CHAPTER IV
RESULTS AND DISCUSSION

The research problem address in this work is the evaluation of the catalytic activity of an organic base and an alkaline earth metal oxide. The performance of these catalysts is compared against the behavior of a typical industrial catalyst such as sodium methoxide. The goal is to establish the optimum reaction conditions for the production of high biodiesel yield as a function of catalyst type and concentration, excess reagent, temperature, and biodiesel quality. The heterogeneous catalysts evaluated in this study is strontium oxide (SrO) as compare to 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which is an organic base with potential for heterogenization. The experimental results obtained from the different experimental series are presented in the following sections.

4.1 Sodium Methoxide as Homogeneous Catalyst-Baseline Data

The aim of this first series of experiments with sodium methoxide was to identify the best reaction conditions for the transesterification reaction of the specific raw canola oil using sodium methoxide ($NaOCH_3$) that maximizes reaction yield and conversion while minimizing soap formation.

The experimental results obtained from this first series of experiments with sodium methoxide are presented below. Each of these experiments was repeated twice and in some cases three times. The standard deviation is provided on the graphs.

4.1.1 Effect of Mixing

The optimum mixing rate for the transesterification reaction that promotes the lowest formation of soap, which is an undesirable product, was determined. Experimental results are presented in Figure 4.1.

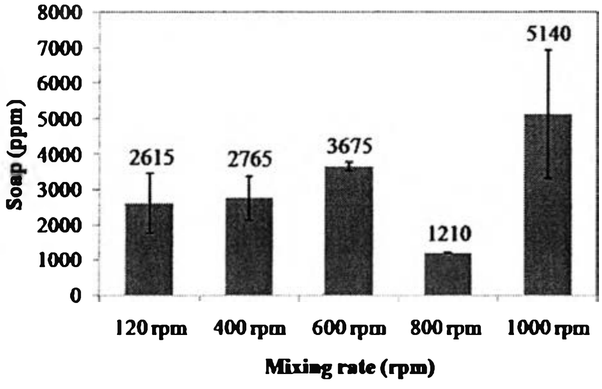

Figure 4.1 Mixing rate effect on soap formation.

As Figure 4.1 shows the optimum mixing rate that promotes the minimum soap formation is at 800 rpm. Once the optimum mixing rate for the transesterification reaction was determined, a set of reactions was repeated under identical conditions at 800 rpm with applying a mixing scheme where the reactants were mixed at 800 rpm for the first 10 min of the reaction and 400 rpm for the rest of the reaction time. The reactions were performed at a temperature of 90°C, 4.8:1 molar ratio of methanol to oil and 0.59% sodium methoxide catalyst by weight of oil.

The results showed that at the optimum speed of 800 rpm induces lower soap formation than the mixing scheme of 800 rpm during the first 10 minutes of the reaction followed by a decrease in the mixing rate to 400 rpm as Figure 4.2 shows. Therefore, the best mixing rate is 800 rpm for the total reaction time.

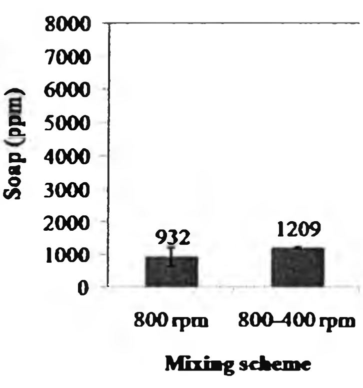

Figure 4.2 Mixing scheme effect on soap formation.

Table 4.1 Mixing scheme effect on reaction yield

Conditions	Mean Yield (%)	Standard Deviation
800 rpm/90°C	92.9	0.0707
800-400 rpm/90°C	93.1	0.1414

Table 4.1 shows that biodiesel yield is slightly higher when the mixing scheme is applied in contrast to the application of a fixed mixing rate during the total reaction time.

Despite, the slight increase in biodiesel yield when the mixing scheme is applied, the use of a fixed mixing rate of 800 rpm during the total reaction time renders less soap formation. Therefore, it is considered that the optimum mixing rate for the transesterification reaction is 800 rpm.

4.1.2 Effect of Reaction Temperature

In this part of the study, the effects of reaction temperatures on soap formation and reaction yield have been evaluated by using three different temperatures 70°C, 80°C and 90°C. The transesterification reactions of raw canola oil have been conducted under identical conditions using the optimum mixing rate of 800 rpm, which was obtained from the previous experimental section. Therefore, the reactions were performed maintaining the following parameter constants: mixing rate 800 rpm, 4.8:1 molar ratio of methanol to oil, and 0.59% sodium methoxide catalyst by weight of oil.

Figure 4.3 indicates that the lowest soap formation was obtained at 90°C. Experimental results show that as the temperature decreases from 90°C to 70°C the concentration of soap produced increases. For instance, at 70°C the highest concentration of soap of 1342 ppm is produced as a secondary product from the transesterification reaction.

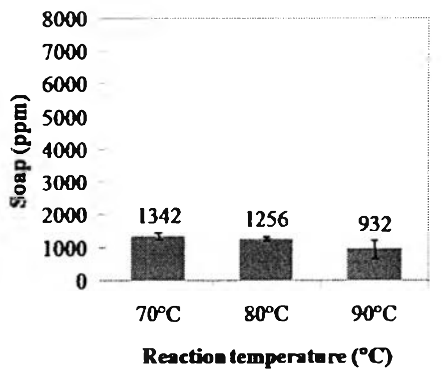

Figure 4.3 Reaction temperature effect on soap formation.

Table 4.2 indicates that temperature affects biodiesel yield. The general trend is that as the temperature increases the reaction yield increases. However, the results show that at 80°C there is a slightly higher in biodiesel yield than at 90°C. However, soap formation at 90°C is lower than at 80°C. Therefore, the best reaction temperature is considered to be 90°C.

Table 4.2 Reaction temperature effect on reaction yield

Conditions	Mean Yield (%)	Standard Deviation
800 rpm/70°C	90.9	1.0607
800 rpm/80°C	93.1	0.0707
800 rpm/90°C	92.9	0.0707
800-400 rpm/90°C	93.1	0.1414

4.1.3 Effect of Methanol to Oil Molar Ratio

In this experimental section, the effect of methanol to oil ratio on soap formation and reaction yield was evaluated by studying the effect of four different methanol to oil ratios: 3:1, 4.5:1, 4.8:1, and 6:1. The transesterification reactions of canola oil were conducted under identical conditions using the optimum mixing rate and reaction temperature previously obtained. Therefore the reactions were performed keeping a fixed mixing rate of 800 rpm, a reaction temperature of 90°C, and 0.59 wt% sodium methoxide catalyst by weight of oil.

Figure 4.4 presents the effect of methanol to oil ratio on soap formation, it indicates that soap formation is favored as the methanol to oil ratio increases. The lowest soap formation is obtained at a methanol to oil ratio of 3:1. However, this methanol to oil ratio also produces the lowest biodiesel yield which can be confirmed by ^{1}H NMR results in the following section. An explanation for this is that a higher excess of methanol to oil ratio is required to shift the transesterification reaction to the right.

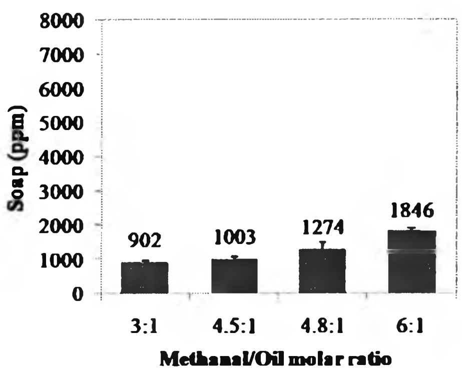

Figure 4.4 The methanol to oil ratio effect on soap formation.

Table 4.3 presents the effect of methanol to oil ratio on reaction yield. The highest biodiesel yield is obtained at a methanol to oil ration of 6:1.

Table 4.3 The methanol to oil ratio effect on reaction yield

Conditions	Mean Yield (%)
3:1 Methanol/Oil	87.0
4.5:1 Methanol/Oil	94.3
4.8:1 Methanol/Oil	93.0
6:1 Methanol/Oil	96.0

These experimental results indicate that an increase in methanol to oil ratio switches the transesterification reaction towards the product side (right).

In this study, the selection of the optimum methanol to oil ratio was based on reaction yield and soap formation. It is necessary to compromise biodiesel yield in order to control soap formation. Otherwise, the further separation and purification step of biodiesel could be complicated by the undesirable production of soap.

4.1.4 Effect of Catalyst Concentration

The effect of catalyst concentration on soap formation and reaction yield was evaluated by studying six different catalyst concentrations. The transesterification reactions of canola oil were conducted under identical conditions using mixing rate (800 rpm), reaction temperature (90°C), and methanol to oil ratio (4.5 to 1) previously identified. Figure 4.5 shows the experimental results. The lowest soap formation is observed at a catalyst concentration of 0.59% by weight of the oil.

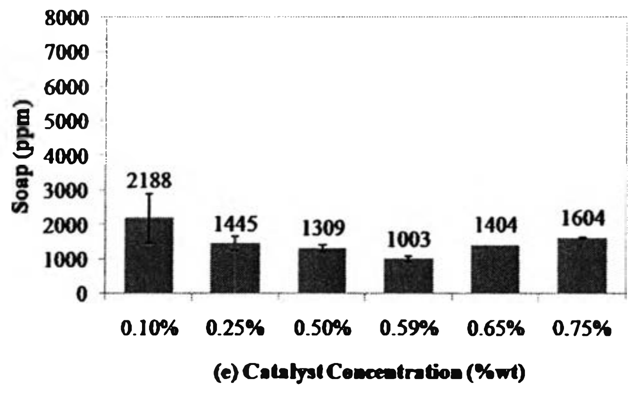

Figure 4.5 Catalyst concentration effect on soap formation.

Table 4.4 shows the effect of catalyst concentration on reaction yield. The highest biodiesel yield is obtained at a catalyst concentration 0.59% by weight of the oil which is consistent with the soap formation results.

Table 4.4 Catalyst concentration effect on reaction yield

Conditions	Mean Yield (%)
0.10% $NaOCH_3$	85.4
0.25% $NaOCH_3$	83.4
0.50% $NaOCH_3$	93.9
0.59% $NaOCH_3$	94.3
0.65% $NaOCH_3$	91.4
0.75% $NaOCH_3$	93.7

The experimental observations allow the establishment of the optimum conditions for the transesterification reaction of the raw canola oil used in this work. These optimum conditions are: mixing rate 800 rpm, 6:1 molar ratio of methanol to oil, 90°C, and catalyst concentration 0.59% by weight of the oil. Table 4.5 summarizes the experimental results.

Table 4.5 Summary of reaction yield and soap formation at various reaction conditions

Conditions	Mean of Biodiesel Yield (%)	Standard deviation Yield	Mean of soap formation	Standard deviation of soap formation
800 rpm/70°C	90.9	1.0607	1341.74	95.92
800 rpm/80°C	93.1	0.0707	1256.22	58.38
800 rpm/90°C	92.9	0.0707	931.84	283.58
800-400 rpm/90°C	93.1	0.1414	1209.04	25.02
3:1 Methanol/Oil	87.0	-	902.36	58.38
4.5:1 Methanol/Oil	94.3	-	1002.62	66.73
4.8:1 Methanol/Oil	93.0	-	1273.91	216.86
6:1 Methanol/Oil	96.0	-	1846.00	58.38
0.10% $NaOCH_3$	85.4	-	2188.07	708.96
0.25% $NaOCH_3$	83.4	-	1444.95	191.84
0.50% $NaOCH_3$	93.9	-	1309.30	83.41
0.59% $NaOCH_3$	94.3	-	1002.62	66.73
0.65% $NaOCH_3$	91.4	-	701.83	-
0.75% $NaOCH_3$	93.7	-	1604.19	16.68

Figure 4.6 shows the states of final product after settling overnight. The product mixture separated into two layers: crude ester layer in the liquid state (upper layer) and glycerol layer (bottom layer) as shown in Figure 4.6(A). The states of final product are in agreement with the results reported by Leung. et al. (2006). They reported that the glycerol, which is a viscous liquid at ambient temperature and pressure, tended to form a mixture of glycerol and soap in solid state when more and more solid soaps sank to the bottom as shown in Figure 4.6(B and C). Thus, the separation of the top crude ester layer from the bottom glycerol layer had to be decanted or drawn out from the top of the separation unit, and could not flow out directly from the bottom of the separation unit.

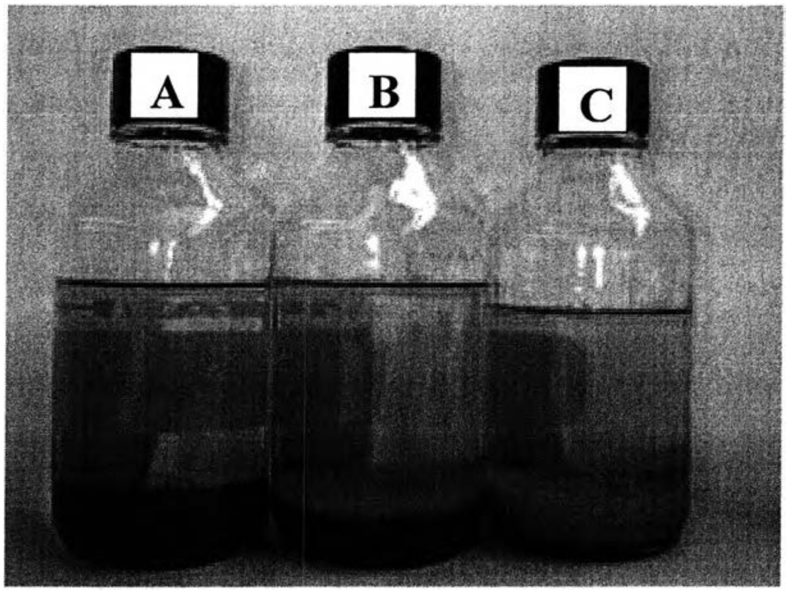

Figure 4.6 States of the final product mixtures settled overnight (A) the good quality of biodiesel, (B) the biodiesel with a soap formation on glycerol phase and (C) the biodiesel with a solid state of catalyst and soaps.

4.2 Optimization of Process Parameters

The experimental design for this part of the study has been established based on the results obtained from the first series of experiments with sodium methoxide. The effects of three independent variables such as catalyst concentration, methanol to oil molar ratio, and temperature on biodiesel yield were evaluated aiming to determine the optimum reaction condition of three catalyst types ($NaOCH_3$, TBD, and SrO). The experimental results obtained from this study are presented in the following sections.

4.2.1 Effects of Catalyst Type and Catalyst Concentration

The concentration of the catalyst was the first parameter studied. The effect of each catalyst type ($NaOCH_3$, TBD and SrO) on the transesterification of canola oil was investigated using the following catalyst concentrations: 0.59, 1.00 and 1.50 wt% (based on raw canola oil weight) for $NaOCH_3$: 1.53, 2.29, and 3.05 wt% for TBD (based on raw canola oil weight), and 1.00, 3.00, and 5.00 wt% (based on the weight of raw oil) for SrO. The optimal conditions for transesterification using each type of catalysts were evaluated. During the reaction the following parameters were maintained at constant: a mixing rate of 800 rpm, a methanol to oil ratio of 6:1, a reaction temperature of 90°C, and a reaction time of 1 hour.

Experimental results shown in Figures 4.7, 4.9, and 4.10 indicate that as the catalyst concentration increases, biodiesel conversion increases. This behaviour is clearly observed in the first period of reaction (first 20 min of reaction). On the other hand, after 20 min of reaction, if $NaOCH_3$ concentration increases from 0.59 to 1.50 wt%, the yield of biodiesel product decreases as shown in Figure 4.7. It seems that an excess amount of $NaOCH_3$ promotes further saponification of triglycerides, thereby reducing biodiesel yield as confirmed by the soap formation results shown in Figure 4.8. Excess $NaOCH_3$ concentration led to a reduction in the product yield and also added an extra cost to the process due to removal of excess catalyst and soaps at the post-treatment stage of product purification. Therefore, $NaOCH_3$ concentration should be controlled carefully.

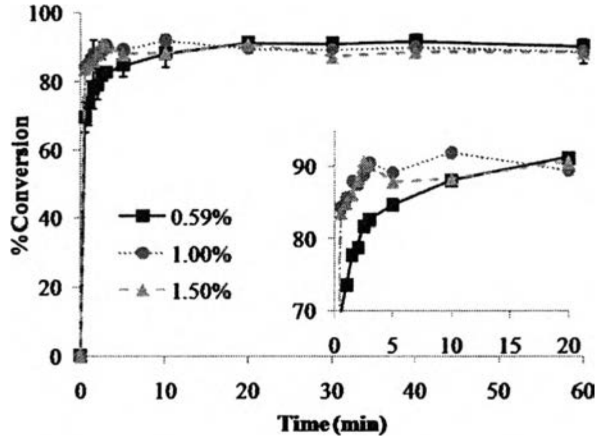

Figure 4.7 Effect of $NaOCH_3$ concentration on canola oil conversion (methanol to oil molar ratio 6:1, temperature 90°C, mixing rate 800 rpm).

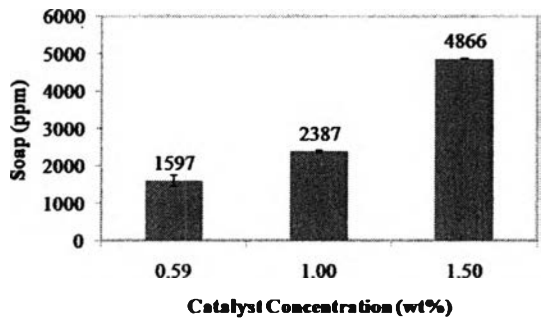

Figure 4.8 Effect of $NaOCH_3$ concentration on soap formation (methanol to oil molar ratio 6:1, temperature 90 °C, mixing rate 800 rpm).

In the case of TBD, the results indicated that the increase of TBD concentration does not have a significant effect on biodiesel yield after 20 min of reaction. On the other hand, if the first 20 min of the reaction are considered, the use of 2.29 wt% TBD renders higher biodiesel yield than that of 1.53 wt% as shown in Figure 4.9. However, TBD concentrations of 2.29 and 3.05 wt%, biodiesel yield are 90.38% and 90.00% respectively. Therefore, the optimal catalyst (TBD) concentration is considered to be 2.29 wt%. The use of this concentration would reduce the cost of biodiesel production, in terms of catalyst savings.

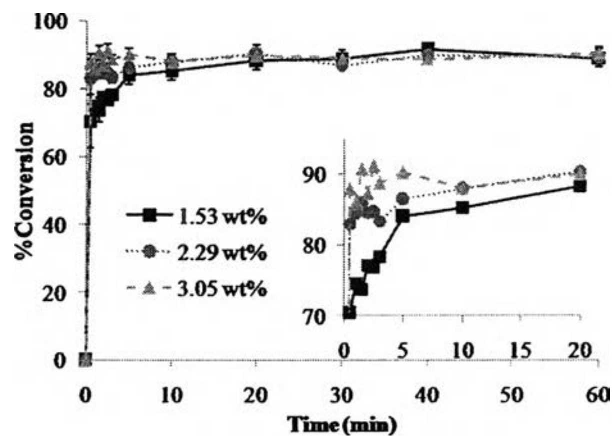

Figure 4.9 Effect of TBD concentration on canola oil conversion (methanol to oil molar ratio 6:1, temperature 90°C, mixing rate 800 rpm).

In the case of SrO, the experimental results showed that an increase of SrO concentration increases biodiesel yield as shown in Figure 4.10. The use of 1.00 to 3.00 wt% SrO turns into a higher biodiesel yield, during the first 20 min of the reaction, of 88.27% to 88.75% respectively. On the other hand, a concentration of SrO of 5 wt% renders a biodiesel yield of 94.28% at the same reaction time, which is significantly higher compared to the yield obtained from 1.00 and 3.00 wt% of catalyst addition. However, Liu. et al. (2007) have also studied the effect of catalyst concentration in biodiesel yield for the transesterification of soybean oil to biodiesel using catalyst concentrations in the range of 0.5 to 3 wt%. They have reported that the maximum biodiesel yield was obtained by adding 3 wt% SrO, which reached 92% at 5 min.

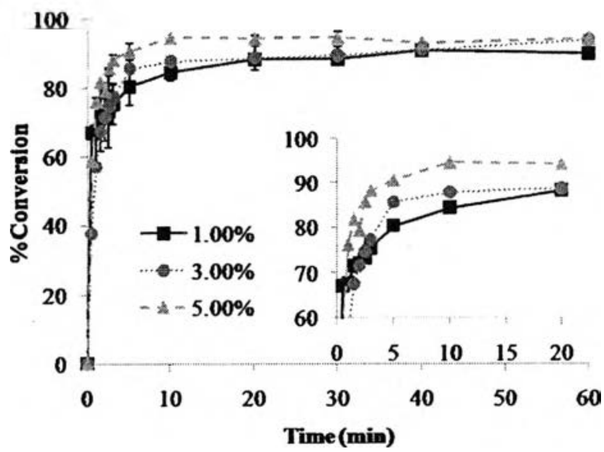

Figure 4.10 Effect of SrO concentration on canola oil conversion (methanol to oil molar ratio 6:1, temperature 90 °C, mixing rate 800 rpm).

These experimental results for the catalyst concentration effect indicate that the optimum catalyst concentrations are 0.59 wt%, 2.29 wt% and 5.00 wt% for $NaOCH_3$, TBD, and SrO, respectively.

4.2.2 Effect of Methanol to Oil Molar Ratio

The alcohol to vegetable oil molar ratio is one of the most important factors that can affect the biodiesel conversion. The effect of methanol to oil ratio on biodiesel yield was evaluated by fixing the optimum catalyst concentrations determined from the previous section. The experiments were conducted using three different molar ratios of methanol to oil; 3.5:1, 4.5:1, and 6:1 for both $NaOCH_3$ and TBD as well as 4.5:1, 6:1 and 12:1 for SrO. From the stoichiometric transesterification reaction, three moles of methanol are required per mole of triglyceride to yield three mole of biodiesel and one mole of glycerol. The theoretical molar ratio of methanol to triglyceride should therefore be 3:1. However, the experimental results indicate that the reaction rate increases when the molar ratio of methanol to oil is increased as shown in Figures 4.11, 4.13, and 4.14. Figure 4.11 shows that with a concentration of 0.59 wt% $NaOCH_3$ at 90°C, an increase of the methanol to oil molar ratio from 3.5:1 to 6:1 increases a biodiesel yield from 84.95% to 91.23% after the first 20 min of reaction. Moreover, it was observed that for a high methanol to oil molar ratio a longer time was required for the subsequent separation stage because separation of the ester layer from the glycerol layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier. Therefore, increasing the molar ratio of methanol to oil beyond 6:1 did not increase the biodiesel conversion, but complicated the ester recovery process and raised the cost for methanol recovery (Leung and Guo., 2006). As a result the optimal methanol to oil molar ratio was 6:1 for $NaOCH_3$ catalyst.

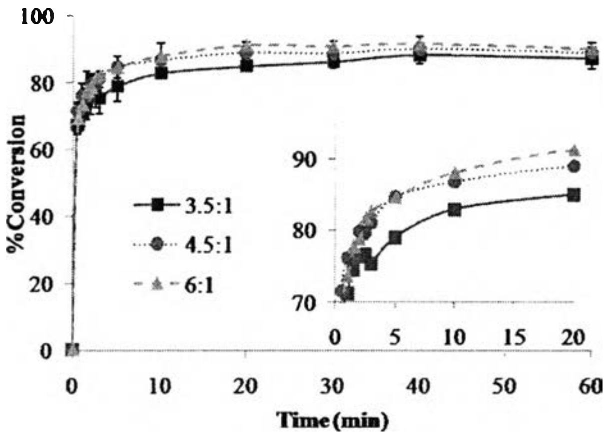

Figure 4.11 Effect of methanol to oil molar ratio on canola oil conversion ($NaOCH_3$ 0.59%, temperature 90°C, mixing rate 800 rpm).

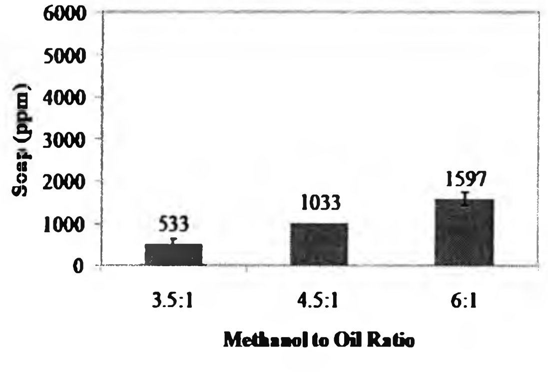

Figure 4.12 Effect of methanol to oil molar ratio on soap formation ($NaOCH_3$ 0.59%, temperature 90 °C, mixing rate 800 rpm).

In the case of TBD (2.29 wt% TBD at 90°C), a molar ratio of methanol to oil shows little effect on the canola oil conversion at 20 min of reaction as shown in Figure 4.13. As the methanol to oil molar ratio is increased from 3.5:1 to 6:1, the biodiesel yields are at 91.05%, 89.91%, and 90.38%, respectively. This shows that methanol to oil molar ratio has no significant effect on biodiesel yield during the range studied in this work. Therefore, to decrease the cost for biodiesel production, the optimal methanol to oil molar ratio was chosen to be 3.5:1 for TBD catalyst.

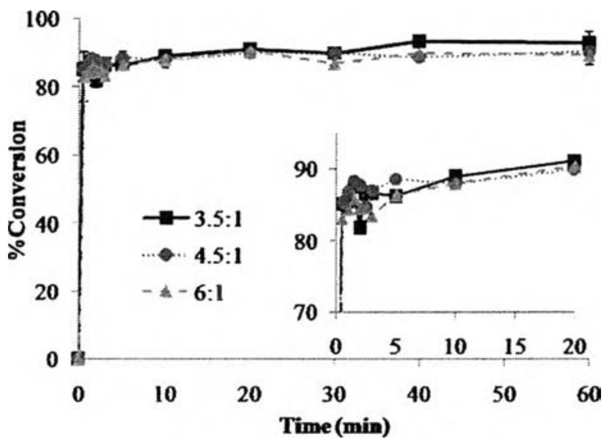

Figure 4.13 Effect of methanol to oil molar ratio on canola oil conversion (TBD 2.29 wt%, temperature 90 °C, mixing rate 800 rpm).

Finally, in the case of SrO, methanol to oil molar ratio were varied from 4.5:1 to 12:1 as shown in Figure 4.14. If the first 20 minutes of the reaction are considered, when methanol to oil molar ratio is increased, the biodiesel yield increases. However, when the amount of methanol to oil ratio is 12:1, glycerol separation becomes more difficult, thus decreasing the biodiesel yield. These experimental observations are in agreement with the results presented by Liu. et al. (2007). Based on the results of transesterification reaction after only 20 minutes of reaction and using a methanol to oil ratio of 6:1 a maximum biodiesel yield of 94.28% is determined. In contrast, the results reported by Liu. et al. (2007) indicated that the optimum molar ratio of methanol to oil was 12:1.

These experimental findings indicate that the optimum molar ratio of methanol to oil is 6:1 for $NaOCH_3$ and SrO, while for TBD the optimum molar ratio is 3.5:1.

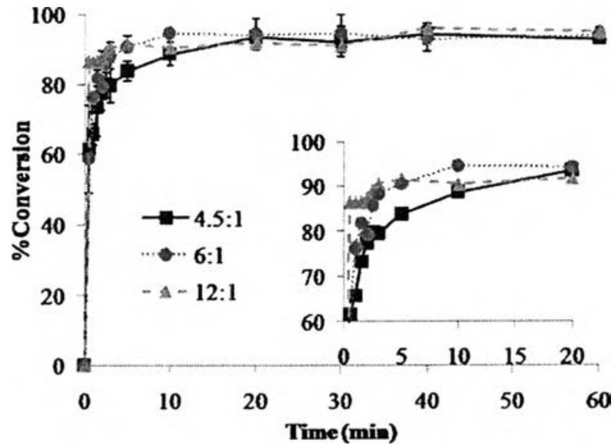

Figure 4.14 Effect of methanol to oil molar ratio on canola oil conversion (SrO 5.00 wt%, temperature 90°C, mixing rate 800 rpm).

4.2.3 Effect of Reaction Temperature

The effect of reaction temperature on canola oil conversion was carried out under the optimal conditions obtained in the previous section (i.e. 0.59 wt% $NaOCH_3$ and 6:1 methanol/oil molar ratio; 2.29 wt% TBD and 3.5:1 methanol/oil molar ratio; 5 wt% SrO and 6:1 methanol/oil molar ratio). In this part of the study, the effect of reaction temperature on biodiesel yield was evaluated by using three different reaction temperatures; 60°C, 70°C, and 90°C. Figures 4.15, 4.17 and 4.18 illustrate the effect of reaction temperature on product yield for $NaOCH_3$, TBD, and SrO, respectively.

For $NaOCH_3$, after 5 min of reaction, biodiesel yields at 60°C, 70°C, and 90°C were 82.21%, 81.63% and 84.60%, respectively. These results demonstrate the significant influence of temperature on biodiesel yield. However, after 20 min of reaction under the mentioned temperatures, the biodiesel yields were found to be 87.27%, 85.03%, and 91.23%, respectively. Figure 4.15 indicates that the highest biodiesel yield under these conditions is reached after almost 20 min of reaction time, thus indicating that temperature had positive influence on the transesterification of canola oil.

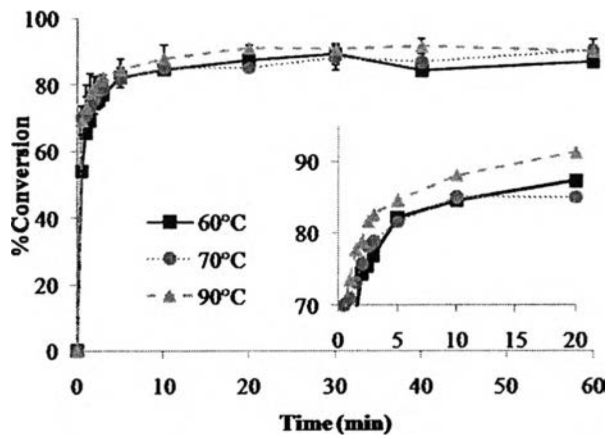

Figure 4.15 Effect of reaction temperature on canola oil conversion ($NaOCH_3$ 0.59 wt%, methanol to oil molar ratio 6:1, mixing rate 800 rpm).

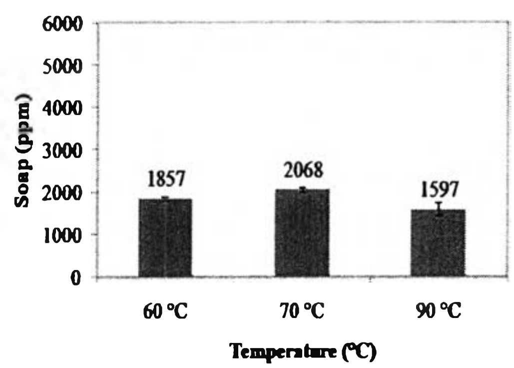

Figure 4.16 Effect of reaction temperature on soap formation ($NaOCH_3$ 0.59 wt%, methanol to oil molar ratio 6:1, mixing rate 800 rpm).

In the case of the TBD, reaction temperatures in the range of 60 to 90°C were evaluated. The results indicate that reaction temperature has no significant effect on biodiesel yield as shown in Figure 4.17. Therefore, to reduce energy usage for biodiesel production, it is reasonable to consider 60°C as the optimum reaction temperature for biodiesel production using TBD as the catalyst.

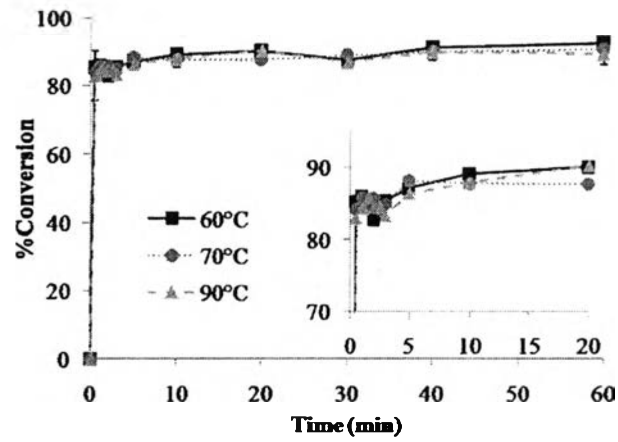

Figure 4.17 Effect of reaction temperature on canola oil conversion (TBD 2.29 wt%, methanol to oil molar ratio 3.5:1, mixing rate 800 rpm).

The effect of reaction temperature on biodiesel production using SrO as the catalyst was studied by varying reaction temperatures in the range of 60 to 90°C as shown in Figure 4.18. The results indicate that after 20 min of reaction, an increase in reaction temperature from 60 to 90°C, results in increasing biodiesel yield from 91.70 to 94.28%. Therefore, the optimal reaction temperature for SrO is 90°C.

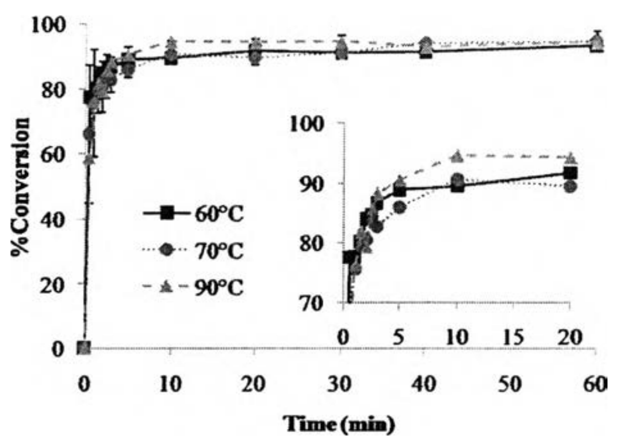

Figure 4.18 Effect of reaction temperature on canola oil conversion (SrO 5 wt%, methanol to oil molar ratio 6:1, mixing rate 800 rpm).

Experimental results indicate that biodiesel yield increases as reaction temperature increases. Biodiesel yields of 90% at 90°C within the first 20 min of reaction were obtained for $NaOCH_3$ and TBD. The same biodiesel conversion was observed for SrO, but during the first 5 min of reaction, which means that SrO is more sensitive to reaction temperature than $NaOCH_3$ and TBD. A higher temperature leads to a drastic decrease in viscosity of canola oil that favors the solubility of the oil in methanol, promoting a better conversion of triglycerides to biodiesel. Therefore, the optimal reaction temperatures are 90°C for $NaOCH_3$ and SrO, but 60°C for TBD.

The effect of the three types of catalysts evaluated on the transesterification was compared in terms of biodiesel conversion. Figure 4.19 presents the results of the optimal conditions for the transesterification of canola oil using $NaOCH_3$, TBD, and SrO. The three catalysts exhibited similar trends on biodiesel conversion, but different amounts of catalyst were required for achieving the same conversion. TBD gives the same catalytic activity as $NaOCH_3$. However, it takes more catalyst concentration than $NaOCH_3$. SrO seems to possess the best activity but it takes much more catalyst concentration than TBD and $NaOCH_3$.

The maximum biodiesel conversions reached are 91.23%, 91.05%, and 94.28% after 20 min of reaction at the optimal reaction conditions for $NaOCH_3$, TBD, and SrO, respectively.

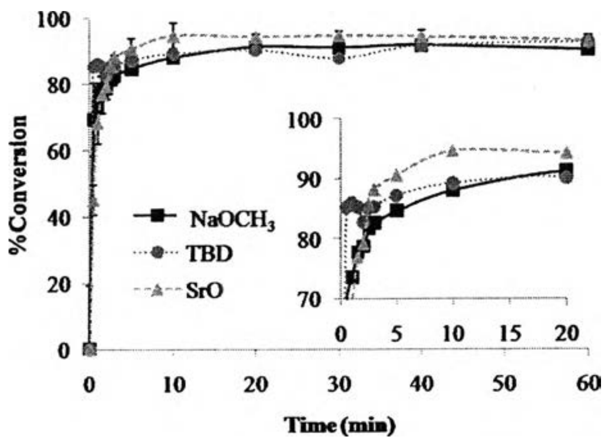

Figure 4.19 The progress of reaction under the optimal conditions for $NaOCH_3$, TBD and SrO.

4.3 SrO reusability

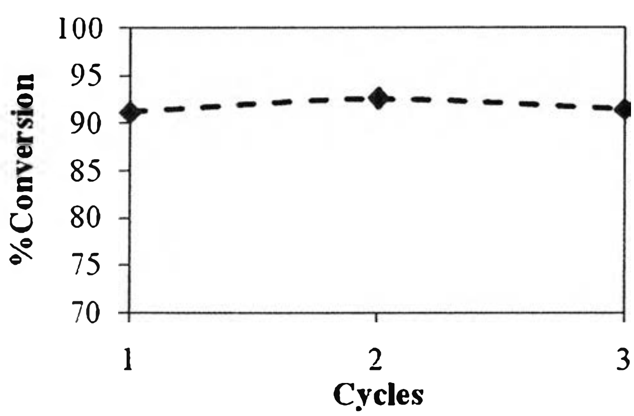

Figure 4.20 The performance of SrO resusability.

Figure 4.20 shows that the SrO is likely to maintain its catalytic activity after 3 cycles of reaction with the biodiesel yield of 90%. Therefore, SrO can contribute to a decreasing cost of biodiesel production due to its long catalyst lifetime and good stability.

4.4 The Synergistic Effect of Catalyst Combinations

In this part the synergistic effect of heterogeneous catalyst combinations on the transesterification yield, conditions, reaction time, and product quality was investigated.

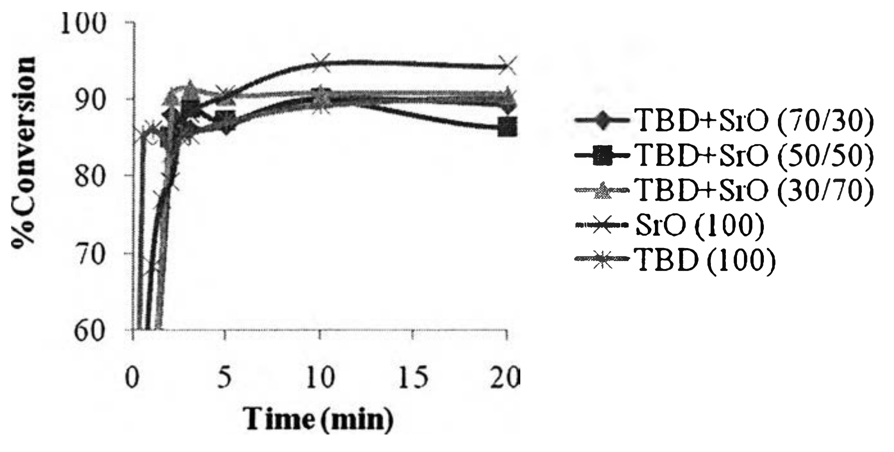

Figure 4.21 The performance of catalyst combination (SrO mixed with TBD).

Figure 4.21 shows the biodiesel yields obtained from the transesterification of canola oil using the combination of TBD and SrO as catalysts. Based on the results the best combination of 30% TBD and 70% SrO is observed with each 5 wt% catalyst concentration. When compared to 100% SrO, the combination does not improve biodiesel conversion. On the other hand, the particular combination improves the conversion if compared to 100% TBD.

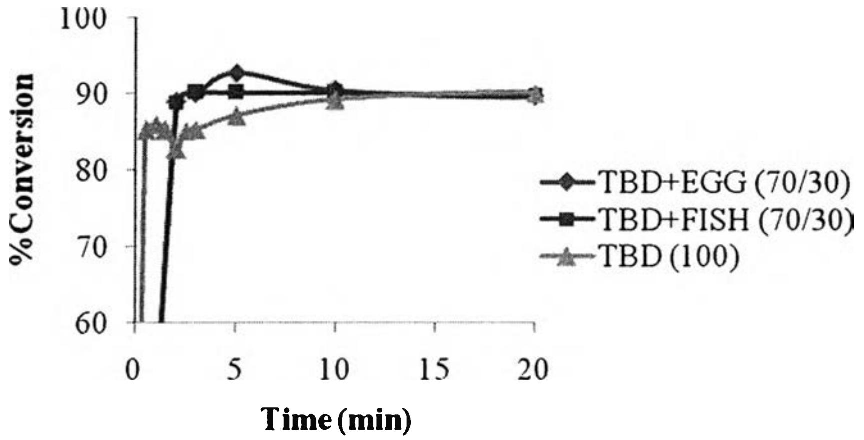

Figure 4.22 The performance of catalyst combination (TBD mixed with animal shell: egg shell and lobster shell).

Figure 4.22 illustrates that the catalytic activity of TBD is increased by mixing it with animal shells in a TBD:egg shell proportion of 70:30 and TBD:lobster shell of 70:30 during the first minute of the reaction. Therefore, the combination of TBD with animal shells does improve the conversion.

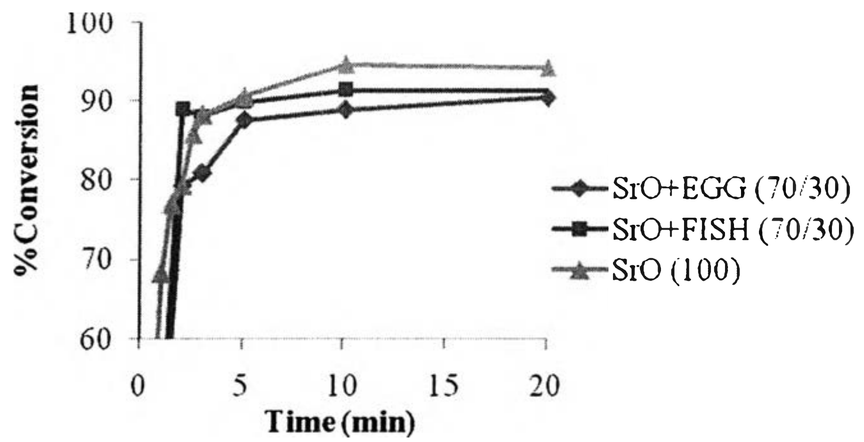

Figure 4.23 The performance of catalyst combination (SrO mixed with animal shell: egg shell and lobster shell).

Figure 4.23 presents that the catalytic activity of the SrO is not increased by mixing it with animal shells. Therefore, the combination of TBD with lobster shell does not improve the conversion.