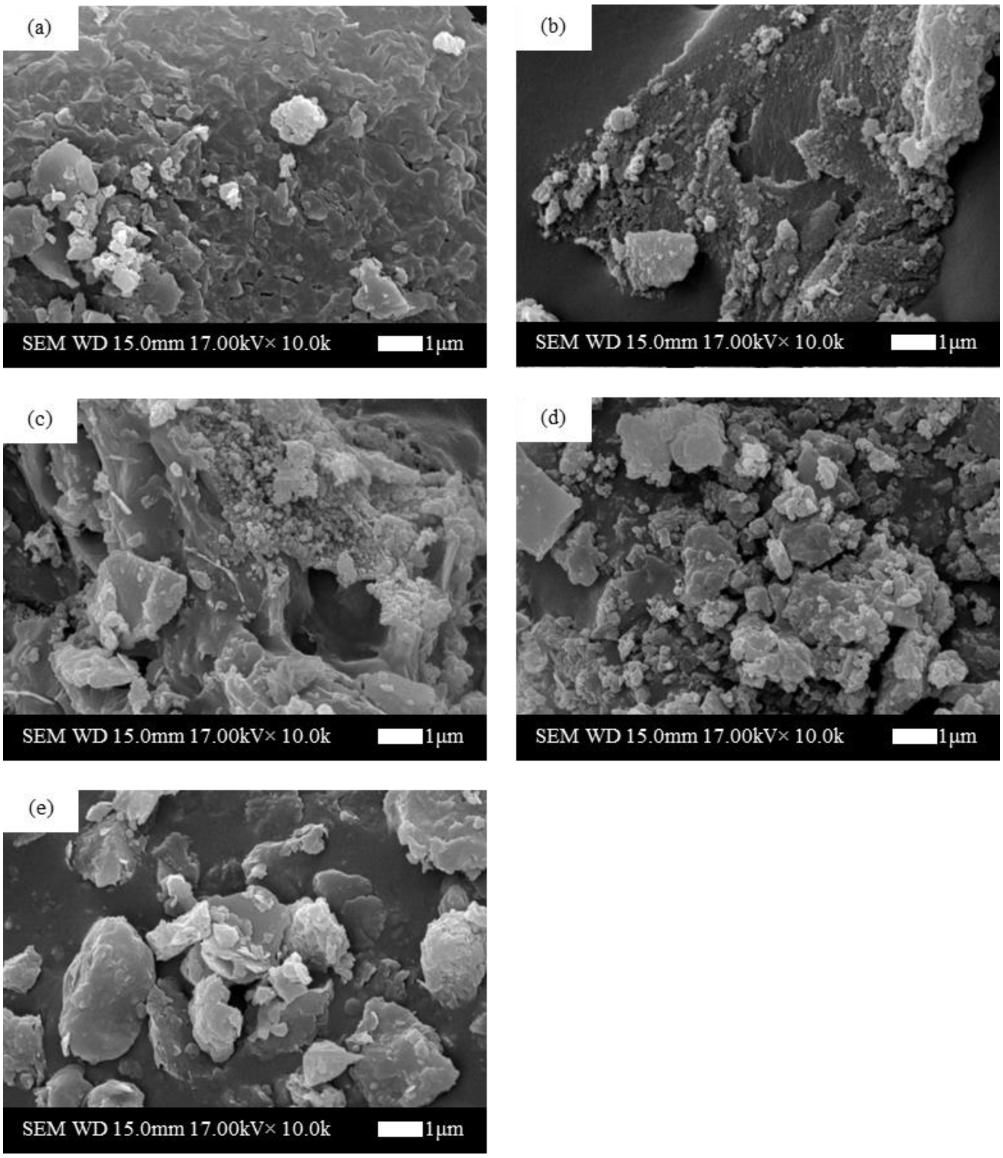

Figure 4 SEM morphologies of the dolomite catalysts calcined at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C and (e) uncalcined sample

WCO in different sources has displayed the difference in kinematic viscosity and acid value because of dissimilar usage.

In terms of the effect of different calcination temperatures (600 to 900°C), the results were found that calcination temperatures were significantly affected on the pyrolytic yield of products in all reaction temperatures (450, 500, and 550°C), as shown in Figure 5. It was clearly seen that CTD calcined at higher temperatures led to a high gas production because $CaCO_3$ in dolomite increasingly turned into CaO at higher calcination temperatures. CaO in dolomite can react in terms of breaking the carbon chain to small molecules. Moreover, it might be due to the occurrence of the reactions between hydrodeoxygenation, decarboxylation, and decarboxylation during the pyrolysis process [9].

The maximum pyrolytic yield was conducted at a reaction temperature of 500°C by using the CDT catalyst calcined at 700°C. The results showed a liquid product of about 91% by volume compared with entering WCO. A high reaction temperature enhanced the cracking reaction of free fatty acid by breaking the carbon chain to small organic compounds on the surface of catalysts [26]. On the other hand, the pyrolysis process, reacted at the low reaction temperature, caused a coke formation on catalyst surfaces. The reaction of the pyrolysis process can be divided into two cracking processes. Firstly, the primary cracking change from the liquid phase to the gas phase was called evaporation. Then, the second cracking under the high reaction temperature of the gas phase on the surface of catalysts was produced smaller molecules of hydrocarbons in gas products, which processes were similar to Chang et al. report [7].

Simultaneous thermal analysis was used to characterize WCO and pyrolytic products. The TGA curve measured up to 700°C is shown in Figure 6. The TGA curve was conducted under an oxygen atmosphere (air zero) at 20 to 700°C, with a heating rate of 10°C/min [27]. The TGA result of WCO presented that a molecule of WCO started loss of weight at about 200°C, which was similar to Borugadda & Goud report [28]. Then, at 250 to 500°C, WCO weight was sharply decreased because of heavier hydrocarbon evaporation and the reaction of WCO with oxygen to produce CO and CO_2, as consisting of a single continuous step of thermal decomposition as Borugadda & Goud report [28]. Also, WCO suddenly evaporated at approximately 325°C, the same as the result of Patil et al. research [29]. Thus, the WCO evaporation or primary cracking was selected at 500°C because WCO was almost converted to the vapor phase. Then, the vapor phase continuously reacted over the CTD in a packed bed reactor at different reaction temperatures.

As selected reaction temperature at 500°C, pyrolytic products reacted over catalysts calcined at different temperatures (600, 700, 800, and 900°C). Following Figure 6(a), pyrolytic oils were decomposed completely at 520°C, while WCO was done at

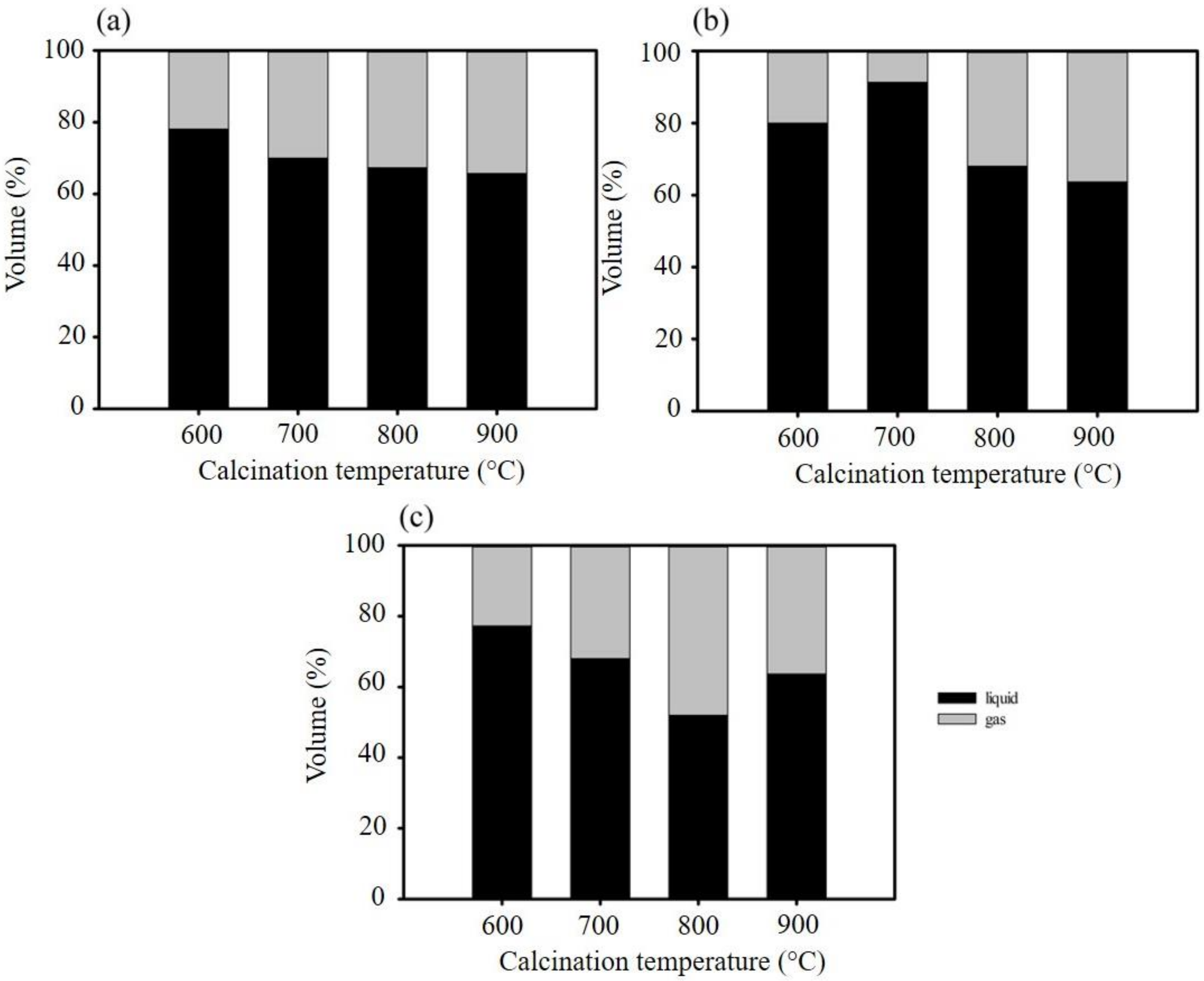

Figure 5 Volumatic percentage of products at different reaction temperatures: (a) 450°C, (b) 500°C and (c) 550°C

almost 600°C, which might be due to smaller molecules of pyrolytic oil. Percent weight losses of WCO and pyrolytic oils at a temperature 300°C were about 5% and 90%, respectively. Moreover, there was an insignificant difference in each different calcined temperature. Figure 6(b) shows the percent weight loss of pyrolytic oils in different reaction temperatures over the CTD calcined at 700°C. The results were found that pyrolytic oil decomposed about 90% weight from 25 to 300°C. Then, it was totally gone at 500°C. Before distillation, water was firstly separated from pyrolytic oil. Water product was formed by decarboxylation, hydrodeoxygenation, and hydrocracking reactions [30]. Many reactions can occur in the pyrolytic process. Firstly, the bioorganic molecules were converted to smaller gas molecules. Then, the smaller molecules were decomposed by the thermal reaction in hot temperature before a catalytic process (secondary process). The products, such as H_2, CO, CO_2, CH_4, C_nH_m, $C_xH_yO_z$, and soot-like carbon, can be produced after thermal reactions [31]. After that, secondary reactions can occur over catalysts before the pyrolysis vapor was quenched in the condenser at the high temperature in the packed bed reactor. Also, H_2 can be produced from this secondary reaction, including tar cracking shift reaction [32]. This secondary reaction could produce incondensable gas, including CO, H_2 and small molecule of hydrocarbons. The reactions can be expressed in Equation (3) to (12), according to Lojoiu et al. [31] and Dai et al. [33] discussions for H_2 production during the pyrolysis process.

$$\mathrm{Tar} \rightarrow CH_4 + H_2O + C_nH_m + H_2 \tag{3}$$

$$C + H_2O \rightarrow CO + H_2 \tag{4}$$

$$C + CO_2 \rightarrow 2CO \tag{5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$

Water-gas shift (WGS) equilibration:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{7}$$

$$C + 2H_2 \rightarrow CH_4 \tag{8}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{9}$$

Boudouard reaction:

$$2CO \rightarrow C + CO_2 \tag{10}$$

$$C_mH_n + 2nH_2O \rightarrow nCO_2 + [2n + (m/2)]H_2 \tag{11}$$

$$C_mH_n + nH_2O \rightarrow nCO + [n + (m/2)]H_2 \tag{12}$$

Thus, H_2 can be produced and then continuously reacted with bio-oil following hydrodeoxygenation reaction (Equation (13)), decarboxylation reaction (Equation (14)) and decarboxylation reaction (Equation (15)) to produce hydrocarbon compounds.

Hydrodeoxygenation:

$$R\text{-}COOH + 3H_2 \rightarrow R\text{-}CH_3 + 2H_2O \tag{13}$$

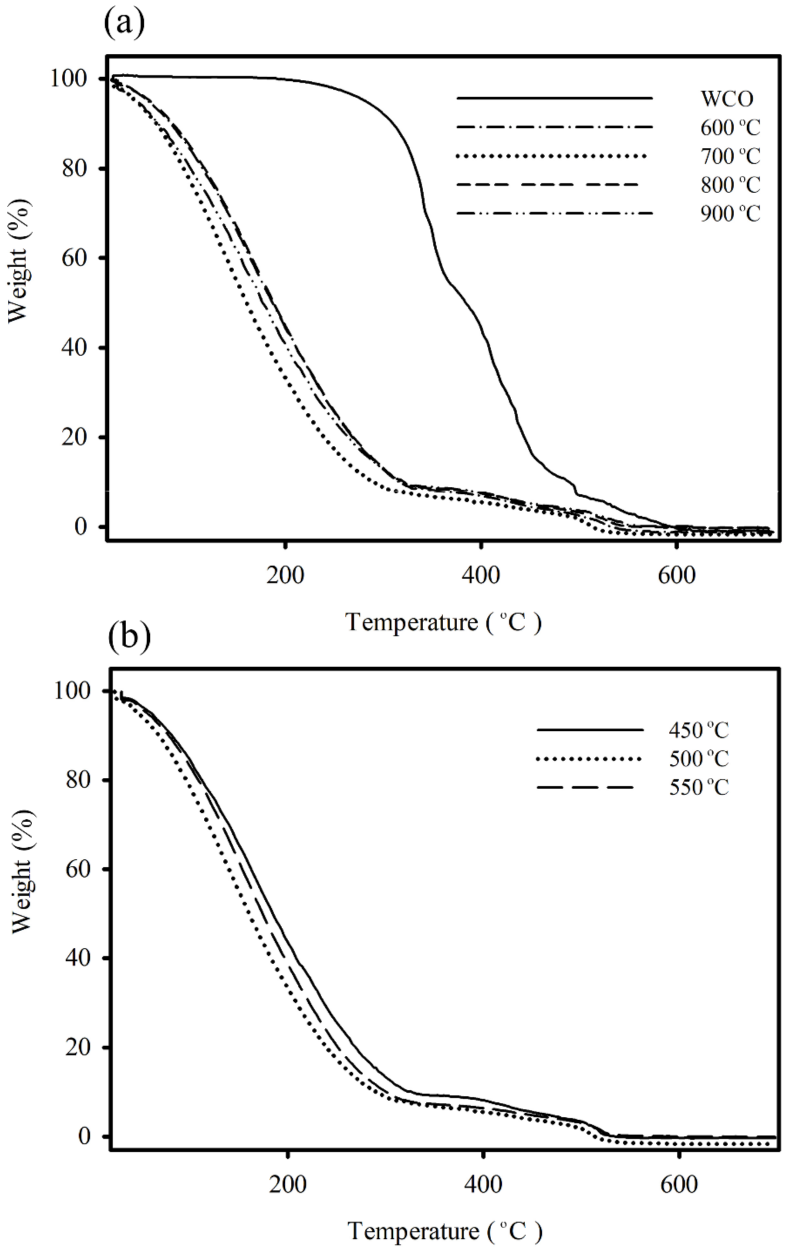

Figure 6 Percent weight loss of pyrolytic oil conducted at 500°C with different calcined catalysts comparing to WCO (a), and weight loss of pyrolytic oil conducted at different reaction temperatures using CTD calcined at 700°C (b)

Decarbonylation:

$$R\text{-}COOH + H_2 \rightarrow R\text{-}H + CO + H_2O \qquad (14)$$

Decarboxylation:

$$R\text{-}COOH \rightarrow R\text{-}H + CO_2 \qquad (15)$$

According to hydrodeoxygenation and decarboxylation reactions, water was produced by CaO as a catalyst in these reactions. Hydrocarbons were formed following the removal of carboxylic acid and carbonyl group in fatty acid by CaO catalysts. Hydrocarbon compounds from decarboxylation and decarboxylation reactions were paraffin and olefin, respectively. Afterward, the cracking process, hydrogen transfer, and isomerization were appeared, resulting in smaller hydrocarbon products. Primary cracking of the pyrolysis process can promote decarboxylation, decarboxylation, dehydration, isomerization, and aromatization reactions, which can convert biomass-derived oxygenates into aromatic hydrocarbons [34, 35]. Therefore, this study was not necessary to add hydrogen gas for secondary cracking over the catalytic process. Pyrolytic oils about 100 mL of each condition were distilled as regarding ASTM D86 standard, and distillation temperatures of every 10 mL of distilled products were recorded. Distilled oil, produced by using CTD calcined at 600°C, was about 90% of pyrolytic oil due to large molecules, while pyrolytic products produced by CTD calcined at higher calcination temperatures (700 to 900°C) were distilled almost 100%, as shown in Figure 7.

During the distillation, biofuel products were separated by using the different distillation temperatures (biogasoline, 75 to150°C [36], biokerosene, 150 to 250°C [37] and biodiesel, 250 to 350°C [38]), and the results are displayed in Figure 8. There was an insignificant difference at 450°C of reaction temperature with every calcination temperature. Biogasoline and biokerosene increased continuously with increasing calcination temperatures contributing to fewer diesel products with higher reaction temperatures (500 and 550°C). It can be explained that smaller hydrocarbon products occurred when increased calcination temperatures of CTD because $CaCO_3$ further transformed to CaO, as confirmed by XRD and SEM results.

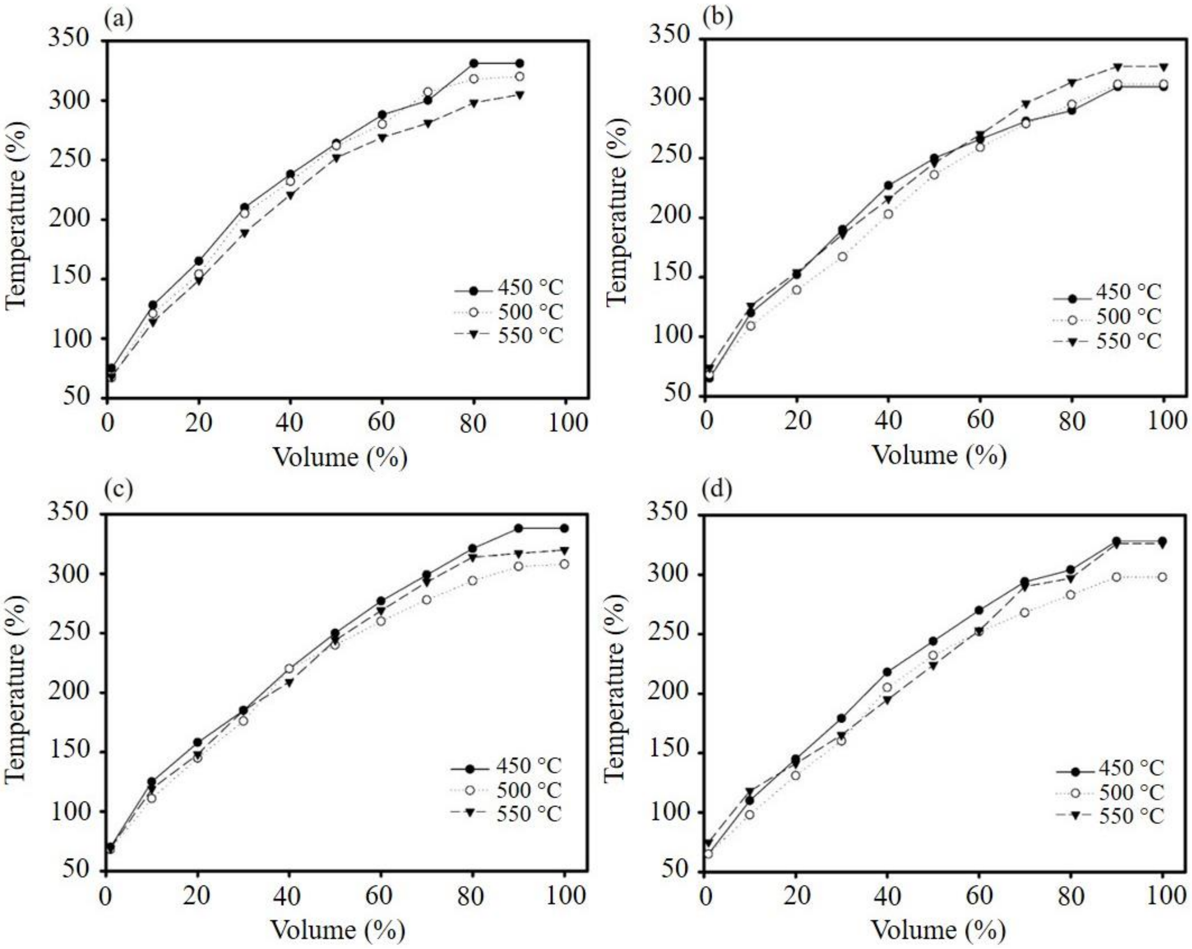

Figure 7 Relationship between temperature and volume of distilled oil following ASTM D86 at different calcination temperatures of dolomite: (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C

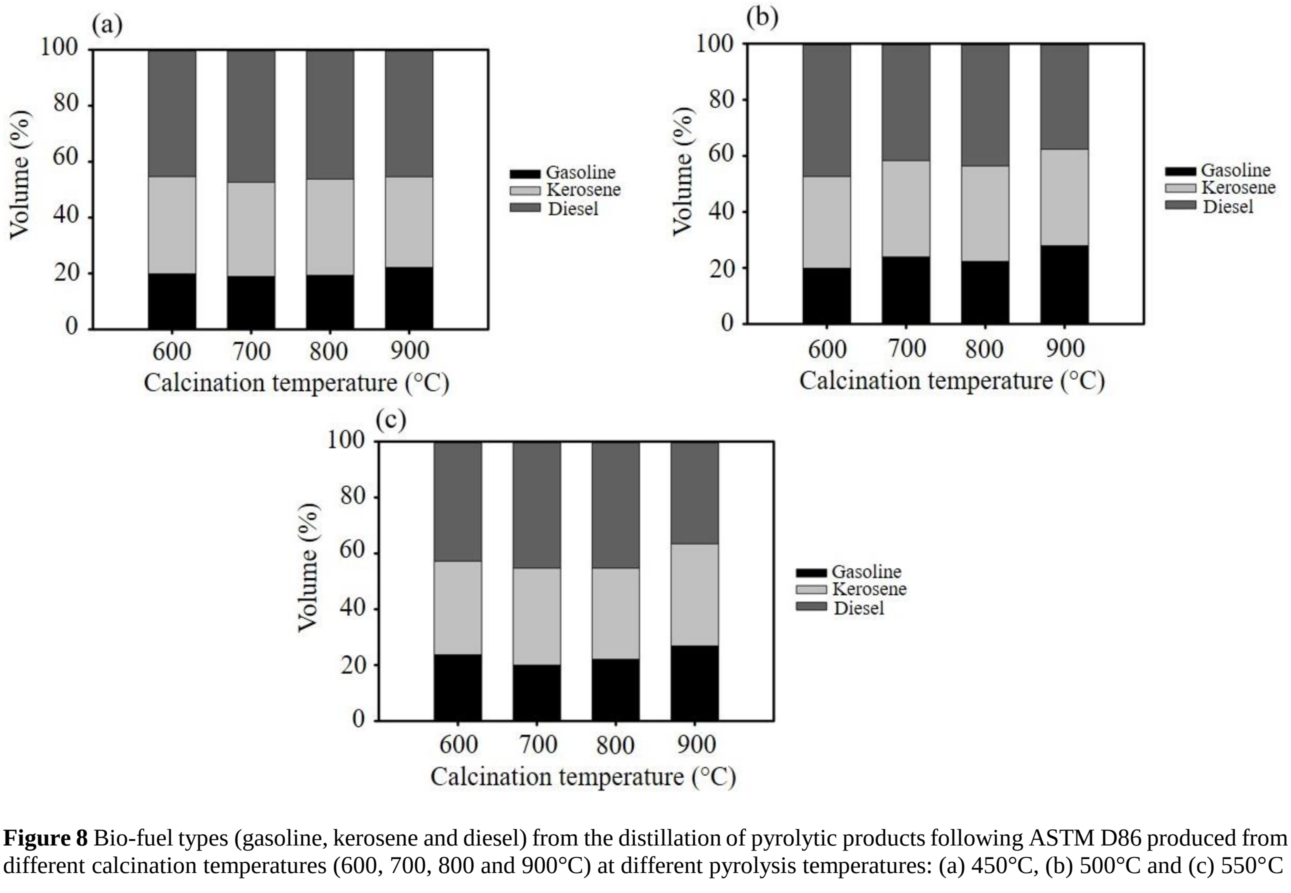

Figure 8 Bio-fuel types (gasoline, kerosene and diesel) from the distillation of pyrolytic products following ASTM D86 produced from different calcination temperatures (600, 700, 800 and 900°C) at different pyrolysis temperatures: (a) 450°C, (b) 500°C and (c) 550°C

Then, CaO, an active site in the decarboxylation process, can promote the secondary hydrocarbon-cracking process. Thus, biofuel products were shown in small hydrocarbon compounds relating to Xie et al. report [39].

3.3 Biofuel analysis

Biofuel, distilled from pyrolytic products using CTD calcined at 700°C and reacted at 500°C, was selected for product analysis. The results were found that the kinematic viscosity of biogasoline, biokerosene, and biodiesel was in the range of standard values. The kinetic viscosity of each product was 0.444, 0.974, and 3.091 cSt of biogasoline, biokerosene, and biodiesel, respectively, comparing with kinetic viscosity standards for gasoline 0.40 to 0.71 cSt, kerosene < 2.00 cSt and diesel 1.80 to 4.10 cSt. The heating values of biogasoline, biokerosene, and biodiesel were 46.25, 49.91, and 47.74 MJ/kg, respectively. The heating values of all biofuel types were higher than standard values, which were 44-46 MJ/kg for gasoline, 43 MJ/kg for kerosene, and 42-46 MJ/kg for diesel. On the contrary, the acid values of all biofuel products were obviously higher than the standard values, which the acid values standard for gasoline, kerosene, and diesel should be about 0.0162, 0.015, and 0.5 mg KOH/g, respectively. In our results, the acid values of biogasoline, biokerosene, and biodiesel were about 7.11, 10.19, and 9.35 mg KOH/g, respectively. These high acid values of biofuel value might be due to the high oxygenated compound. Importantly, it can result in corrosion of the engine. Thus, decreasing the acidity of biofuel products must be required by mixing with fossil fuel or using the hydrodeoxygenation reaction. In addition, biofuel can be produced from CTD catalyst calcined at 700 and 900°C with the same reaction temperature (500°C). The acidity of gasoline over CTD calcined at 900°C was about 5.25 mg KOH/g, which was lower than the product reacted over CTD calcined 700°C and WCO. It might be due to the CTD calcined at 900°C representing CaO phase, which the oxide form of this CaO phase may decrease the acidity of biofuel products [6]. That may be the reason for the acidity of the CTD calcined at 900°C that showed lower.

4. Conclusions

The effect of calcination temperature of Thai dolomite was significant on catalytic performance. The specific surface area and pore volume decreased with increasing the calcination temperatures. $CaCO_3$ was wholly transformed into CaO at 900°C. Additionally, liquid pyrolytic products were reduced with increasing the calcination temperatures and increasing the reaction temperature except CTD calcined at 700°C and reacted at 500°C that gave the highest liquid product. The pyrolytic products showed that a small hydrocarbon molecule occurred when using CTD calcined at higher calcination temperatures, which were confirmed by increasing biogasoline and biokerosene and decreasing biodiesel. The kinetic viscosity and the heating value for each product were 0.444, 0.974, and 3.091 cSt and 46.25, 49.91, and 47.74 MJ/kg of biogasoline, biokerosene, and biodiesel, respectively, which showed under standard values. While the acidity of biofuel indicated higher than standard values, therefore, decreasing the acidity of biofuel products must be required for the next challenge in the future, for example, using the hydrodeoxygenation reaction. However, CTD calcined at higher temperatures gave lower acid values because of the occurrence of the CaO phase.

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