

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Pure Natural Materials as Heterogeneous Catalysts

CS1 and CS2 are crustaceans shells obtained from local markets of Fredericton, New Brunswick, Canada. Calcium, magnesium, phosphorus, carbon, strontium and oxygen were found as main components of the cuticles and sodium, chloride, strontium and silicon in minor amounts for these samples. For CS1, the organic matrix was found to vary between 10.4% and 38.2% of the dry weight, the mineral content varied between 50.0% and 88.6% and the loss of CO₂ was found to vary between 16.1% and 36.0% of dry weight and consisting mainly of calcium carbonate (Boßelmann *et al.*, 2007). For CS2, the protein content was found to vary between 33% and 40% of the dry weight, the chitin content varied between 17% and 20% and the ash content of CS2 was found to be relatively constant with an average value of $34 \pm 2\%$ of the dry weight (Ruth Hagen Rødde *et al.*, 2008).

AS is egg shell obtained from household. The chemical composition (by weight) of AS has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) (Stadelman, 2000).

The last two types of mollusk shell used for this experiment were MS1 and MS2. Both of these shells were obtained from the beaches of Prince Edward Island, Canada. MS1 and MS2 are composed of primarily calcium carbonate crystals laid down in a protein matrix (Wheaton, 2007).

A reaction temperature of 60°C and a reaction time of 60 minutes were used for these experimental runs. The amount of the catalyst used was set to 10% by weight of oil. All of natural materials for this experiment consisted of different types of animal shells; CS1, CS2, AS, MS1, and MS2. At these reaction conditions, these natural materials did not show any catalytic activity. Because the major component of animal shells is CaCO₃. Kousu and his coworkers (2008) reported that CaCO₃ itself is not active for the transesterification of vegetable oil even at long reaction times.

The yield of this reaction is the percentage by weight of the biodiesel contained in the reaction mixture. Table 4.1 indicates that for the reaction conditions used in these experiments the animal shells tested as catalysts for the transesterification reaction of canola oil did not show any catalytic activity. There was no conversion of the the canola oil.

Table 4.1 Animal shells as catalysts for the transesterification of canola oil

Catalysts	Catalyst by weight of oil (wt%)	Reaction temperature (°C)	Reaction time (minutes)	Biodiesel yield (%)
CS1	10	65	60	No conversion
CS2	10	65	60	No conversion
AS	10	65	60	No conversion
MS1	10	65	60	No conversion
MS2	10	65	60	No conversion

All of the natural materials used for this experimental section contain calcium carbonate as a major component, some of the other metal carbonates and phosphates, traces of transition metal including M1, M2, and M3, and some alkaline metal; sodium, potassium. These metals are very active for transesterification in the form of oxide but not in the form of carbonate. The results in Table 4.1 confirm this explanation. However, Saetang (2008) reported that the combination of M1O and CS1 could improve the biodiesel yield compared to the use of M1O alone. This leads to the use variety of metal oxide mixed with natural materials as well as metal carbonates and the other types of metal oxide as catalyst for biodiesel production.

4.2 Synthetic Heterogeneous Catalysts

The performance of several metal oxides as catalysts during the transesterification reaction of canola oil using methanol were evaluated. The metal oxides tested were: M1O, M2O, M3O, M4O, and M5O. The complex metal oxides

tested were: barium-strontium-titanium oxide, and barium-yttrium-tungsten oxide. The reaction conditions used in this experimental phase were: reaction pressure: 15 psig, mixing rate: 800 rpm, reaction time: 30 and 60 minutes, and reaction temperatures: 45, 55, and 65°C. The catalyst concentration was varied from 0.5-3.0% by weight of oil.

4.2.1 Metal Oxide Catalysts

The preliminary performance of the commercial metal oxides was tested at the following reaction conditions: reaction temperature: 65°C, reaction time: 30 minutes, and catalyst concentration: 3.0% by weight of oil. The results are shown in table 4.2.

Table 4.2 Metal oxides as catalysts for oil transesterification

Catalysts	Catalyst by weight of oil (wt%)	Reaction temperature (°C)	Reaction time (minutes)	Biodiesel yield (%)
M1O	3	65	30	97.33
M2O	3	65	30	97.71
M3O	3	65	30	0.31
M4O	3	65	30	No conversion
M5O	3	65	30	No conversion
Barium-Strontium-Titanium-Oxide	3	65	30	No conversion
Barium-Yttrium-Tungsten-Oxide	3	65	30	No conversion

Metal oxide (M1O) shows high catalytic activity at mild reaction conditions. Previous studies have shown that this metal oxide could achieve more than 90% biodiesel yield in 5 minutes at a concentration of 3% catalyst by weight of oil, at a methanol to oil molar ratio equal to 12:1, and at a reaction temperature of

65°C (Liu *et al.*, 2007). In addition to M1O, there are several types of metal oxides that can be used as catalysts for biodiesel production. In this work, a series of alkaline earth and transition metal oxides (M2O, M3O, M4O, and M5O) including complex metal oxides (barium-strontium-titanium-oxide, and barium-yttrium-tungsten-oxide) were used.

The results presented in Table 4.2 were obtained from the evaluation of the commercial metal oxides. From all the catalysts evaluated only 3 metal oxide catalysts showed activity at the reaction conditions used. The most active metal oxide was M2O rendering 97.7% yield of biodiesel. The biodiesel produced from M1O was slightly less than M2O. The disadvantage of using M2O is that it forms a very toxic solution with alcohol (Gryglewicz, 1999). It has been reported that M3O could achieve a biodiesel yield up to 85%. However, at the mild reaction conditions used in this work, the biodiesel yield obtained using M3O as catalyst was very low (Table 4.2). Then, M2O was rejected due to the toxicity of the solutions of M2O in methanol. Consequently, M1O was chosen as the best synthetic catalyst option for the remaining experiments.

The higher basic strength of the metal oxide could achieve higher yield from transesterification. But, there had the other variables that could affect biodiesel yield. Some literatures reported that M3O could achieve yield up to 90% with higher methanol-to-oil molar ratio, higher reaction temperature and longer reaction time (Viriya-empikul *et al.*, 2010). But, doing this will lead to higher biodiesel production cost. In order to make biodiesel price to be competitive with the fossil diesel, we need the catalyst that work at lower reaction temperature to save more energy cost the same way when we shorten the reaction time. Normally adding more alcohol can improve the biodiesel yield with the traditional theory said that when the reactant increasing, the reaction will shift to the right side (produce more products) to maintain the reaction equilibrium. By the way, there will be more excess alcohol in the system. In fact, we can recover this excess alcohol but we need more energy. These are all conditions that we need to consider for the optimum biodiesel production. For M4O and M5O, they were far from active in the transesterification (Kouzu *et al.*, 2008).

4.2.2 Metal Carbonate as a Catalyst

Three types of pure metal carbonates were evaluated in this experimental section: M1CA, M3CA, and M6CA. M1 and M3 were tested. And M6O which has been reported that it work for tranesterification (Ngamcharussrivichai *et al.*, 2008). At the following reaction conditions: reaction temperature: 65°C, reaction time: 30 minutes, and catalyst concentration: 3.0% by weight of oil were used in this section, these metal carbonates did not show catalytic activity so that a methyl ester signal could not be observed using ¹H-NMR.

At least 2 kinds of metal carbonates which contain the same metal as metal oxide catalyst tested in he previous section (M1 and M3) that work for tranesterification, were selected. The results obtained from this section were similar to the first section when used only natural materials as a catalyst. Biodiesel yield could not be found that mean there had no treanesterification in the mixture. In this way, it confirmed that metal carbornates itsself were not active for the transesterification (Kouzu *et al.*, 2008).

4.3 **Combination of Natural Materials and Metal Oxide Catalysts**

The use of M1O as a heterogeneous catalyst for biodiesel production shows potential due to many of its advantages. However, this is an expensive catalyst that might restrict its use at a commercial scale. Thus, the combination of this expensive catalyst with other materials could reduce the overall cost of the catalyst while maintaining its catalytic activity during the transesterification of vegetable oil. Fish shell is a biodegradable waste produced during fishery and from seafood industrial processes. Different mixtures of M1O powder to CS1 powder were evaluated on the base of 1% total catalyst combination by weight of canola oil.

4.3.1 M1O and Crustacean Shell with Different Reaction Times

The ratio of M1O-to-CS1 powder varied from 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1 for a total concentration of 1 wt% catalyst mixture by weight of canola oil. The results are shown in Figure 4.1, and 4.2 at 45°C reaction temperature and reaction time 30 and 60 minutes respectively.

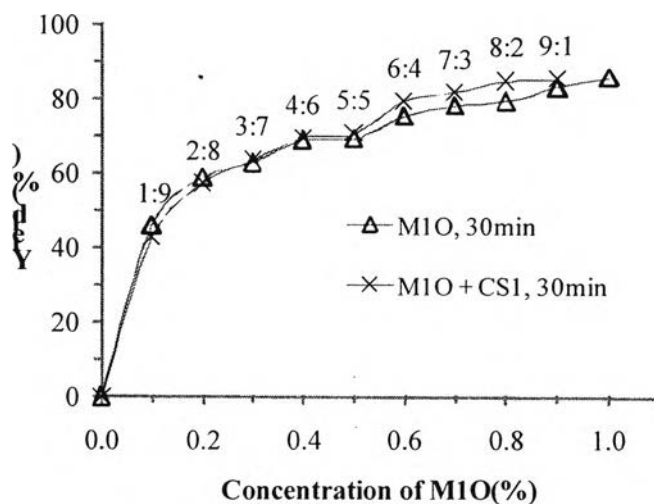


Figure 4.1 Performance of M1O and combination of M1O and CS1 as catalysts at 45°C at a heating rate of 5°C.min⁻¹ and 60 minutes reaction time. The triangle and cross symbols represent the biodiesel yield for M1O and mixtures of M1O with CS1 as catalysts respectively.

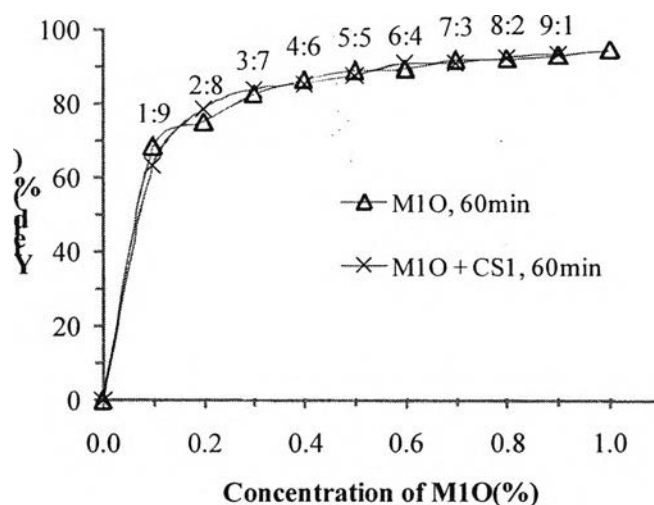


Figure 4.2 Performance of M1O and combination of M1O and CS1 as catalysts at 45°C at a heating rate of 5°C.min⁻¹ and 60 minutes reaction time. The triangle and cross symbols represent the biodiesel yield for M1O and mixtures of M1O with CS1 as catalysts respectively.

Only the reaction times were set to be different for this experimental section in order to study the effect of reaction time. At 30 minutes reaction time, the

combination of M1O and CS1 could improve biodiesel yield from the ratio of M1O-to-CS1 powder that varied from 5:5, 6:4, 7:3, 8:2, and 9:1 equal to 1.63%, 4.33%, 3.80%, 5.66%, and 2.55% respectively. In comparison with 60 minutes reaction time, the maximum yields were lower for less reaction time. But, our objective is to find the maximum improvement. Then, we desired to choose 30 minutes as reaction time for the rest of the experiments.

4.3.2 M1O and Crustacean Shell with Different Reaction Times

The ratio of M1O-to-CS1 powder varied from 5:5, 6:4, 7:3, 8:2, and 9:1 for a total concentration of 1wt% catalyst mixture by weight of canola oil. Because of the results from previous section, we selected only 5 ratios that work for biodiesel yield improvement. In this section, we studied about the effect of the different reaction temperature. By theoretically, higher reaction temperature could improve the yield (Saetang, 2008). The results are shown in Figure 4.3, 4.4, and 4.5 for 45°C, 55°C, and 65°C reaction temperature respectively.

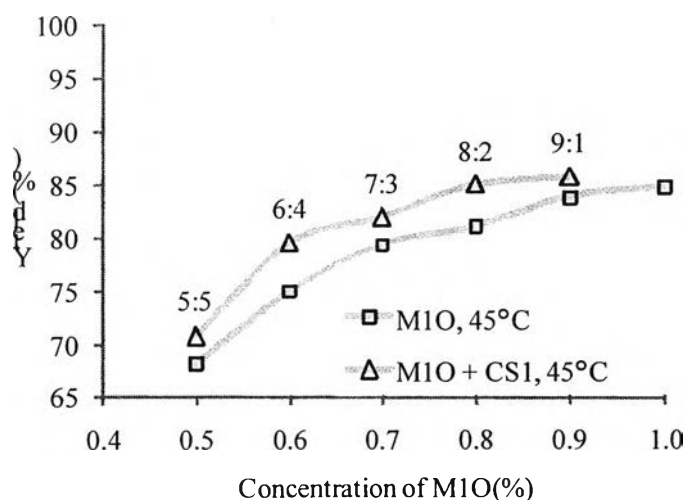


Figure 4.3 Performance of M1O and combination of M1O and CS1 as catalysts at 45°C at a heating rate of 5°C.min⁻¹. The square symbols and triangle symbols represent the biodiesel yield for M1O and mixtures of M1O with CS1 as catalysts respectively.

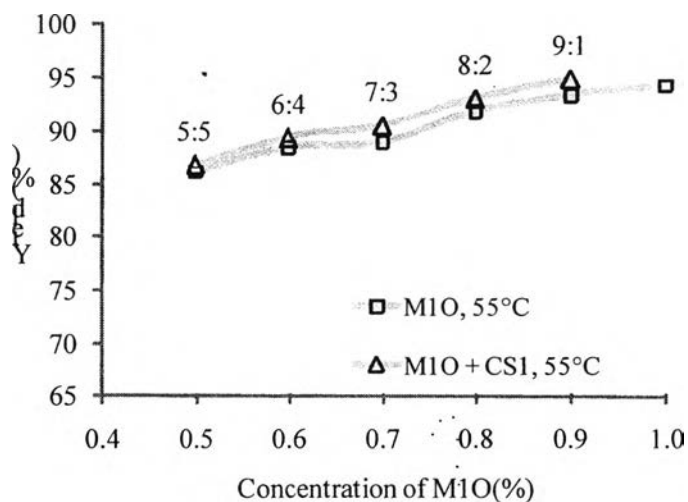


Figure 4.4 Performance of M1O and combination of M1O and CS1 as catalysts at 55°C at a heating rate of 5°C.min⁻¹. The square symbols and triangle symbols represent the biodiesel yield using M1O and mixtures of M1O and CS1 as catalysts respectively.

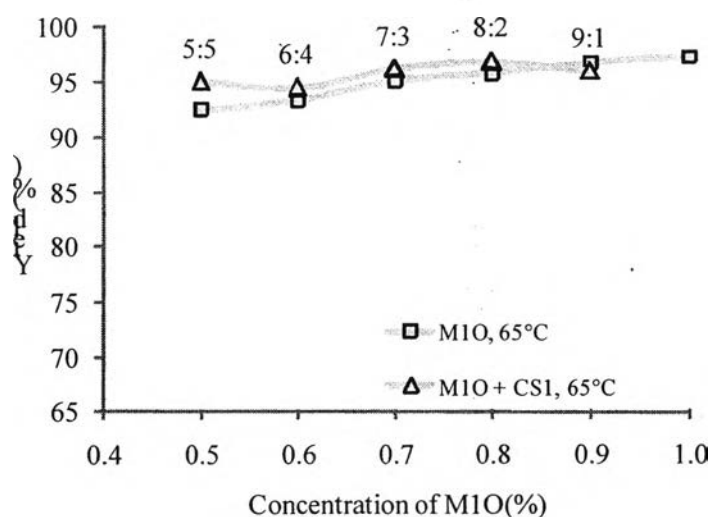


Figure 4.5 Performance of M1O and mixtures of M1O and CS1 as catalysts at 65°C at a heating rate of 5°C.min⁻¹. The square symbols and triangle represent the biodiesel yield of M1O and mixtures of M1O and CS1 as catalysts respectively.

For both pure M1O and the combination of M1O and CS1 power, biodiesel yield increased as the concentration of M1O increased in the mixture for each reaction temperatures. The reaction seemed to reach the equilibrium state when

the biodiesel yield was around 85% for 1% of the catalyst mixture. This catalyst mixture increased the yield of biodiesel by 2-3% when the reaction temperature was 45°C as Figure 4.4 shows. When the reaction temperature increased by 10°C from 45°C to 55°C, all of the catalysts could achieve higher yield compared to the results from 45°C. The highest yield was around 93% obtained from 1% of pure M1O. This number was close to the result from the combination of M1O and CS1 powder with the ratio of 9:1. However, most combinations could improve only 0.5-1.0% compared to pure M1O at this temperature. Figure 4.5 shows the reaction performance when a reaction temperature of 65°C was used. This was the highest reaction temperature evaluated in this research. The methyl ester yields were higher than 95% in many of the experimental runs and none of them showed a biodiesel yield below 92% as expected. The catalyst mixture did not increase the biodiesel yield significantly at this temperature. Based on these experimental observations, the reaction temperature for the rest of the experiments was set at 45°C in order to determine the highest improvement of the catalyst mixtures during the transesterification of canola oil at mild reaction conditions.

The possible explanation for this result could be the metal compound which contain in CS1 (M1 and M3) (Boßelmann *et al.*, 2007) affect to the reaction. Most of these metals are in the carbonate form that did not work for transesterification as a catalyst by itself. Doing combination with M1O could improve the yield as shown in Figure 4.1, 4.3, and 4.4. But, the main objective of this research work is to find the combination that work as a yield booster. More researches need to be done in order to investigate the reaction mechanisms for transesterification with this catalyst combination.

4.3.3 The Other Clustacean Shell Used to Formulate Catalyst Mixtures

The success of use CS1 as a catalyst additive to improve the yield of biodiesel production leaded us to find another possible candidate for the experiment. CS2 was made from the other kind of clustaceans which are smaller from the one that used to make CS1. One similar thing for these materials are the habitat of the clustaceans. They all came from the sea which has more elements can be found in the shell compare to the others that live in fresh water.

The ratio of M1O-to-CS2 powder varied from 5:5, 6:4, 7:3, 8:2, and 9:1 for a total concentration of 1wt% catalyst mixture by weight of canola oil and these ratios were used for the rest of the combination testing. The results are shown in Figure 4.6 at 45°C reaction temperature and 30 minutes reaction time.

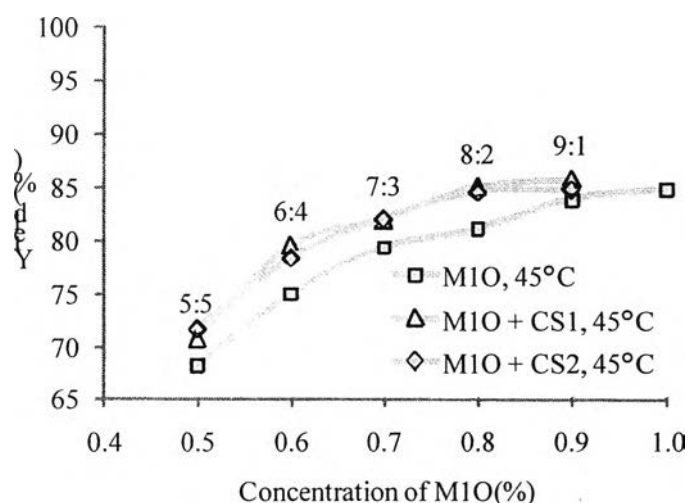


Figure 4.6 Performance of M1O, mixtures of M1O and CS1, and mixtures of M1O and CS2 as catalysts at 45°C at a heating rate of 5°C.min⁻¹. The square symbols, triangle, and diamond symbols represent the biodiesel yield of M1O, mixtures of M1O and CS1, and mixtures of M1O and CS2 as catalysts respectively.

The results obtained from this experimental section has shown the same trend of biodiesel yield production improvement. That means the shell of clustacean that live in the sea worked as a catalyst additive. And the chemical composition of these shells are similar (Boßelmann *et al.*, 2007 and Ruth Hagen Rødde *et al.*, 2008). This could be the reason why these clustacean shell achieved the similar results.

4.3.4 The Animal Shell Used to Formulate Catalyst Mixtures

The animal shell used for this experimental section was egg shell obtained form household use. In 2000, Stadelman reported that egg shell usually contain calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate

(1%) and organic matter (4%). AS was prepared the same way as CS1 and CS2. The powder with average particle size equal to 90 micron was used.

The ratio of M1O-to-CS2 powder varied from 5:5, 6:4, 7:3, 8:2, and 9:1 for a total concentration of 1wt% catalyst mixture by weight of canola oil and these ratios were used for the rest of the combination testing. The results are shown in Figure 4.7 at 45°C reaction temperature and 30 minutes reaction time.

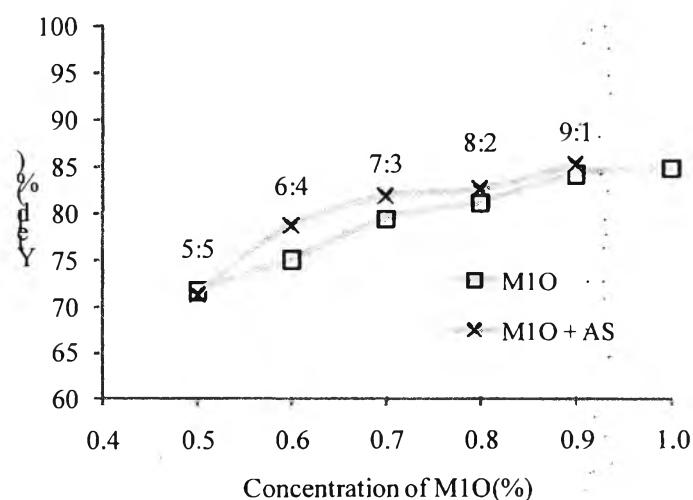


Figure 4.7 Performance of M1O and mixtures of M1O and AS as catalysts at 45°C at a heating rate of 5°C.min⁻¹. The square and cross symbols represent the biodiesel yield of M1O and mixtures of M1O and AS as catalysts respectively.

Stadelman (2000) reported that AS has calcium carbonate as a major component (94%) and magnesium carbonate, calcium phosphate, and organic matter as minor components. It is possible that calcium carbonate obtained from egg shell helped in the reaction. At certain ratios of the catalyst combination, the improvement of biodiesel yield could be observed. This result shows the same trend as the use of crustacean shell combined with M1O. But, the improvement of biodiesel yield from this combination was less than the one we obtained from crustacean shells combination. One possible explanation would be the effect from the different in amount of major chemical composition contained in all of natural material used. AS has more calcium carbonate content compared to CS1 and CS2. But, AS lacks of the other trace of metal such as sodium, chloride, strontium and silicon including chitin

which has only in the crustacean shell. However, the effects of chitin to transesterification were not investigated in this study. But, it is possible for the future research to find the roles of chitin for this reaction.

4.3.5 The Mollusk Shell used to Formulate Catalyst Mixtures

In addition, two types of mollusk shell were tested as catalyst additive. These mollusk shell were collected from the local beaches at Prince Edward Island, Canada and prepared in the same way as the other kind of natural materials to make uniform mollusk shell powder.

Figure 4.8 reveals the results for this run. Both of mollusk used were not work in order to improve the yield. No significant increasing of the yield could be observed.

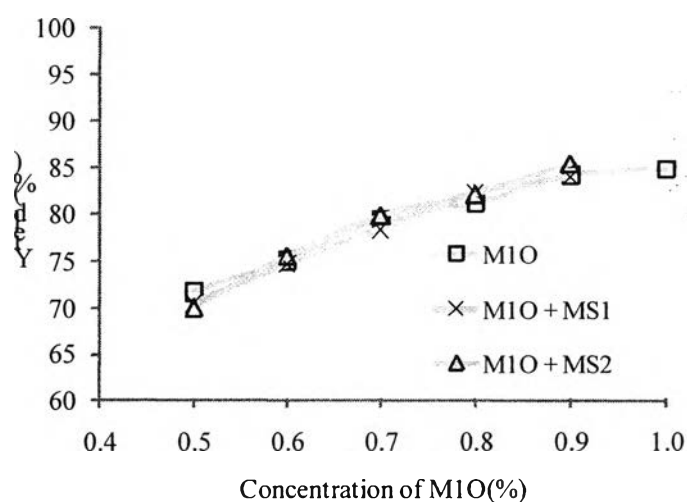


Figure 4.8 Performance of MIO, mixtures of MIO and MS1, and mixtures of MIO and MS2 as catalysts at 45°C at a heating rate of 5°C.min⁻¹. The square symbols, cross symbols, and triangle symbols represent the biodiesel yield of MIO, mixtures of MIO and MS1, and mixtures of MIO and MS2 as catalysts respectively.

MS1 and MS2 did not work as a catalyst additive in order to improve yield even they have the similar types of chemical compositions to the other kind of natural materials. It is possible that carbonate of M3 contained in these mollusk shell

could not be activated with the same mechanism as the other combinations. However, these powder need to be characterized in order to find the exact chemical compositions including the others chemical and physical properties in the further reserch. But for this study, mollusk shells without any modification of chemical properties, seem to be useless as a catalyst additive for biodiesel yield improvement.

4.4 Combinations of Metal Oxides and Synthetic Heterogeneous Catalysts

For this experiment, the possibility of using low cost synthetic catalysts mixed with e reactive catalysts in order to reduce the overall cost of heterogeneous catalysts for transesterification of canola oil was investigated. The first set of the experiments was conducted by using M1O mixed with M3O and M4O. M2O was rejected due to its toxicity when mixed with methanol. And metal carbonates were found as major component of fish shell, animal shell, and mollusk shell. Some synthetic metal carbonates were also tested as catalyst mixers.

4.4.1 M1O and Other Metal Oxides

The metal oxides selected for this experiment were M3O and M4O. The combination of M1O and M3O improved the biodiesel yield by 2-4% compared to pure M1O. The synergistic effects of the combination of M1O and M3O should be further evaluated to establish the reaction mechanisms that cause the increased biodiesel yield. The M1O:M4O combination did not show improved catalytic activity when compared to M1O alone. The results are shown in Figure 4.9.

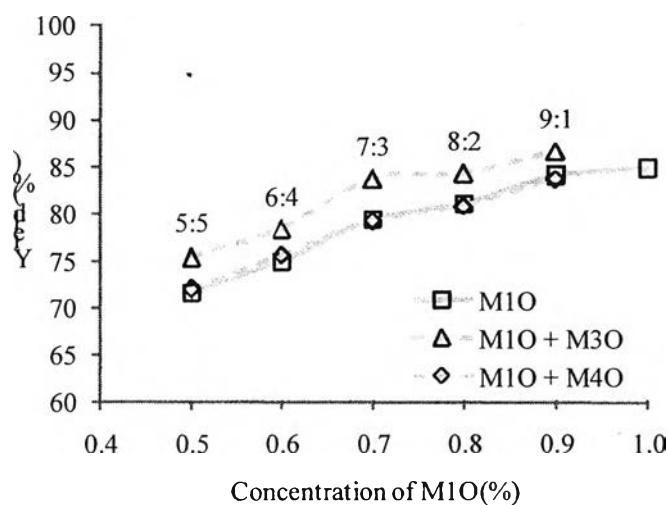


Figure 4.9 Performance of M1O and combination of M1O and various metal oxides as catalysts at 45°C, 30 minutes reaction time and set up heating rate of 5°C.min⁻¹. The square, triangle and diamond symbols represent the biodiesel yield obtained using M1O, combinations of M1O and M3O, and combinations of M1O and M4O respectively.

Only 2 types of metal oxides were selected for this experimental section. The results from the previous section, demonstrated that M3O alone did not work well as a catalyst at our conditions (reaction pressure: 15 psig, mixing rate: 800 rpm, reaction time: 30 minutes, and reaction temperatures: 45°C.). However, M3O could work if more methanol, higher reaction temperature, and/or longer reaction time are used (Liu *et al.*, 2008). Additionally, M4O itself was far from active in the transesterification (Kouzu *et al.*, 2008). The results from this experiment confirmed this reason. Mixing M4O with M1O which is very active for tranesterification did not work in order to improve yield of biodiesel production.

4.4.2 M1O and Metal Carbonates

The last series of experiments conducted in this work consisted on the use of metal carbonates as co-catalyst with M1O for canola oil transesterification. Previous results demonstrated that the combination of M1O and CS1 could significantly improve biodiesel yield. The major components of animal shell are carbonate compounds, thus three types of metal carbonates were selected: M1CA,

M3CA, and M6CA. It was found that the combination of M1O and M1CA improved the yield of the reaction by 3-4% as shown in Figure 4.10. The same trend was observed when mixtures of M1O:M1CA and M1O:M3CA were used. But the mixtures of M1O:M6CA did not show any improvement under the reaction conditions used for this experimental section.

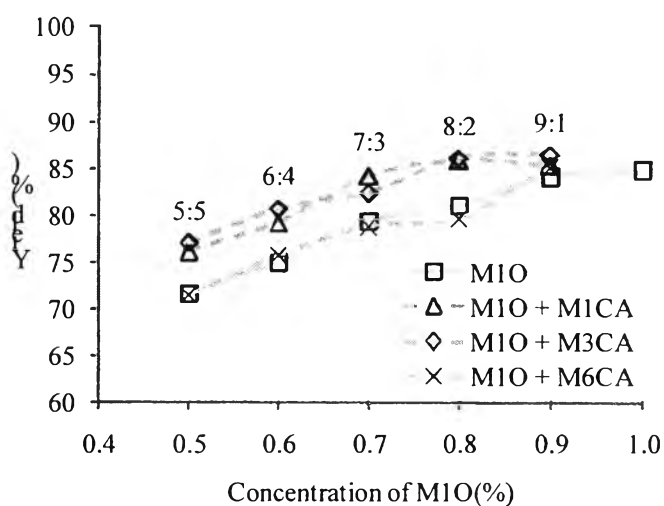


Figure 4.10 Performance of M1O and combinations of M1O and various metal oxides as catalysts at 45°C, 30 minutes reaction time at a heating rate of 5°C.min⁻¹. The square, triangle, diamond and cross symbols represent the biodiesel yield obtained using M1O, combinations of M1O and M1CA, combinations of M1O and M3CA, and combinations of M1O and M6CA respectively.

M1CA and M3CA contain the same metal which worked as catalysts for transesterification in the form of oxide. But metal carbonate itself is not active for transesterification (Kouzu *et al.*, 2008). These chemicals worked as catalyst additives in order to improve the yield and reduce the amount of expensive catalyst used for transesterification. The results show that synthetic metal carbonates work as well as the natural materials which contain the same type of metal carbonate (M3CA). In addition M1CA was selected because it contain the same active metal as M1O that worked very well as heterogeneous catalyst for transesterification and it worked as well as M3CA. The results obtained from this experimental section reveal the alternative option for an expensive catalyst. However, the economical

optimization needs to be done in order to find the most active and the cheapest catalyst combination for transesterification.

Table 4.3 Summary of biodiesel production yield obtained from various mixtures at 45°C, and 30 minutes reaction time

Catalysts	Biodiesel yield obtained at MO-to-Natural materials ratio (%)					
	5:5	6:4	7:3	8:2	9:1	10:0
M1O + CS1	70.80	79.51	81.91	84.98	85.67	84.79
M1O + CS2	71.62	78.34	82.03	84.52	84.80	
M1O + AS	71.25	78.61	81.81	82.52	85.11	
M1O + MS1	69.90	75.43	79.74	82.03	85.34	
M1O + MS2	70.30	74.50	78.13	82.05	83.84	
M1O + M3O	75.42	78.36	83.61	84.22	86.53	
M1O + M4O	72.01	75.58	79.12	80.68	83.52	
M1O + M1CA	76.15	79.14	84.10	85.80	85.23	
M1O + M3CA	76.94	80.66	82.32	86.00	86.40	
M1O + M6CA	71.39	75.63	78.70	79.57	85.03	

Table 4.3 shows the summary of biodiesel yield from transesterification of canola oil with methanol with all catalyst combinations at 45°C, and 30 minutes reaction time.